

Chapter 5

Experimental

5.1 Introduction

The aim of the study was to investigate the possibility of an alternative method to Spectrographic techniques for the determination of impurities in Ruthenium. Parameters that could be altered were investigated and optimised to obtain calibration curves for the analysis of the impurities in Ru base matrix. The supply voltage was kept constant at 220 V and the analysis gap (gap between the sample and electrode) adjusted between 3 and 4 mm. The optional parameter settings available were as follows:

Capacitance (μF) 2.2, 4.7, 6.9, 10.0, 12.2, 14.7.

Resistance (Ω) 1, 15

Inductance (μH) 30, 130

Frequency (Hz) 300

These conditions could be applied to the pre-spark and SAFT conditions. The pre-spark or HEPS was to ensure the homogenising process. The pre-spark conditions were determined and remained the same throughout the experiment. The sensitivity of the analytical channels and the background equivalent concentrations were monitored. The capacitance, resistance and inductance were varied where applicable. Calibrations were established for the various analytical elements using optimised conditions. Production samples were measured and compared with the analysis of other techniques. Due to the confidentiality agreement signed with the company supplying standards and samples, results will be presented graphically instead of in tables, in order not to compromise confidentiality.

5.2 Samples

Pure metal salts and purified final metal samples were received for analysis. Salts received for analysis from the plant were ignited and reduced prior to analysis. If the

samples were moist they were placed under an infrared lamp to avoid spitting of the sample before ignition at 900 °C. The sample was placed in a porcelain crucible over a Bunsen burner. A lid placed on the crucible and hydrogen passed over the sample through a glass capillary to replace the oxygen and create a reduced atmosphere. While the sample was cooled to room temperature it was kept in a hydrogen atmosphere. The sample was shaken using a ball type milling action to ensure homogeneity. Loss of ignition was recorded and taken into account in the final analysis. Samples were pressed at 70 tons to prepare them for analysis on the spark spectrometer. The pure, refined metal powder for final analysis was pressed into pellets at 70 tons per square inch.

5.3 *Optimisation of parameters*

5.3.1 *HEPS (High Energy Pre-spark)*

Pre-spark used high discharge energy and the analysis was done using lower discharge energy. The capacitance was five times greater during pre-spark than during the analysis. The resistance remained the same. Pre-spark burn spot was larger (6 mm) than during integration (3 mm). This ensured that only material from the region that had been re-melted during prespark to obtain homogenisation was analysed [1].

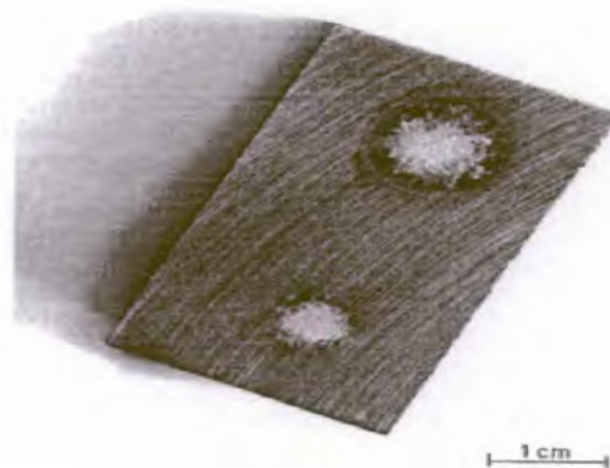


Fig.5.1 Burn spots on a sample, top – HEPS and bottom – analytical integration [2].

The duration of the low energy discharge was of secondary importance, as a state of quasi-homogenous layer was obtained and this supported the fact that the solid state does not alter over longer sparking times, which was what the principle of the HEPS was based on. Samples with low conductivity, when heated in the burn spot, caused the surface to disintegrate. Disintegration of the material can cause results to be incorrect. The problem can be overcome by using lower energy per discharge.

The parameters for the HEPS remained constant as per the manufacturers' factory settings. Resistance at 1 Ohm (Ω), Inductance 130 (μ H) micro Henry Capacitance at 12,2 (μ F) microfarad and Frequency at 300 (Hz) Hertz.

5.3.2 Intensity versus integration time

Experimental – HEPS

Samples containing reasonable amounts of impurities were sparked at different integration times until a steady state was reached.

The sample was used for the determination of the pre-spark time. The spark conditions were as follows:

Table 5.1 R = Resistance Ω Ohm; C = Capacitance Microfarad; L = Micro Henry; F=Frequency Hertz

	Pre-Spark	Spark	SAFT
R	1	1	1
L	30	130	130
C	12.2	2.2	4.7
F	300	300	300

Resistance (R): The ratio of the potential difference between the ends of a conductor to the electrical current flowing in the conductor. All materials except super conductors resist the flow of an electrical current, converting a proportion of the electrical energy into heat. The extent to which a conductor resists the flow of a given current depends on its physical dimensions; the nature of the material of which it is made, its temperature, and in some cases the extent to which it is illuminated [3].

Capacitance (C): The property of a system of electrical conductors and insulators, which enables it to store electrical discharge when a potential difference exists between the conductors. It is measured by the charge, which must be communicated to such a system to raise its potential by one unit. The SI Unit for capacitance is farad [3].

Inductance (L): The property of an electrical circuit as a result of which an electromotive force is generated by a change in the current flowing through the circuit, or by a change in the current of a neighboring circuit with which it is magnetically linked. The SI unit of inductance is henry. An inductance in a closed circuit, such that a rate of change of current of 1 ampere per second, produces an induced electro motive force of 1 volt [3].

Experimental – intensity versus time

Sample S8 contained the following concentrations in ppm: Fe 200, Na 200, Ca 200, Si 200, Cu 85, Al 200, Mg 200, Te 100, As 100, Bi 100, Mo 100, Sn 50 and Co 50.

Sample 7 contains the following concentrations in ppm levels: Pt 200, Pd 200, Rh 200, Ir 200, Au 200, Os 120, Ag 200, Zn 200, Pb 100, Sb 100, Mn 100, Ti 100, Cr 100.

Both samples were sparked using the same conditions and the integration time varied from 1 to 10 seconds, increasing the time by 1-second intervals.

5.3.3 Effect of different gating parameters

When a sample is sparked, a background signal is obtained which is synchronous with the discharge current curve. When sparking a sample with concentrations above the background equivalent the intensities of the atom and ion lines differ. The intensities of the ion lines were also synchronous with the current and thus the spectral background. This was due to the high temperatures (current) required for the excitation of the ion lines (15 eV). The number of ions is also proportional to temperature and the intensities of the atom lines appear with a delay time. The intensity curve against time (as described in detail in chapter 3, 3.9.2, 49) is basically

determined by the excitation energy and not by the vapourisation enthalpy. Thus the temperatures for Fe 371.9 nm (3.3 eV) and Cd 228.8 nm (5.3 eV) in a Cu base are very similar against time, although the vapourisation temperatures differed considerably.

The aim was to optimise the delay conditions to reduce spectral interference from ion lines or to eliminate it so that the atom line of the element of interest appeared clearly above the background. The system has to be optimised to produce the best signal to background ratio.

Experimental – optimising gating parameters

The test was performed on pressed Ru powder standards. Impurities in solution of the various elements and varied concentrations were added to very pure ruthenium. These samples were dried at very low temperatures and blended mechanically by shaking the mixture in a mixer-mill and then ground it in a rotary mill. Standards were pressed at 70 ton. Five samples were used for the test work. Sample preparation was as has been discussed in chapter 5, 5.2, 83.

Sample 1 was a blank (99.9 % purity).

Sample 7 and 9 contained different concentrations of Ag, Au, Cr, Ir, Mn, Pb, Pt, Pd, Rh and Sb.

Sample 8 and 10 contained different concentrations of Al, As, Bi, Ca, Cu, Fe, Mg, Mo, Na, Ni and Sn.

Two different samples were analysed to confirm any trends.

Ideally I would have liked to have the samples melted but the facilities available could not reach the high temperatures required for melting the Ru standards. Secondly, due to the high value of the material security was tight and the samples were not allowed to be taken from the premises. The standard parameters were; 1 Ω Resistance, 30 μ H, frequency 300 Hz, Capacitance 4.7 microfarads.

Tests were performed with the 15 Ω and 1 Ω resistor.

The system makes use of a 16-channel integrator board. The times set up for the experiment were at intervals of 16 μ s ranging from 16 μ s to 176 μ s. All the other

parameters stayed constant. The samples were analysed using a 5 second pre-spark and then SAFT parameters for the analysis.

Table 5.2 Spark Analysis For Traces (SAFT) conditions

Parameters	R	L	C	F
SAFT Conditions	1 / 15 Ω	130 μ H	4.7 Microfarad	300 Hertz

5.3.4 Internal standardisation

The internal standard is generally a constant amount of an element, which is added to all samples, blanks and calibration standards used for the analysis. Alternatively, it can be a major constituent of the sample and standards in a large amount, so that it is assumed that the amount is constant throughout. The calibration curve was obtained by plotting the ratio of the analyte signal as a function of the analyte concentration of the standards. Internal standardisation was widely employed in quantitative emission spectroscopy as a way of improving precision and accuracy [4]. The procedure involved calculating the ratio of the intensity of the analyte emission line to that of a second element also present in the sample or added intentionally. Guidelines have been proposed for matching the physical properties of the analyte and the reference elements so that this ratio was insensitive to fluctuation of the experimental parameters.

Greenfield [5] reported a high degree of correlation between two emission signals for elements, which had similar excitation energies, or in the case of ions, a similar sum of ionisation and excitation energy.

In spark emission a reference line is often the base, matrix element. If no element could be found which was suitable as a reference because of variations in the sample composition, a constant quantity of an element not present in the sample (external reference) was added during sample preparation. The reference line is exposed to the same, or similar, changes as the analytical lines, in radiation produced [6].

Changes in the radiation can be due to the composition of the sample itself, changes in viscosity, processes in the discharge gap or faults in the radiation off take.

A suitable reference line should adhere to the following criteria:

- The intensity ratio of the line pair should not be affected by interference from other lines.
- The ratio should be dependant only on the concentration and not on discharge parameters, so that the lines were associated with the same ionisation state, and should have similar excitation energies. Analyte and reference should have similar ionisation energy.
- Vapourisation of the reference element should take place in a manner similar to that of the analytes. This applies particularly for methods with total vapourisation, or if a steady state has not been obtained.

In the case of spark emission, it was found that with elements mainly or entirely precipitated from the base, matrix element (e.g. B, P, S, Pb, Sb in Fe base), the RSD (relative standard deviation) was not improved by relating the analytical line to a reference line [6]. Thus for precipitated elements the sample surface must be heated sufficiently for it to be vapourised. This was achieved by using optimum HEPS conditions. In the case of dissolved elements and the base metal, the crystalline structure must first be destroyed and then vapourised.

In samples where the base metal was close to 100 %, and the intensity of the background at a "clean" (no interferences) wavelength, the total discharge radiation or zero order radiation was used. Since these variables take intensity changes in the spectral background into account, they were suitable as a reference for low concentrations, if the proportion of the spectral background in the total measurement signal was significant. The reference is primarily intended to compensate for changes in the vapourisation behavior and probability of transition, and only secondarily for instability due to absorption or in the geometry of the radiation source with resultant fluctuations in the signal from the photo multiplier tubes due to inadequate radiation off take [6]. Therefore the spectrometer calibrations and the intensity ratio of the analytical line to the reference line are plotted against the

concentration ratio of the analyte to the reference (base material or background position) [6].

5.3.5 Analytical gap 3 mm and 4 mm

As in Chapter 4, fig. 4.6, 69 the temperature distribution generated at the spark stand can be seen. The electrode, made from tungsten, can be set at either a 3 mm or 4 mm gap (the gap between the sample and the electrode). Under these conditions the temperature generated at the spark is estimated to be between 1000 and 10 000 Kelvin. The best excitation was expected for atomic lines from 5000 to 8000 Kelvin and best excitation for ionic lines at 10 000 Kelvin. The experiment was done using sample 9 and 10. Sample 9 contained Ag, Au, Cr, Ir, Mn, Pb, Pt, Pd, Rh and Sb. Sample 10 contained Al, As, Bi, Ca, Cu, Sn, Mg, Mo, Na, Ni, Si and Fe. The sparking conditions of the instrument remained the same, with only the gap (distance between the electrode and the sample) changing: 3 mm and 4 mm distances were used.

Table 5.3 Sparking conditions used during 3 and 4 mm gap determinations

Sparking Conditions								
	C (μF)	R (ohm)	L (μH)	Freq (Hz)	Air Gate(μS)	Air Delay(μS)	UV Gate(μS)	UV Delay(μS)
Flush	0	0	0	0	64	144	64	144
Pre-Spark	12.2	1	30	300	64	144	64	144
Spark	2.2	1	130	300	64	144	64	144
SAFT	4.7	1	130	300	64	64	64	64

5.3.6 Contamination from another base material

When a sample is first measured with a high concentration or even another base and then a pure sample, the concentration for the pure sample will most probably be incorrect due to contamination. With repeated sparking, contamination asymptotically approaches zero. If the degree of contamination is not acceptable, it is necessary to change the stand components, which are in contact with the discharge space. It is

inevitable that trace amounts of all the PGM will be analysed in the various base materials i.e. Pt, Pd, Rh, Ir, Au will be measured in Ru. The next sample might be a Pt sample and Ru will then be required as an impurity. Cross contamination must be prevented at all times.

Experimental – cross contamination:

To investigate the degree of cross contamination between Pt, Pd, and Ru, samples of 99.9 % purity were used. A pure Ru sample was sparked and without changing plates, a pure Pt sample was sparked and the Ru in the sample monitored, until a stable signal was established. A pure Pd sample was then sparked and the Pt monitored. Then a pure Ru sample was sparked and the Pd monitored.

The same exercise was repeated using the Ru base plate, electrode and chamber accessories when sparking the Ru sample, monitoring the Pd. The Pt sample was sparked using the base plate etc. and monitoring the Ru and the Pd sample sparked with the appropriate base plate monitoring the Pt. Sparking conditions remained the same throughout this investigation. Raw intensities were recorded to determine the extent of cross contamination and to establish operating procedures.

5.4 Creating calibration graphs

Creating standards for analysis was probably the most important aspect of the calibration. Calibration standards were prepared in three different ways. A composite sample was used for the basic standard. This material was very pure (99.99 %) and the impurities were known.

The first set of standards was prepared by using stock solutions of the various impurities. Ten standards were made up in this batch. Twenty grams of material was used for each standard and then the samples were spiked with precious metals and base metals in varying concentrations. The standards were dried overnight at 100 °C in a drying oven or evaporated using an infrared lamp. The standards were homogenised in a sample shaker, which used a ball type milling action, and then pressed at 70 ton.

The second set of standards was prepared by using the Ru composite sample and pressing that at 70 ton. Five grams of a certified reference material from Johnson Matthey was pressed on top of the Ru composite sample at 80 ton. 10 Samples with varying concentrations of impurities were prepared in this way. The third set of standards was prepared by adding the impurities as metal to the ruthenium composite and then melting the material in an inductive or arc furnace. Calibration using optimised conditions as found in varying parameters as well as the mathematical procedure will be discussed in more detail in the next Chapter.

5.5 Comparisons of samples analysed

Ultimately, the new method was required to be used in production. Samples analysed had to be compared with those from other techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) and spectrographic (Spec) analysis. Metal salts were analysed for internal use to control the process. Analysis of the final refined pure metals was analysed by the spark spectrometer and sold to customers on their purity value. Samples from the different mines were analysed by the participating mines and these were referred to as interchange samples.

A composite sample was also sent for analysis internationally and these samples were referred to as a round robin. Various precious metal refineries in South Africa, the United Kingdom and Russia participated in these analyses. Company A (South Africa) was responsible for the analysis done by the Spark Spectrometer, B (South Africa) for analysis done on a Spectrograph, C (South Africa) conducted analysis on ICP, D (South Africa) conducted analysis on a spectrograph and ICP, E (United Kingdom) conducted analysis on ICP, F (Russia) conducted analysis on spectrograph and F (United Kingdom) conducted analysis on a spectrograph. Results of the analyses of these samples were compared to each other.

5.6 References

- [1] K.A. Slickers, **Automatic Atomic-Emission-Spectroscopy**, Second Edition (1993), 328
- [2] K.A. Slickers, **Automatic Atomic-Emission-Spectroscopy**, Second Edition (1993), 137-138
- [3] E.B. Uvarov, D.R. Chapman, **A Dictionary of science**, Maryland, A.S.A. (1943), 329, 61, 196
- [4] S.A.Meyers, D.H. Tracy, **Improved performance using Internal standardization in Inductively coupled plasma emission spectroscopy. Spectrochimica Acta, Vol. 38B No.9** Norwork, USA, (1983), 1227
- [5] S Greenfield, **Developments in Atomic Plasma Spectrochemical Analysis**, Heyden, London, Philadelphia (1981), 1
- [6] K.A. Slickers, **Automatic Atomic-Emission-Spectroscopy**, Second Edition (1993), 226 - 238

Chapter 6

Calibration

6.1 Introduction

Calibration comprises the measurement of calibration samples and the determination of the functional relationship between the intensity of the line of an analyte and its concentration in the sample. The functional relationship includes the relations between vapourisation, excitation, radiation off-take, dispersion and the measured value. The slope of the calibration curve is largely determined by the radiation source. The standard error of the calibration and limit of detection is affected by the radiation off-take and dispersion [1]. The final concentration of the unknown analyte is critical and dependent on the calibration of the instrument.

Two commonly employed approaches of calibration are found in emission spectroscopy. These are the methods of direct comparison and standard addition [2]. This study dealt only with the direct comparison method. The accuracy of the calibration was dependent on the selection of standards, the quality of their preparation, the accuracy of their data and the response of the spectrometer used for generating and measuring emission of the required elements.

The instrument signal given by the blank sample will very often not be zero. It is thus wrong in principle to subtract the blank value from the other standard values before plotting the graph [3]. The calibration curve is always plotted with the instrument response on the vertical (y) axis and the standard concentrations on the horizontal (x) axis. This is due to many procedures, which assume that all the errors are in the y values and that the standard concentrations (x-values) are error free [3]. In routine instrumental analysis this statement is justified by the assumption that standards can be made up with an error of 1 % or better, whereas the instrumental measurement might have a coefficient of variance of 1-2 % or worse. The second assumption is that the magnitude of the error in y is independent of the analyte concentration, if the

relative errors in the measurement are constant; the absolute errors will increase as the analyte concentrations increase [3].

Most analytical methods are based on a calibration curve in which a measured quantity y is plotted as a function of the known concentration x of a series of standards [9]. The best "straight line" is fitted through the points and the most common way of obtaining such a "straight" line is by using the method of least squares regression. In applying this method, we assume a straight line is a good model for the relationship between the area of a peak (y) and its analyte concentration (x) as given by the equation:

$$y = mx + c$$

Where m is the slope and c is the intercept of the line. These two parameters form part of the model, which is assumed to be a straight line [4].

6.2 Background Equivalent Concentration (BEC) and Limit of Detection (LOD)

It is very important to avoid confusion regarding sensitivity and limit of detection. The sensitivity is generally defined as the slope of the calibration graph and provided the plot is linear, it can be measured at any point on it. The limit of detection is calculated with the aid of the section of the plot close to the origin, and utilises both the slope and the intercept [3].

Reference is made to the Background Equivalent Concentration (BEC) and the Limit of detection (LOD). The BEC is the concentration in the sample, which produces the same line intensity as the spectral background, also referred to as the signal-noise ratio. The BEC is the concentration of analyte required to produce the same signal as the background at a given wavelength. It is a fundamental process and variable since it directly affects the limit of detection. If the analyte concentration is zero, the intensity "U" is the spectral background (dark current produced by electronic noise already subtracted). If "U" is doubled and plotted in the direction of the intensity axis and this point "(U+L)" is projected on the concentration axis, the BEC is obtained. A basic feature of the analytical method is its capacity to determine low concentrations. The quantitative information is the limit of detection [1].

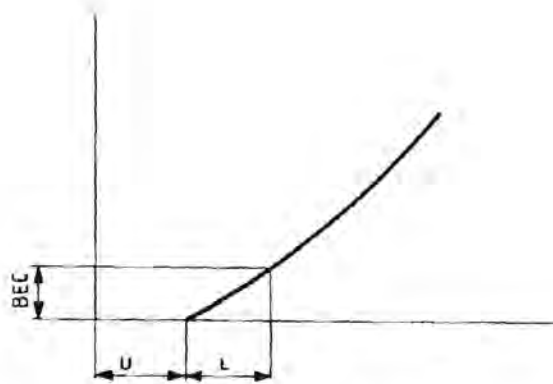


Fig. 6.1 Representation of Background Equivalent Concentration (BEC) [1].

Formula for determining the BEC:

$$\text{BEC} = \frac{C(H) - C(L)}{I(H) - I(L)} \times [I(L) - \text{DC}] - C(L)$$

C(H) = Concentration of high standard

C(L) = Concentration of low standard

I(H) = Intensity of high standard

I(L) = Intensity of low standard

DC = Dark current

The most generally accepted qualitative definition of detection limit is the minimum concentration or mass of analyte that can be detected at a known confidence level [9]. The BEC, LOD and other significant information produced for the calibration on the Spectrolab is based on principles as formulated by Kaiser [5]. The LOD is taken as the equivalent concentration of the absolute standard deviation (ASD) S_0 of the precision of the spectral background in the following form [1]:

$$\text{LOD} = 3 \times \sqrt{2} S_0$$

For the simplified version the $\sqrt{2}$ is omitted. The spectral background can only be given by a sample which "does not contain" the analyte. Slickers [1] say: "there is no such thing. If there is a sample, however, containing the analyte at a concentration

far (<2 times) below the LOD, the method of determining the LOD remains "Clean" as the absolute relative standard deviation is then mainly determined by the spectral background and not by the low analyte concentration". The formula for the LOD does not explicitly contain the spectral background (e.g. Expressed as BEC) i.e. if the spectral background were large but infinitely precise (ASD_0 towards zero) any number greater than the infinitely stable background could be assigned to a concentration in the sample. The LOD as a function of the RSD can be stated directly, in concentrations incorporating the BEC.

$$LOD = 3 RSD_0 \times BEC/100$$

Table 6.1 The LOD as a function of the RSD

RSD ₀	0.50%	1%	1.50%	2%	3%
LOD	BEC/60	BEC/30	BEC/20	BEC/15	BEC/10

Usually, the repeatability of the background is 1 % and therefore LOD = BEC/30 is commonly used as an estimate. The LOD for the method can only improve by reducing the RSD or reducing the BEC [1].

6.3 Spectral interference

Spectrometer measurements can be affected by spectral interference effects, which are systematic additive errors and must be corrected.

Spectral interference effects are [6]:

- i) Line overlaps: Effects due to line overlaps with inadequate resolution of the spectrometer optics.
- ii) Band coincidence: Effects arising from bands of poly-atomic particles (e.g. CN, AlO) forming from the gasses surrounding the radiation source or from incomplete, dissociated compounds.
- iii) Background Interference: Effects arising from changes in the spectral background with varying matrix.

- iv) Stray light: Effects arising from reflection in the optical system (stray radiation) or from radiation from other orders. It may be element or non-element specific.

Interference effects arising from i), ii), and iii) increase the measured value, whereas effects from background interference can decrease or increase the measured value.

Although most inter-element effects are non-linear, it is often possible to carry out a linear approximation in the concentration ranges present. If the concentration ranges were not greater than those in which a linear approximation of the non-linear correction was permitted [6].

Interelement effects can arise from the sample itself, as well as the discharge atmosphere.

The effects associated with the sample are as follows:

- i) Precipitates present in the sample that can change.
- ii) Changes may occur in the form of solidification due to differences in the vapourisation rate.
- iii) Other elements may be present in the base element, which may dissolve or precipitate partly or completely.
- iv) Changes due to elements with high vapourisation temperatures, which were present in a low vapourisation temperature base element.
- v) There may be changes in the vapourisation rate due to changes in vapourisation enthalpy. Due to lowering of the melting point by alloy elements, the energy necessary for vapourisation is reduced. Therefore for a given energy conversion in the discharge gap the quantity of sample material vapourised per discharge is increased, which results in increased intensities.
- vi) There may be changes in the vapourisation rate due to changes in thermal conductivity. Alloy constituents affect thermal conductivity in different ways. Low thermal conductivity leads to greater localised heating in the burn spot and therefore increased vapourisation of material and increased intensities.

- vii) When the analytical line is ratioed to a reference line, the effect of changes in vapourisation rates due to changes in enthalpy and thermal conductivity mostly lose their effect on spectrochemical results. This is because the changes in vapourisation rate affect the dissolved analyte to the same extent as the reference.

The effects associated with the sample and the discharge atmosphere is as follows:

- i) Changes in the type of discharge, that is, diffuse or concentrated, may occur due to presence of oxides in the sample.
- ii) Changes in the type of discharge due to constituents of the sample and discharge atmosphere other than oxides may occur.

The effects associated with the sample in the plasma.

- i) Changes in location of optimum excitation of an atomic line in the plasma may occur due to other elements and differences in the imaging of this location in the optics. This was responsible for discrepancies among interelement effects stated in various texts for the same sample programme. Interferences in the plasma must present a maximum at least one point between the electrodes since it is zero at the electrodes. This effect was lost during analysis where there was uniform radiation from the entire radiation source. This is illustrated in Fig. 6.2, 100 [8].
- ii) Changes in the plasma temperature due to other elements with varying ionisation temperatures and resultant changes in excitation probability may also occur. In the presence of elements with low ionisation energy compared to the base element, the plasma temperature dropped so that spectral lines with high excitation energy became stronger. When elements with high ionisation energy compared to the base metal were present together, the plasma temperature increased so that the spectral lines with high excitation energy became stronger and those with low excitation energy became weaker. This interference lost its effect on spectrometric results if homologous lines were used.

Additive correction: Analytical lines, which arise from spectral interferences, can be corrected for if no other wavelength, which is interference free, is available. The

interference factor can be determined by measuring a binary sample (sample that contains the interfering element in rather high concentrations but is otherwise pure). Changes in intensity with respect to the pure sample as a function of the concentration of the interfering element are the basis of the corrections [6].

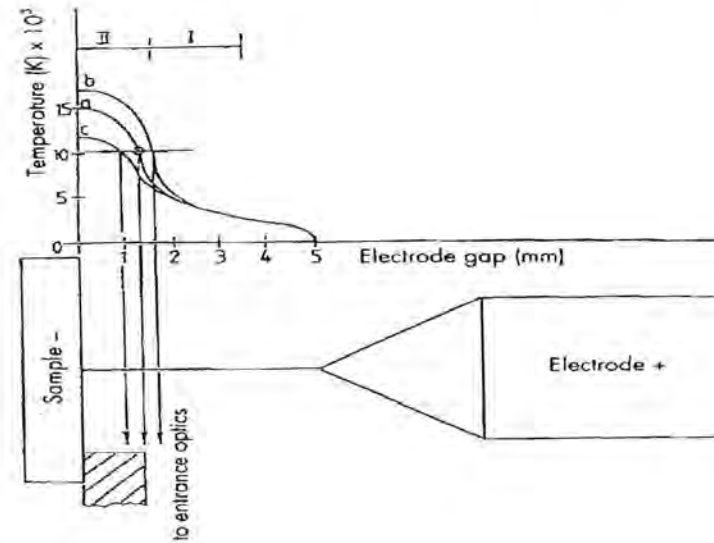


Fig. 6.2 Displacement of location of optimum excitation 1= Atom lines; 11 = Ion lines [8].

6.4 Background correction

In optical systems, which only have, one background slit the intensities of the analytical lines and the background were measured simultaneously. In doing so it was assumed that the background in the background below the analytical lines and the background in the background slit could be reciprocally converted by a factor k [6].

The result was:

$$I_N = I_{EL} - KI_U$$

I_N = Nett Intensity

I_{EL} = Intensity in the channel of the analytical line

KI_U = Background intensity

6.5 *Measurement values for the analytical data*

Once all intensities have been measured by the spectrometer, readings of the measurement capacitors for the analytical channels taken, and analogue signals converted into digital forms, the process of calculating concentrations from intensities takes place. These processes are carried out in a number of steps [6].

6.5.1 *Intensity ratio*

The intensities obtained are usually ratioed to the reference material. This acts as an internal standardisation. It provides compensation for small changes in the spectrometer during the measuring cycle and from measurement to measurement. These changes could be due to variances in the excitation energy of the source, to condensate collecting in the light path and to the window or lens becoming dirty. The typical intensity of the reference was used as a multiplier in order to obtain a specific order of magnitude for the intensity ratios, therefore dealing with whole numbers rather than decimals [6]. The typical intensity is the intensity of the internal standard line (matrix element).

$$\text{Intensity Ratio} = (I_{\text{an}} / I_{\text{ref}}) \times \text{typical } I_{\text{ref}}$$

I_{an} = Intensity of the analyte

I_{ref} = Intensity of the reference

In cases of samples that significantly influence the spectrum background, a background correction could be applied. The differences in the sensitivity of the analysis channel and the background channel can be compensated for by using matching variables. In doing so, the difference between the intensities of the analysis channel and background channel is determined.

6.5.2 Corrected intensity ratio

The effect of the inter element interferences are corrected for. These effects are additive, caused by line interferences or multiplicative corrections caused by inter element / matrix effect [7]. The additive effect caused by line interference is due to light from a spectral line of another element entering the exit slit of the analytical line of interest. This occurs if the two wavelengths are very close together. Spectral lines should be carefully selected to prevent this, however this is not always possible. Inter element corrections can be made to overcome the problem if there is no alternative.

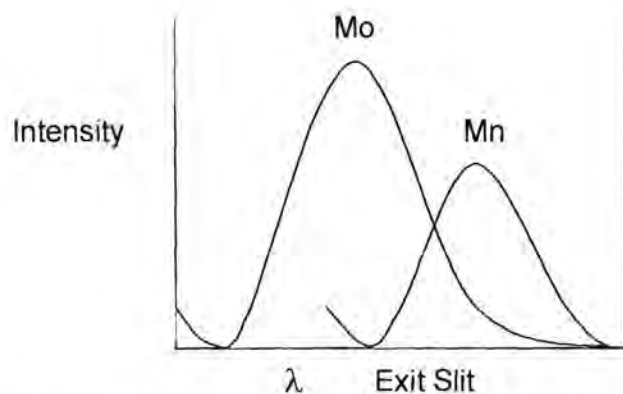


Fig. 6.3 Light of Mn causing interference at the Mo exit slit [7].

The multiplicative effect is caused by matrix effects, which are caused by the physical and chemical nature of the sample. In Fig. 6.3, 102 the intensity of the Mn has to be subtracted from the Mo intensity to correct the calibration standards, which contain Mn on to the calibration curve.

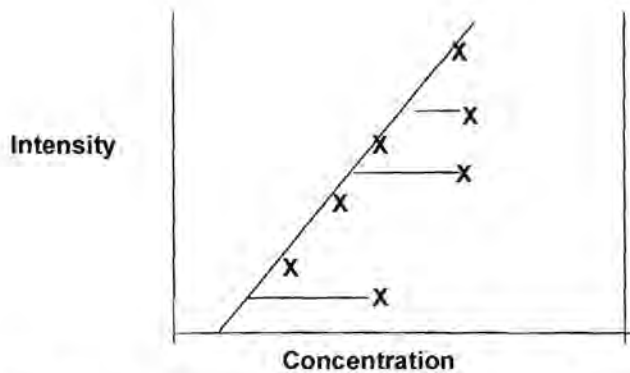


Fig. 6.4 Corrected Intensity calibration curve[7].

6.5.3 Recalibration

The additive and / or multiplicative changes in the sensitivity of the spectrometer (drift) brought about displacements of the calibration curves in the linear scale of the co-ordinate system. To avoid the need for regular new calibrations of the spectrometer it is necessary to follow a procedure, which on the basis of a few samples and mathematical calculations, restores the state of the spectrometer by calculations during the calibrations and corrects for any drift correction. This process is known as recalibration, but is also termed standardisation. The samples, known as recalibration samples, were measured during calibration of the spectrometer. The calibration samples were no longer required for daily analysis. The recalibration samples were to adjust the intensity ratios (actual value) measured "today" to those measured at the time of calibration (nominal value) to compensate for any instrumental drift.

For each calibration curve, a low sample (LS) with low concentration and a high sample (HS) with high concentration were measured in a two-point calibration. For back calculation of the data obtained from the recalibration sample to the nominal state of the spectrometer, a factor was calculated from the ratios of the nominal values to the actual values. The offset shows changes in the zero point. On completion of the recalibration / standardisation, the factor and offset for all analysis channels were stored. These were the basis for subsequent corrections of the measurement values with respect to the nominal state of the spectrometer.

$$\text{Factor} = \frac{\text{Int. HS}_{\text{nom}} - \text{Int. LS}_{\text{nom}}}{\text{Int. HS}_{\text{act}} - \text{Int. LS}_{\text{act}}}$$

$$\text{Offset} = \frac{\text{Int. HS}_{\text{act}} * \text{Int. LS}_{\text{nom}} - \text{Int. HS}_{\text{nom}} * \text{Int. LS}_{\text{act}}}{\text{Int. HS}_{\text{act}} - \text{Int. LS}_{\text{act}}}$$

Using the formula:

Factor = change of the slope of the curve

Offset = parallel drift of the calibration curve

The standardisation intensity ratios were calculated as follows:

Standardisation intensity ratio = Intensity ratio * F + offset.

6.5.4 Concentration calculation

In metal analysis with spark discharge optical emission, the matrix / base element is often used as the reference and for this reason concentration and ratio and intensity ratios were used in this study. The concentration of the matrix element / base element was not calculated by the calibration curve, but was obtained by deducting the sum of the analysed elements from 100 % of the matrix element, on the assumption that all the elements present had been determined. The following equation applies [6]:

$$\sum C_{\text{an}} + C_{\text{b}} = 100 \%$$

C_{an} = Concentration of the analysed element

C_{b} = Concentration of the base element

The concentration of the base element could be obtained by rearranging the equation and taking account of the fact that the concentration ratio of the base to itself was 1 [6]:

$$C_b = 100 \% / 1 + \sum C_{an} / C_b$$

The formula to obtain the concentrations of the analyte from the ratios:

$$C_{an} = C_b \cdot C_{an} / C_b$$

If some analytes (usually those precipitated) were calibrated in absolute values, without a reference, the sum of the analytes (C_{abs}) must be subtracted from the 100 % calculation for the other analytes. The calculation formula to determine the analyte concentration must therefore be modified [6]:

$$C_{an} = (100 - C_{abs}) / (100/1 + \sum C_{an} / C_b) / C_{an} / C_b$$

The relationship between the Intensity ratio and concentration of the calibration sample was mathematically determined during calibration of the spectrometer. By means of the regression calculation, the optimum mathematical polynomial function (first, second or third degree), for all concentration was automatically calculated. For low concentrations the calibration is usually a linear relationship (1ST degree). To calculate the analyte concentration (c), the recalibrated intensity ratio of the required analysis channel (IR) was introduced into the polynomial function:

$$C = a_3 \cdot (IR)^3 + a_2 \cdot (IR)^2 + a_1 \cdot (IR) + a_0$$

Where a_3 , a_2 , a_1 and a_0 are the coefficients of the polynomial function.

6.6 References

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Chapter 7

Results

7.1 Optimisation of parameters

7.1.1 High Energy Pre-Spark

Samples were sparked and parameters were kept constant. During the process samples had to be pressed again as material disintegrated when sparking and created source problems.

Table 7. 1 Intensities of Sample 7 sparked

Seconds	Pt	Pd	Au	Rh	Ir	Os
1	18997	16106	39217	34256	314	7680
2	19909	16183	41855	84190	396	7902
3	29316	23293	60870	121982	586	11893
4	40561	31791	79022	172761	866	15930
5	52901	38745	104330	204569	973	21123
6	60255	45454	123290	236265	1247	25189
7	70256	52018	143184	280135	1368	30353
8	85281	60252	162821	322111	1536	32607
9	90587	66172	182409	346259	1781	35832
10	101370	72944	204097	386193	1965	40903

Table 7.1 Continued. Intensities of Sample 7 sparked

Seconds	Ag	Pb	Zn	Mn	Ti	Cr
1	49677	3091	48718	9552	15720	30202
2	75034	4202	58245	11875	15368	30062
3	104766	5999	73380	17825	22134	43186
4	137110	16601	90037	23392	29483	58228
5	155139	120807	101282	29851	37073	72048
6	183697	15003	112299	35145	43174	82975
7	209639	14360	128655	38434	49924	92646
8	229709	15304	126696	45591	58432	108434
9	269770	17420	148515	48088	62688	118558
10	267941	16539	146493	53314	69287	128761

Table 7.2 Intensities of Sample 8 sparked

Seconds	Cu	Fe	Te	As	Al	Na
1	372068	10959	454	6776	26397	333936
2	438065	21523	600	9211	46730	752031
3	440082	28497	1053	11298	57393	950303
4	496293	33889	1404	16214	82204	1299000
5	527811	42930	1532	18699	83297	1398000
6	584068	50113	1445	20414	97151	1490000
7	629454	59901	2269	24220	101184	1405000
8	710119	73969	2129	28707	138965	1509000
9	737609	74519	2434	30993	132628	1593000
10	798631	82210	2650	34533	138393	1616000

Table 7.2 Continued. Intensities of Sample 8 sparked

Seconds	Ca	Si	Mg	Mo	Sn	Co
1	105613	23634	105466	30587	1346	4422
2	208713	27526	200771	60413	2497	13740
3	290214	37413	250500	82441	3255	20529
4	387243	41102	313486	114349	4389	29134
5	455269	41032	352751	135354	5038	37666
6	548502	44040	396411	164889	6658	45931
7	624099	47588	421945	190052	8326	56751
8	744912	52754	477781	231268	9579	65435
9	826967	56145	522461	246024	11551	73858
10	912861	58407	546634	278720	13169	84283

Four samples were sparked without using the prespark conditions. Two samples containing different concentrations of each element were sparked (elements and concentrations as described in Chapter 5, 5.3.2, 85). Two samples of each element range were used to confirm any trends. The capacitance in each instance was changed and the intensity recorded. In the second instance the inductance, was changed and the sample sparked and the intensities recorded.

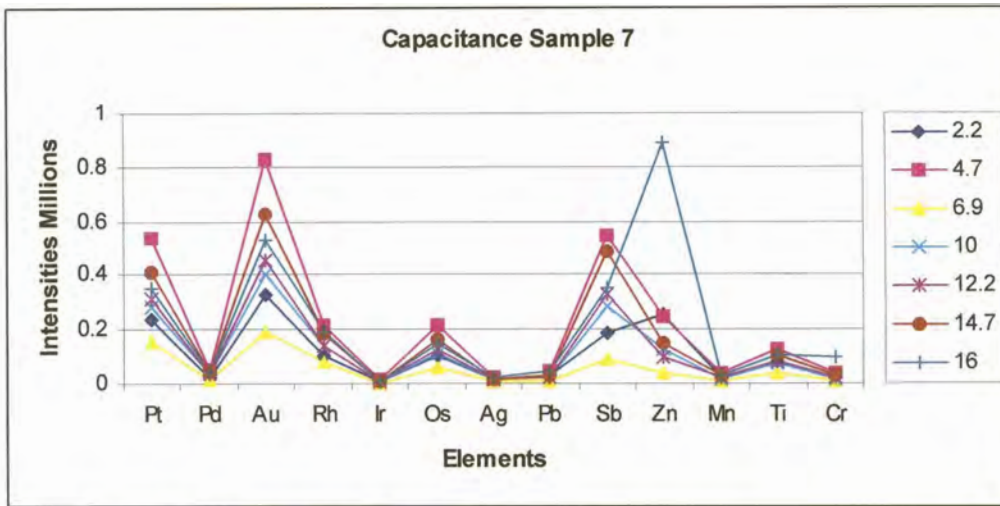


Fig. 7.1 Sample 7 Capacitance in μF variations

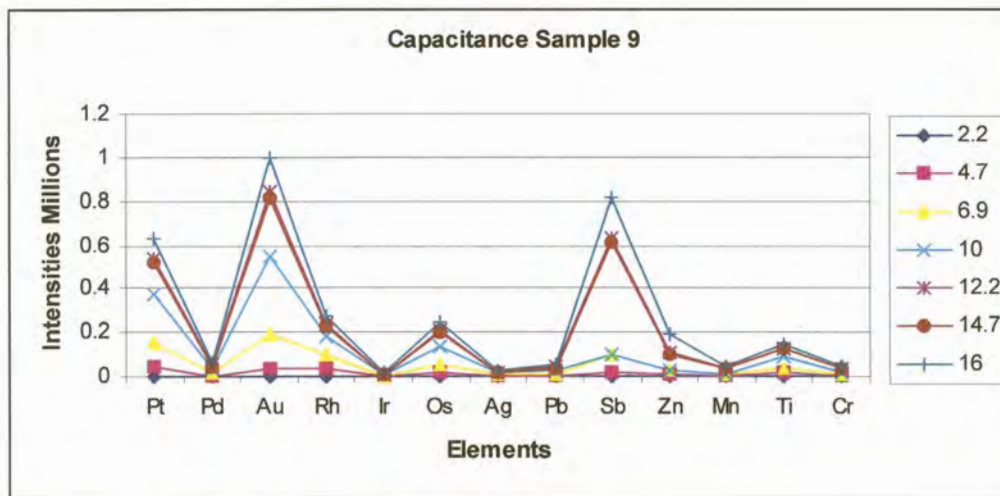


Fig. 7.2 Sample 9 Capacitance in μF variations

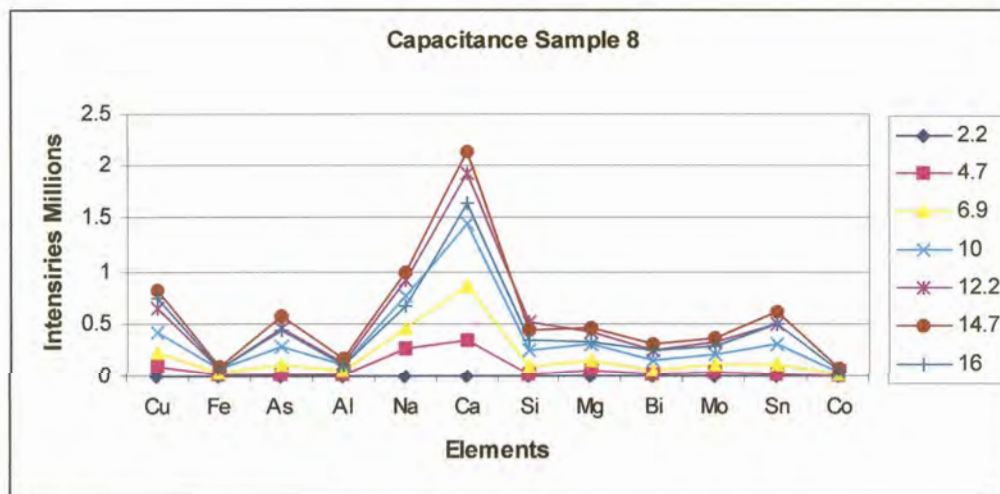


Fig. 7.3 Sample 8 Capacitance in μF variations

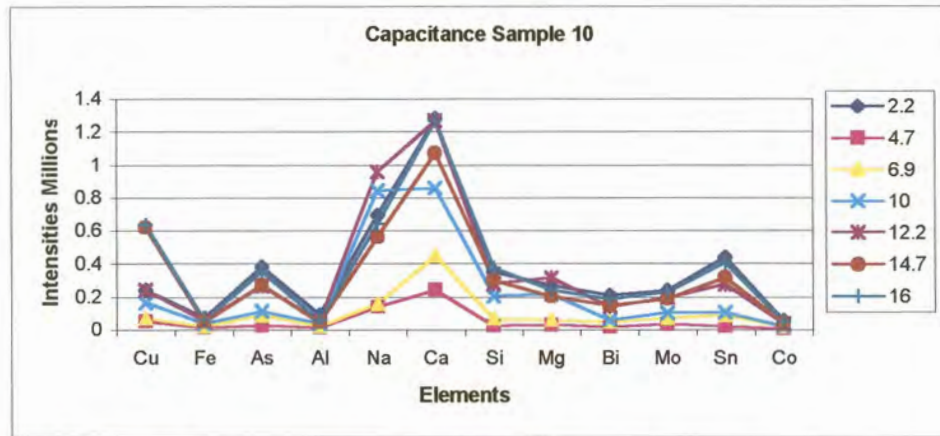


Fig. 7.4 Sample 10 Capacitance in μF variations

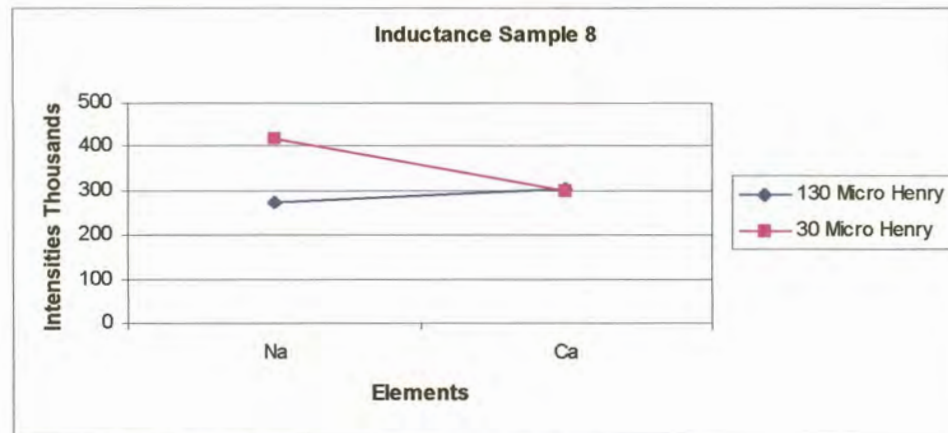


Fig. 7.5 Sample 8 Inductance in μH variations for Na and Ca

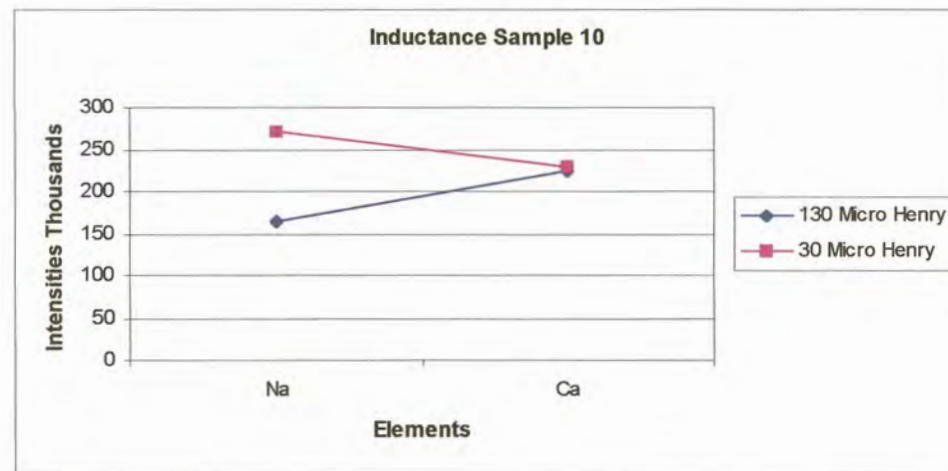


Fig. 7.6 Sample 10 Inductance in μH variations for Na and Ca

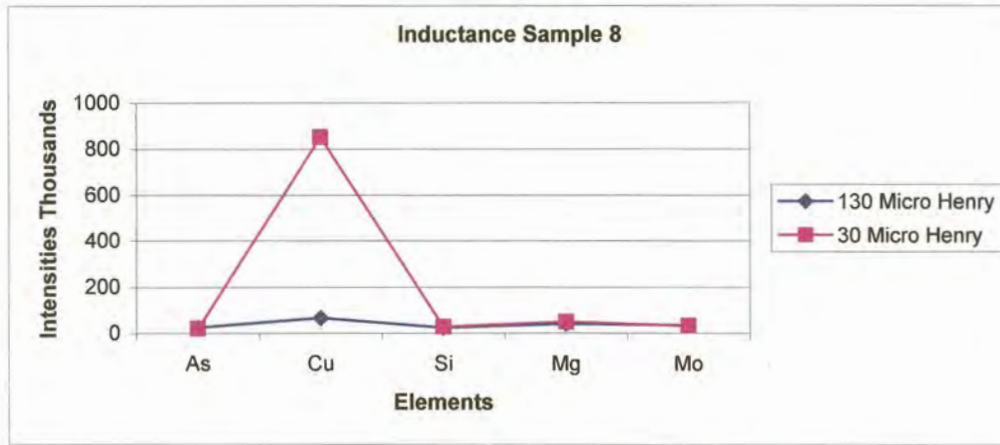


Fig. 7.7 Sample 8 Inductance in μH variations for As, Cu, Si, Mg and Mo

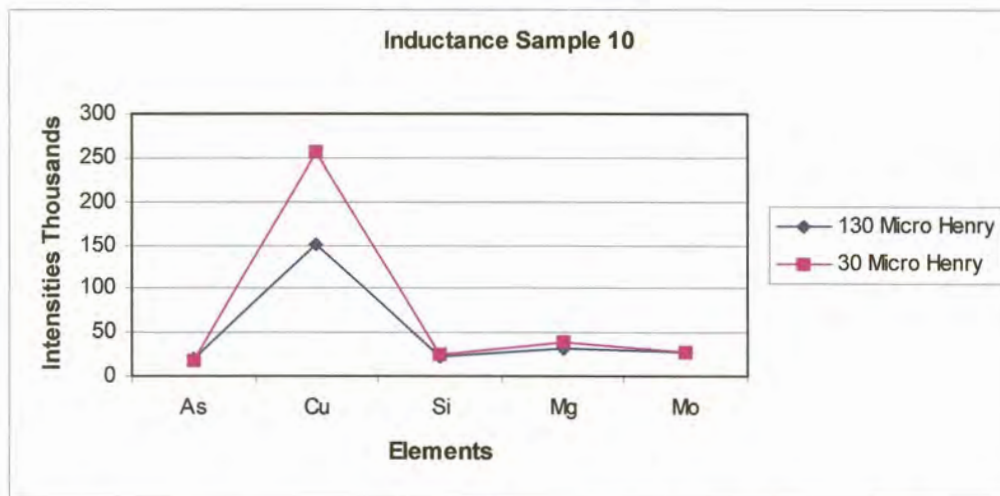


Fig. 7.8 Sample 10 Inductance in μH variations for As, Cu, Si, Mg and Mo

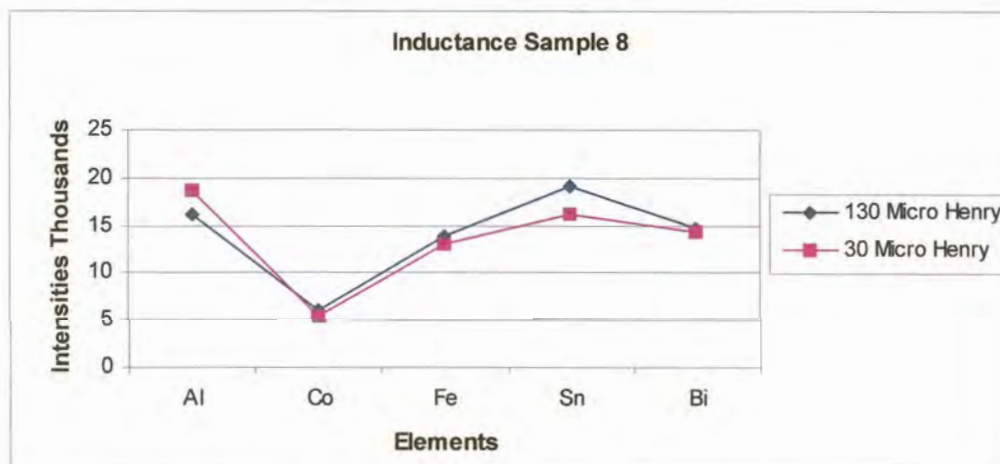


Fig. 7.9 Sample 8 Inductance in μH variations for Al, Ca, Fe, Sn and Bi

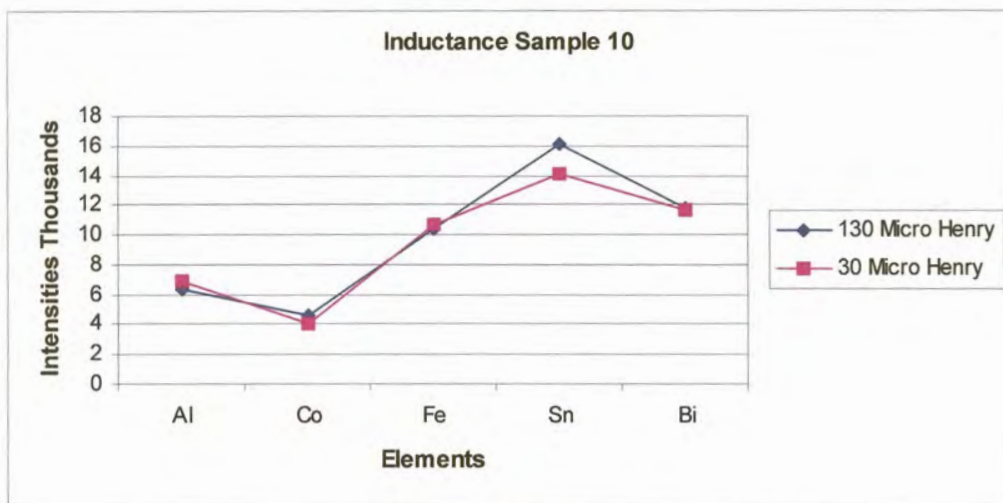


Fig. 7.10 Sample 10 Inductance in μH variations for Al, Co, Fe, Sn and Bi

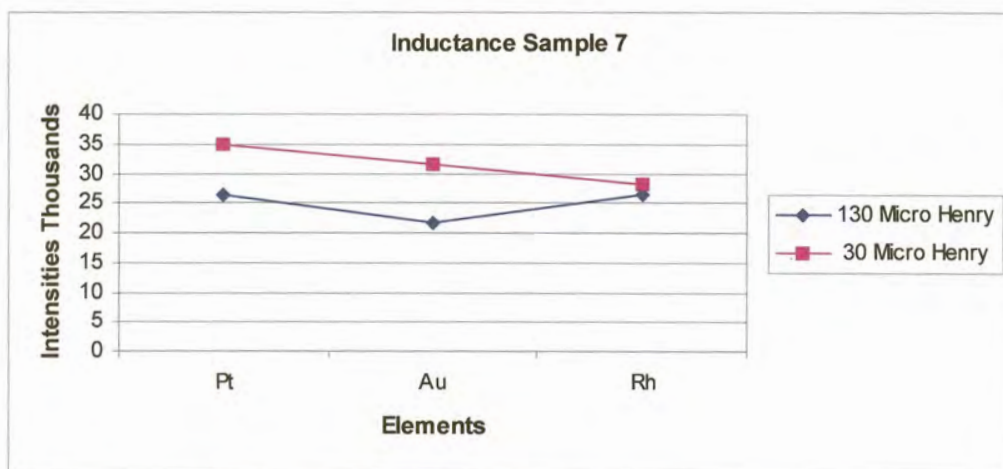


Fig. 7.11 Sample 7 Induction in μH variations for Pt, Au and Rh

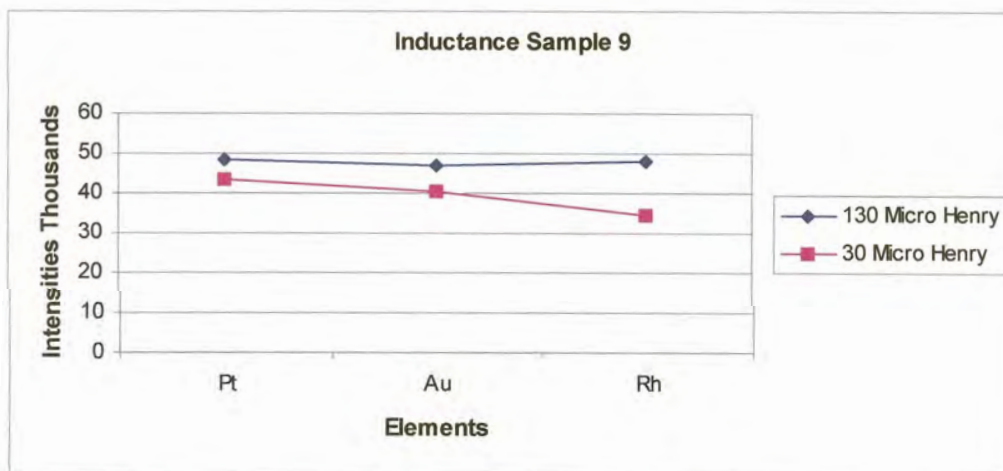


Fig. 7.12 Sample 9 Induction in μH variations for Pt, Au and Rh

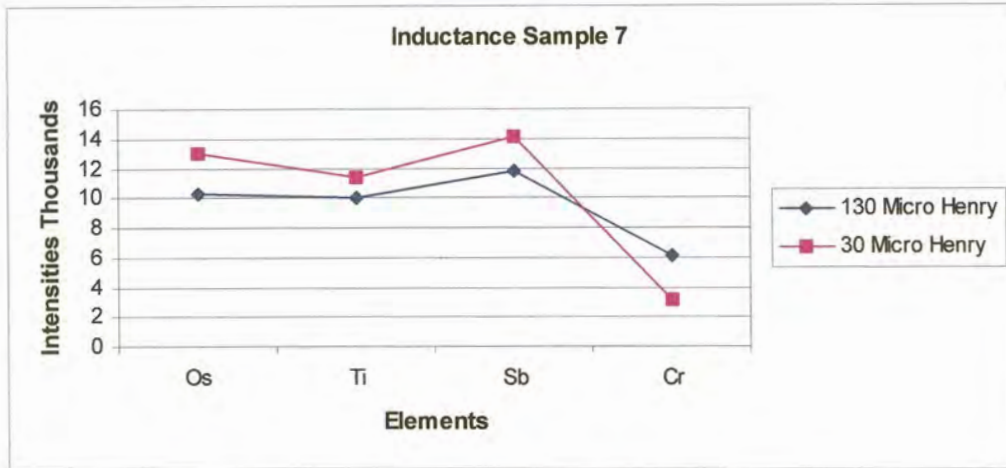


Fig. 7.13 Sample 7 Induction in μH variations for Os, Ti, Sb and Cr

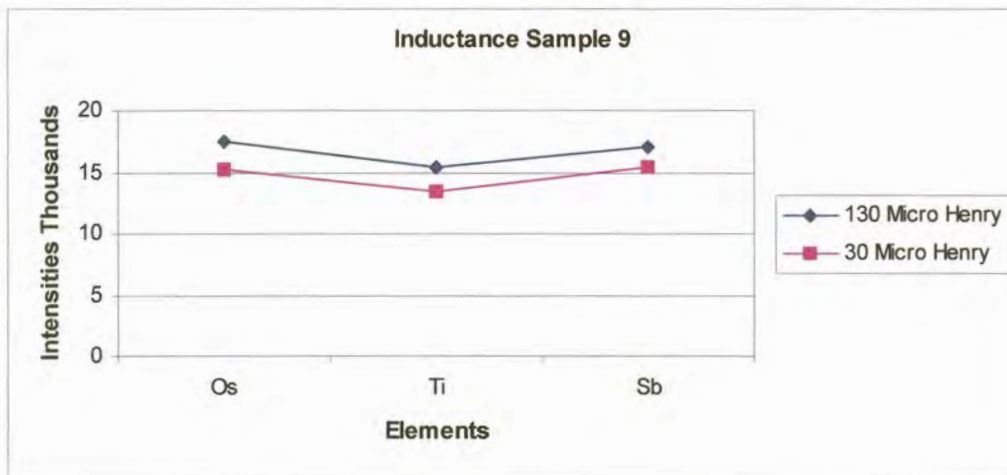


Fig. 7.14 Sample 9 Induction in μH variations for Os, Ti, and Sb

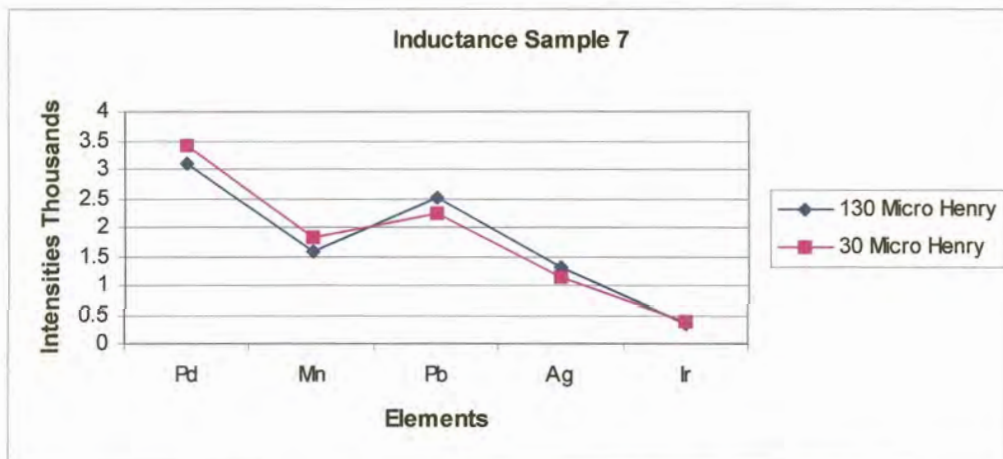


Fig. 7.15 Sample 7 Induction in μH variations for Pd, Mn, Pb, Ag and Ir

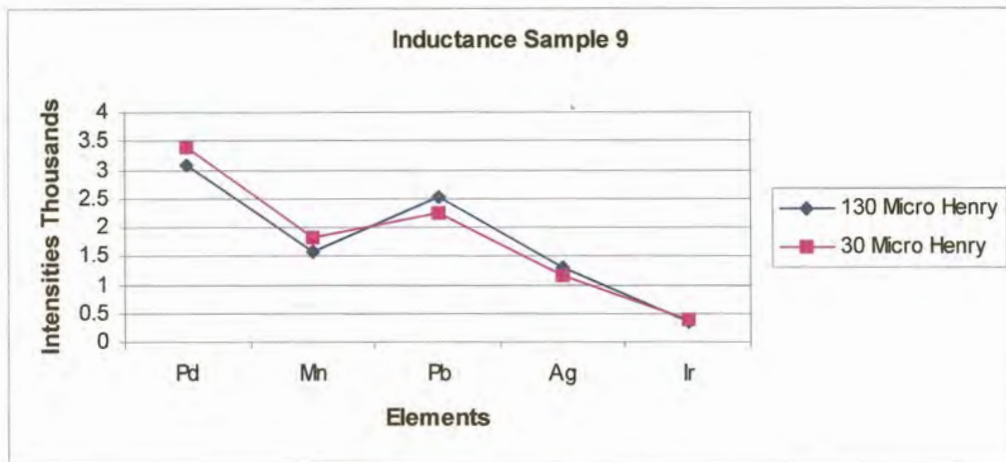


Fig. 7.16 Sample 9 Induction in μH variations for Pd, Mn, Pb, Ag and Ir

7.1.2 Effect of integration time

Sample 7 and 8 were sparked using different integration times. Sample 8 was sparked once for 10 seconds, then once for 3 seconds using SAFT conditions, twice for 3 seconds and then three times for 3 seconds integration time. The two and three times integration cycles took place during the same single spark sequence. Sample 7 was conducted the same way; except that the first spark was twice for 5 seconds instead of once for 10 seconds. The square of s , is known as the variance: $s = \sqrt{s^2}$. The % relative standard deviation (% RSD) of a set of observations is the positive square root of the variance of the observations and is given by $100 s/x$ (also refer to as the coefficient of variance)

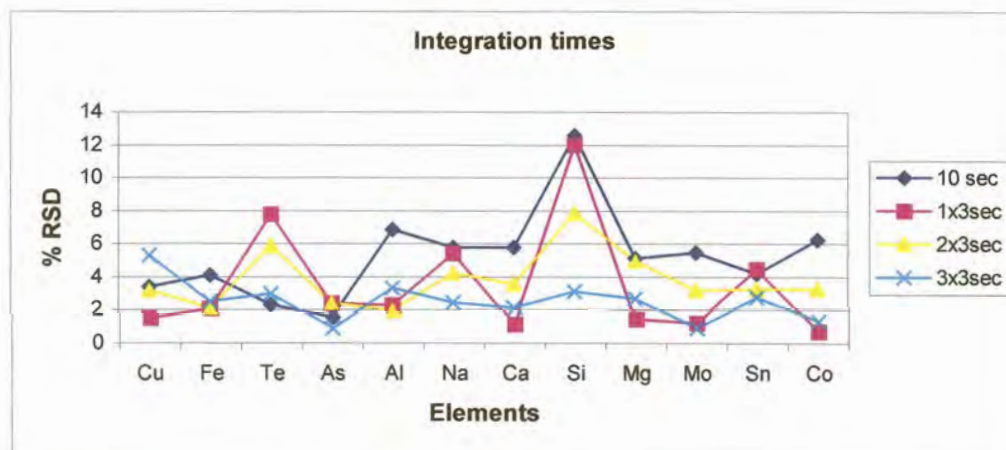


Fig. 7.17 Different Integration time Sample 8

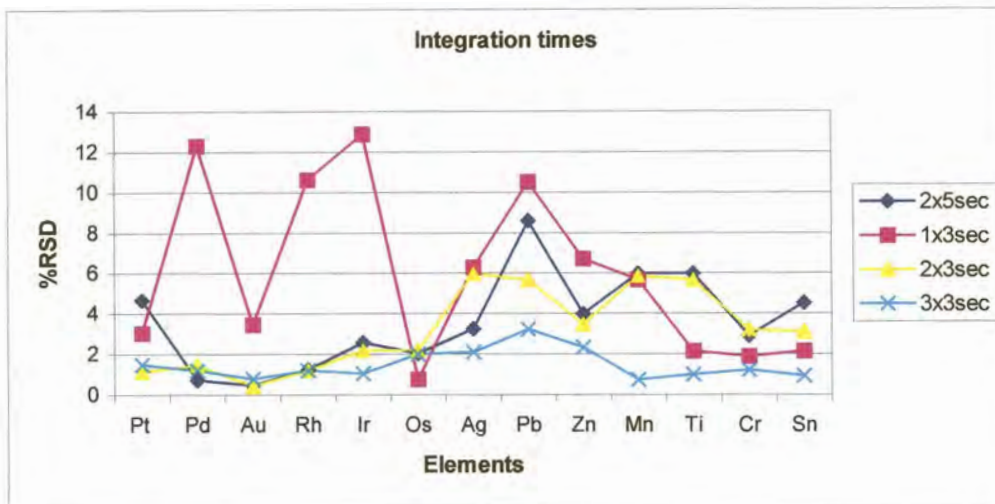


Fig. 7.18 Different Integration times Sample 7

7.1.3 Effect of different gating parameters

Sample 7 and 9 contained the same elements in different concentrations likewise sample 8 and 10. Sample 8 contained the following concentrations in ppm: Fe 200, Na 200, Ca 200, Si 200, Cu 85, Al 200, Mg 200, Te 100, As 100, Bi 100, Mo 100, Sn 50 and Co 50. Sample 7 contained the following concentrations in ppm levels: Pt 200, Pd 200, Rh 200, Ir 200, Au 200, Os 120, Ag 200, Zn 200, Pb 100, Sb 100, Mn 100, Ti 100, Cr 100.

Two samples were analysed to confirm any trends. Signal to background ratios were plotted against the “delayed time”. The background intensity is subtracted from the sample intensity and divided by the background intensity to obtain a signal to background ratio. Intensities are not plotted against the delay time to ensure that any difference in background at the various delay times are corrected for. Parameter changes of the resistance at 1 Ω and 15 Ω were compared. The delay times are measured in microseconds.

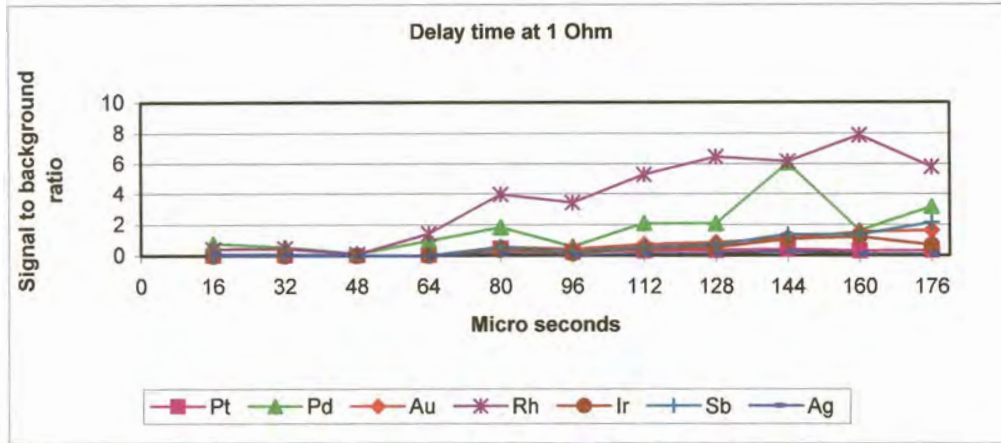


Fig. 7.19 Sample 7 -1 Ω

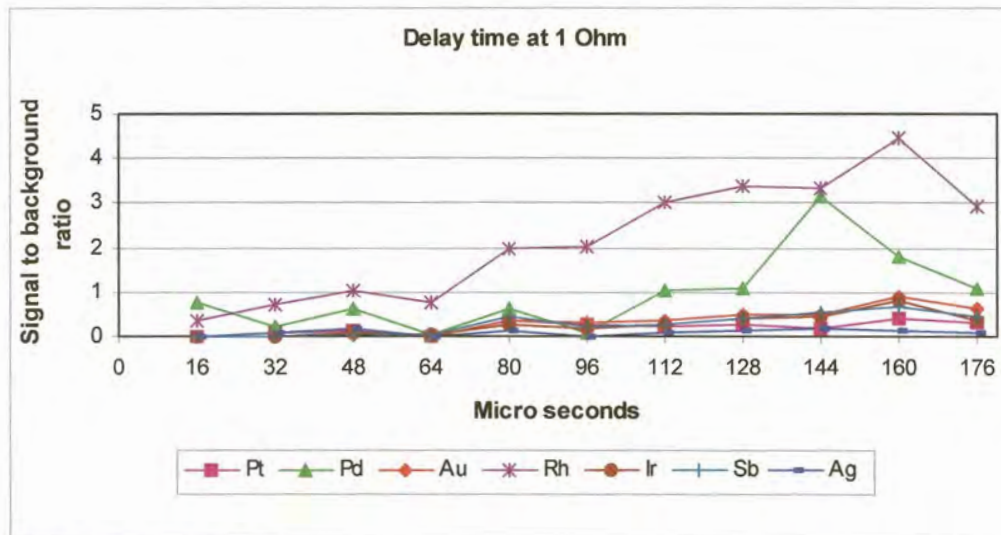


Fig. 7.20 Sample 9 - 1 Ω

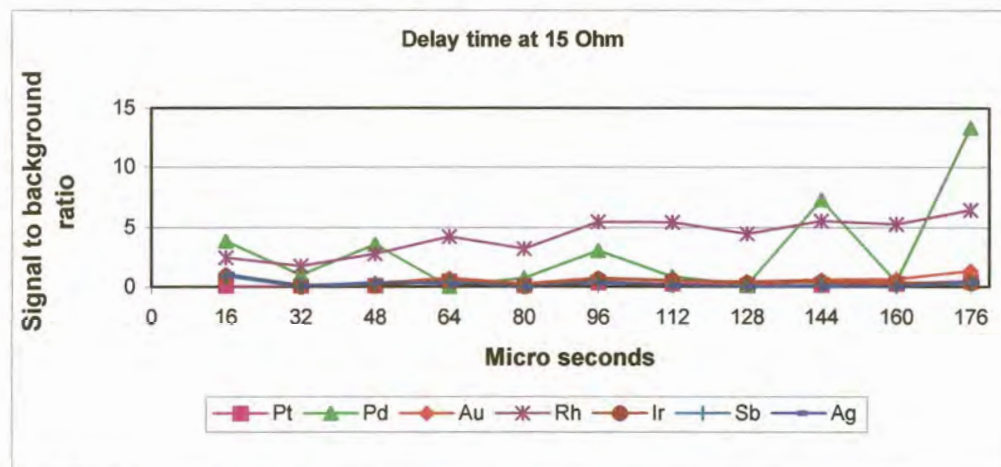


Fig. 7.21 Sample 7 - 15 Ω

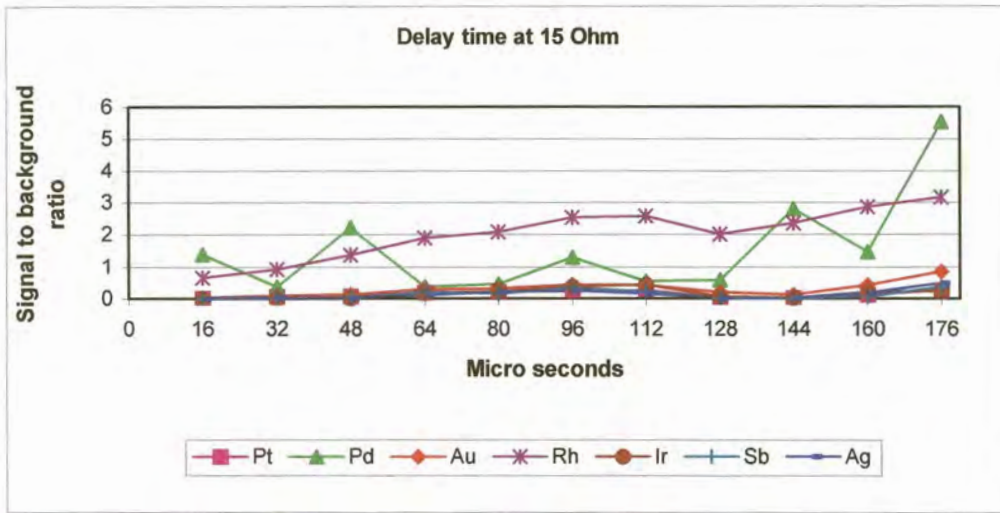


Fig. 7.22 Sample 9 – 15 Ω

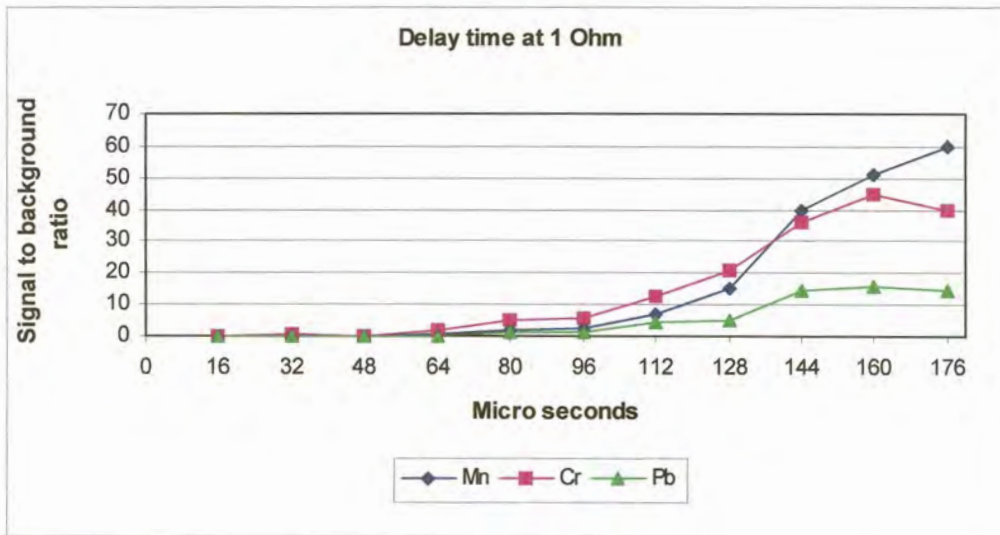


Fig. 7.23 Sample 7 - 1 Ω

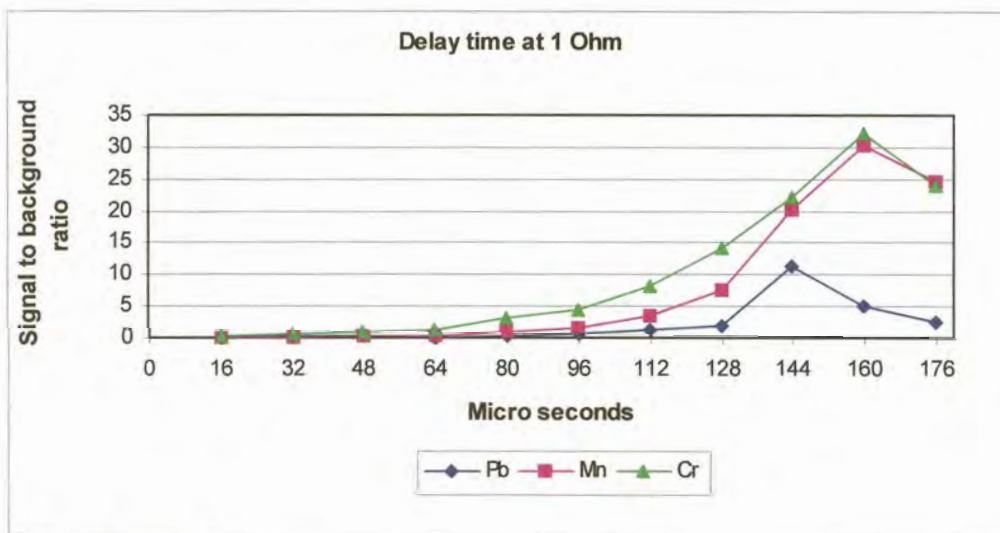


Fig. 7.24 Sample 9 – 1 Ω

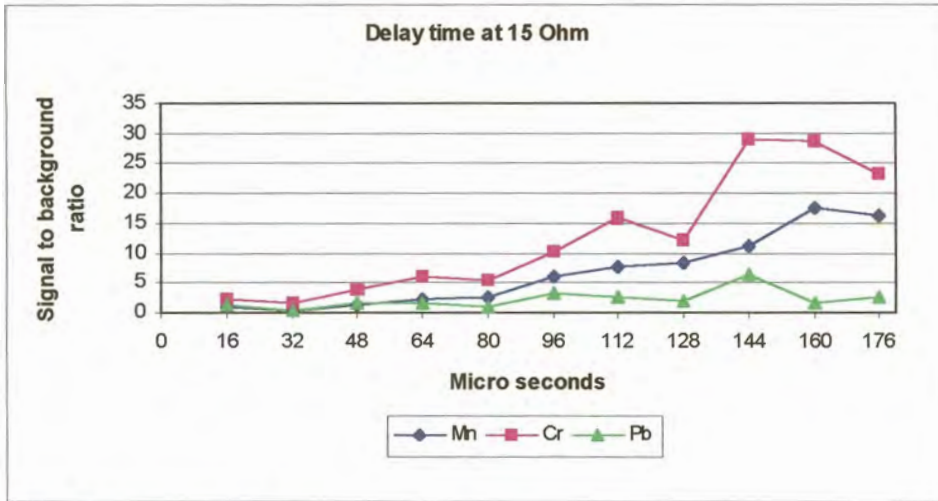


Fig. 7.25 Sample 7 – 15 Ω

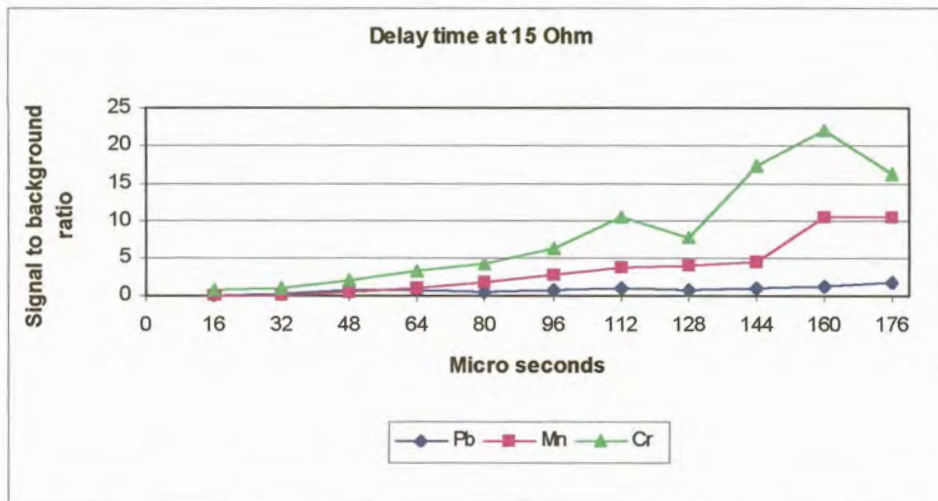


Fig. 7.26 Sample 9 – 15 Ω

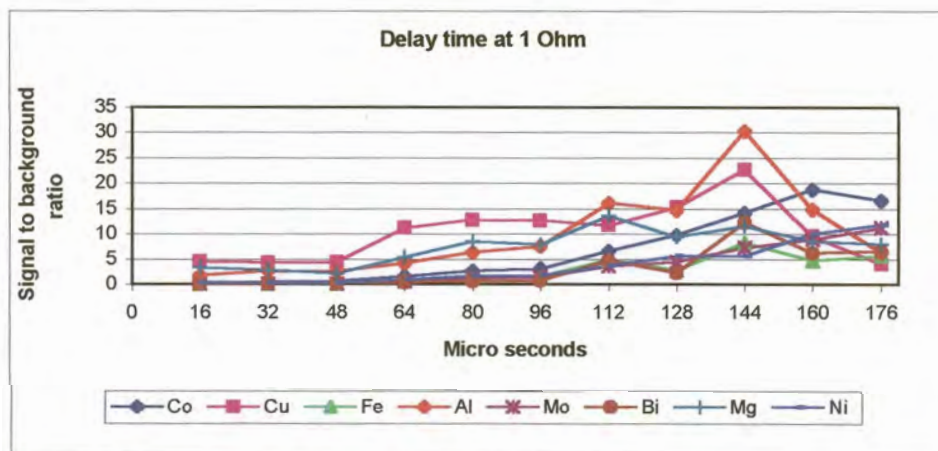


Fig. 7.27 Sample 8 – 1 Ω

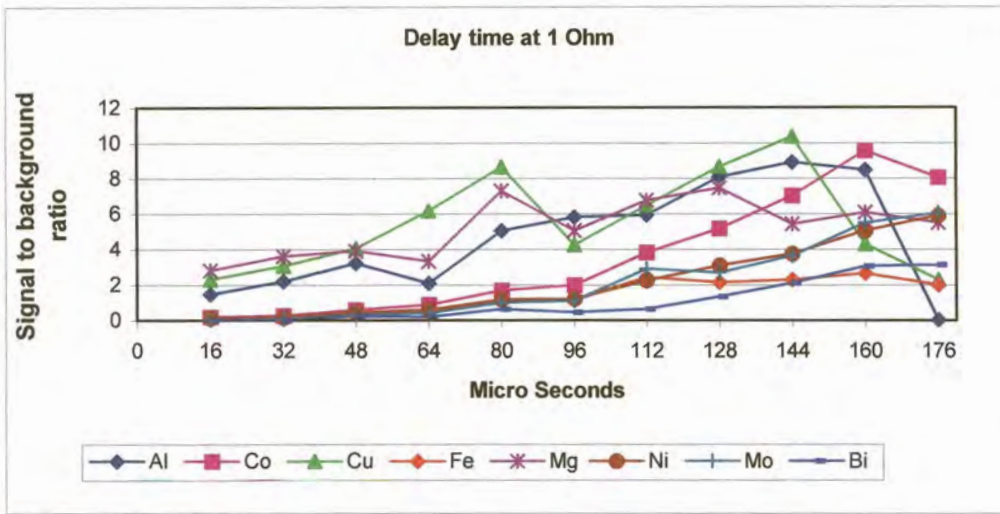


Fig. 7.28 Sample 10 – 1 Ω

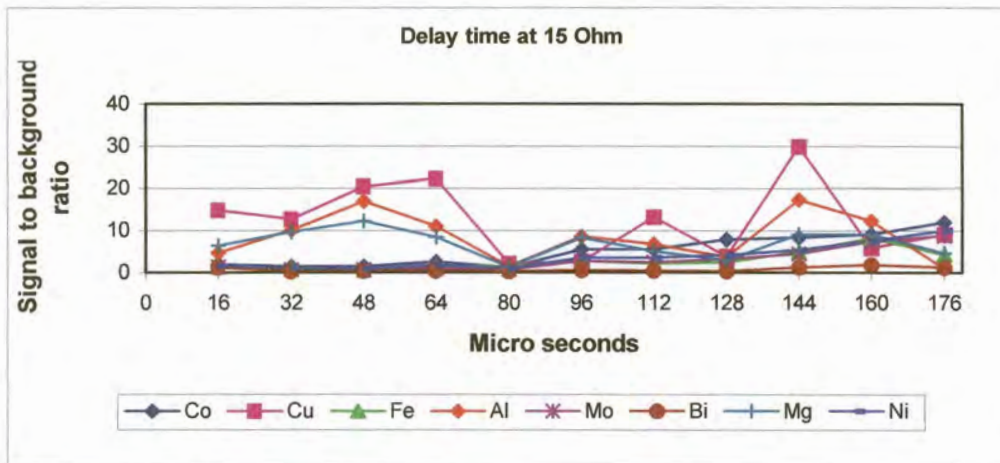


Fig. 7.29 Sample 8 – 15 Ω

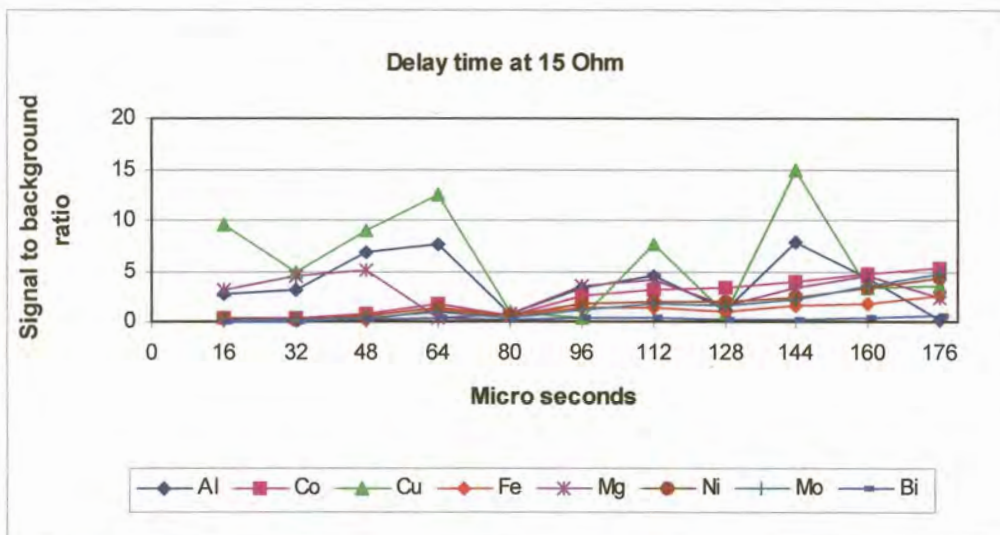


Fig. 7.30 Sample 10 – 15 Ω

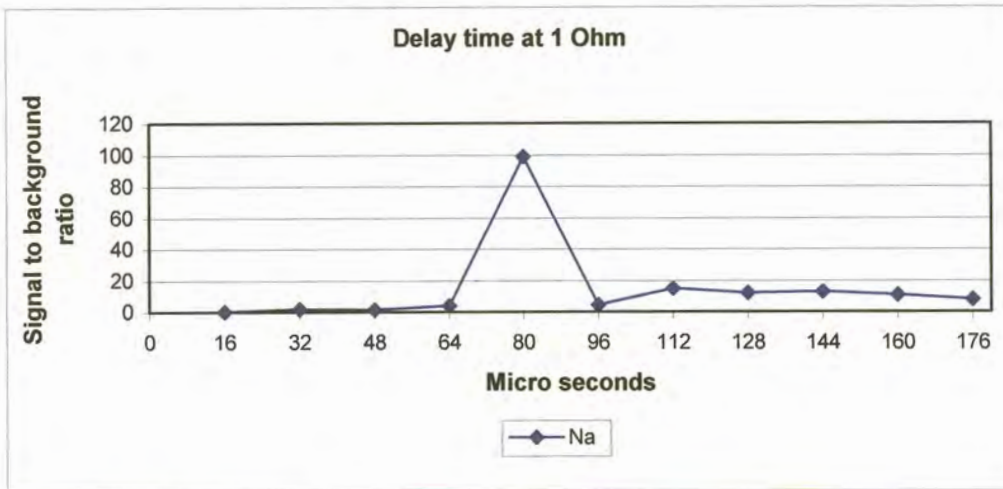


Fig. 7.31 Sample 8 -1 Ω

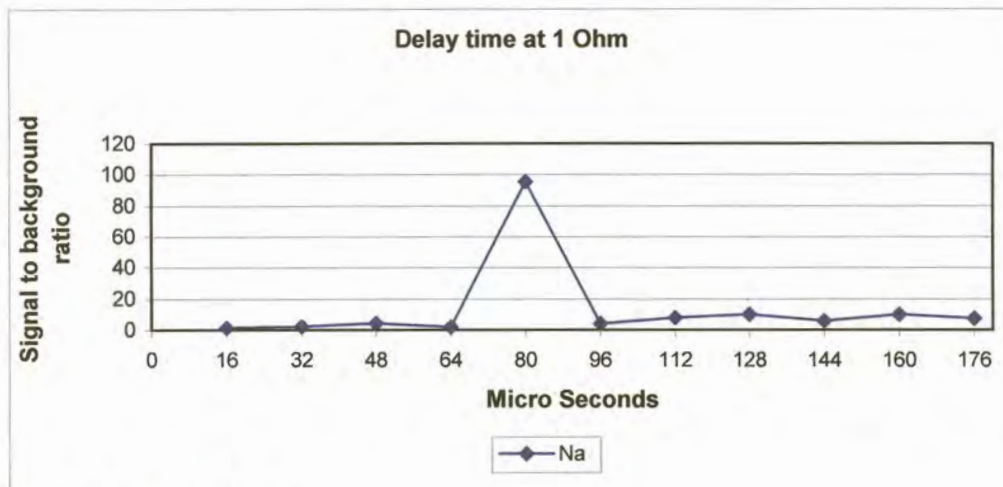


Fig. 7.32 Sample 10 -1 Ω

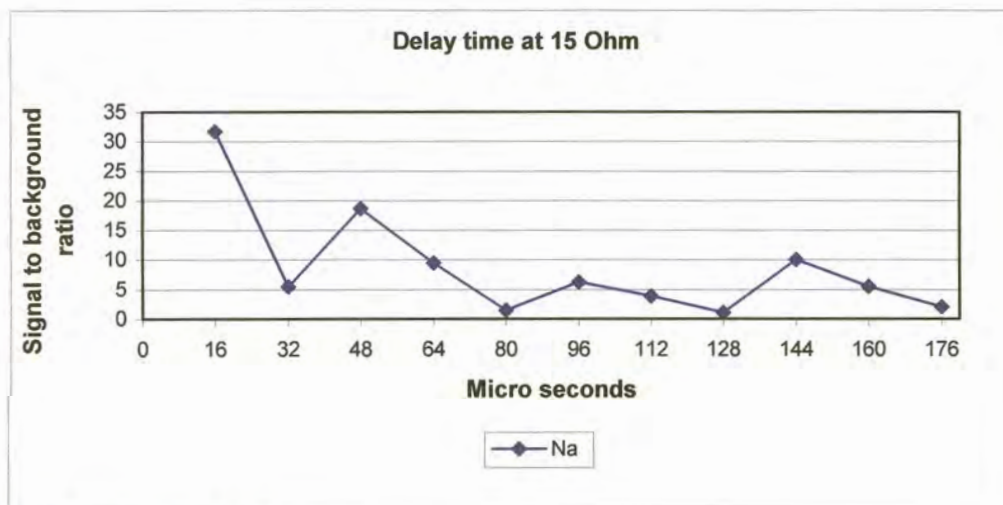


Fig. 7.33 Sample 8 -15 Ω

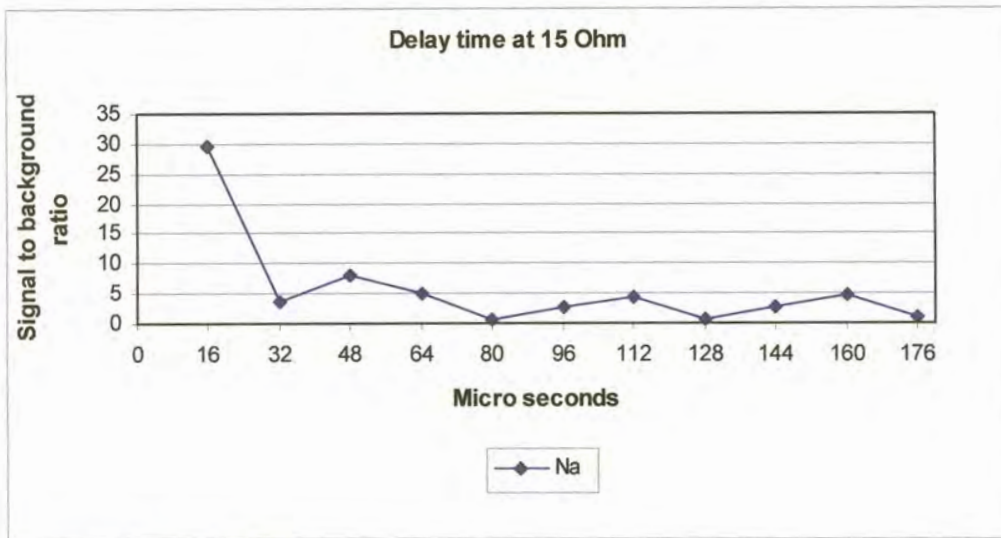


Fig. 7.34 Sample 10-15 Ω

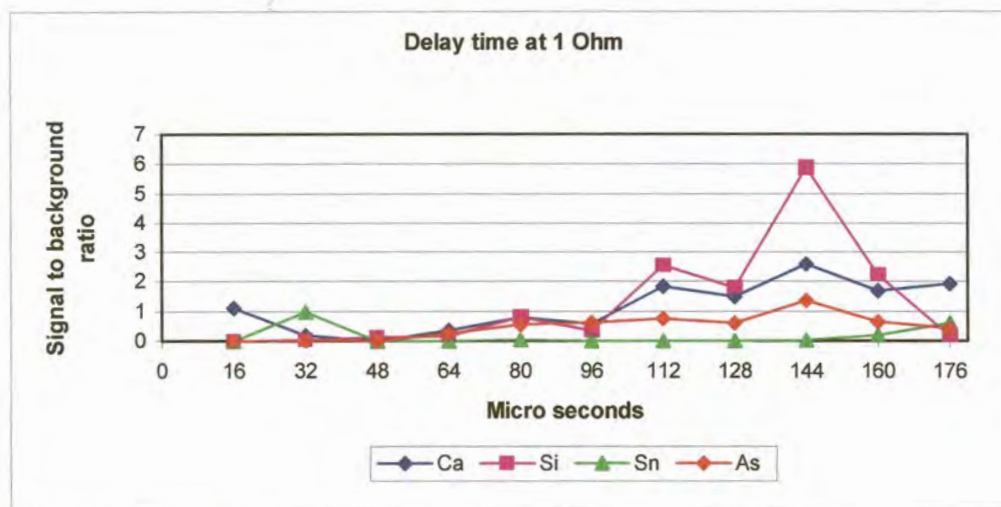


Fig. 7.35 Sample 8 -1 Ω

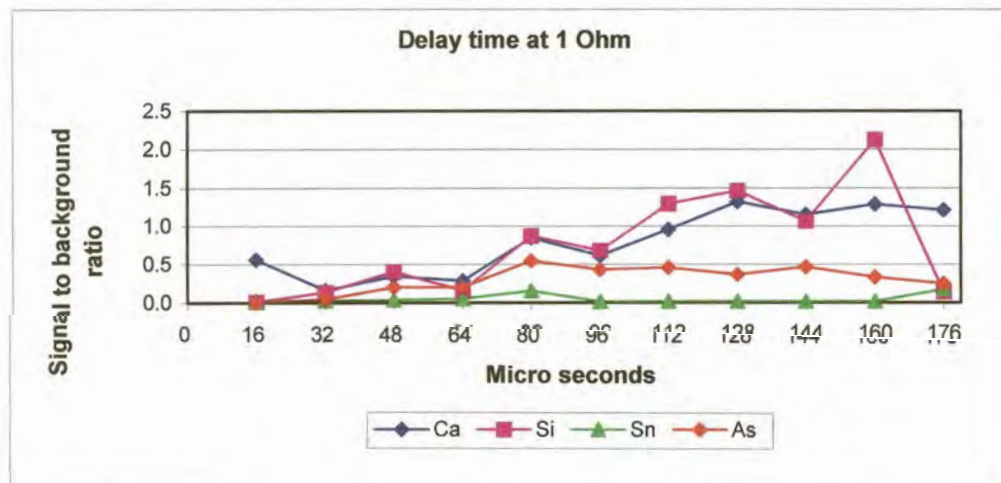


Fig. 7.36 Sample 10 -1 Ω

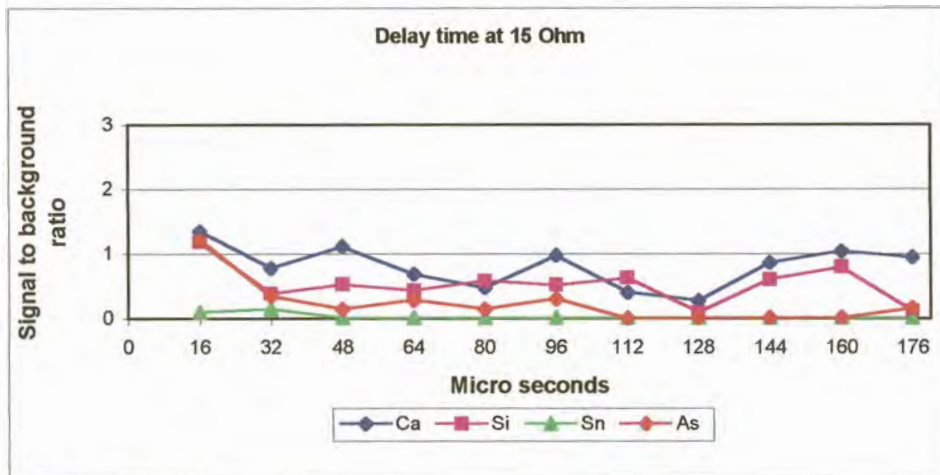


Fig. 7.37 Sample 8 – 15 Ω

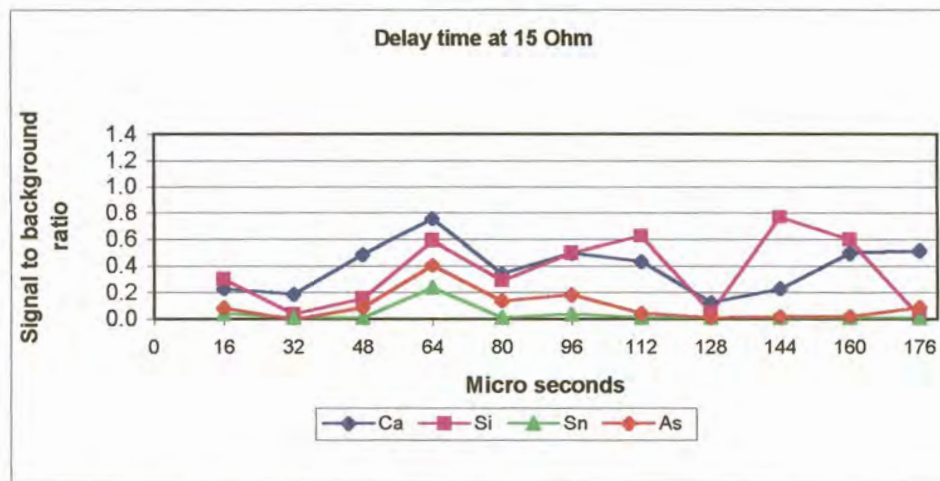


Fig. 7.38 Sample 10 -15 Ω

7.1.4 Internal standardisation

The Intensity ratio of the analytical line to the reference line was generally plotted against the concentration ratio of the analyte to the reference element. In this case it was Ruthenium. Ruthenium as a reference line is not available in the in the Ultra violet region, there are no Ruthenium lines available in this region. A background position at the 310-nanometer wavelength is used in this optical system as the internal standard and the analytical line is ratioed to this background position.

7.1.5 Analytical gap

Samples 9 and 10 were sparked using the same conditions changing only the gap between the sample and the electrode to 3 mm and 4 mm. The signal to background ratio was recorded. All the analytical lines are atom lines.

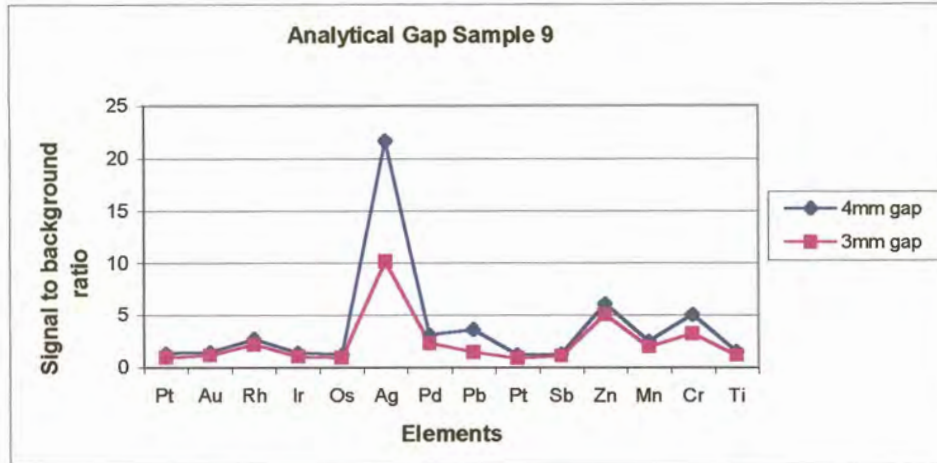


Fig. 7.39 Analytical gap between the sample and electrode for sample 9

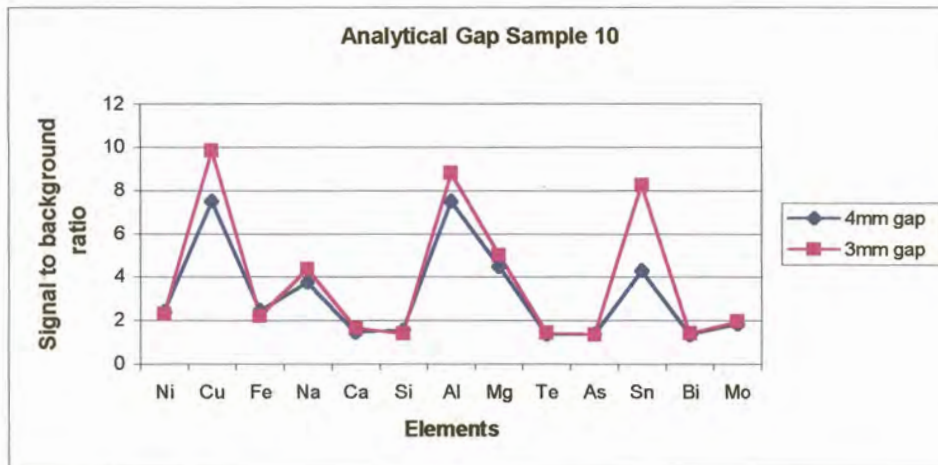


Fig. 7.40 Analytical gap between the sample and the electrode for sample 10

7.1.6 Contamination from other base material

Table 7.3

Pure Pt, Pd and Ru sample is sparked on the same base plate, monitoring the element of the previous sample to evaluate how many sparks are required before a stable signal is achieved

Sample sparked	Pt	Pd	Ru
Base Plate	Ru	Ru	Ru
Monitoring element	Ru	Pt	Pd
Spark number 1	412407	577722	189787
Spark number 2	277828	368768	120182
Spark number 3	241861	301456	90914
Spark number 4	216640	300390	75427
Spark number 5	198708	269518	77213
Spark number 6	96161	210648	85465
Spark number 7	72248	194675	66175
Spark number 8	64843	193314	63236
Spark number 9	68375	214059	58833
Spark number 10	51666	214578	56065
Spark number 11	47458	213676	56101

Table 7.4

Pure Pt, Pd and Ru sample is sparked on a base plate corresponding with the pure sample, monitoring the element of the previous sample to evaluate how many sparks are required before a stable signal is achieved

Sample sparked	Pt	Pd	Ru
Base Plate	Pt	Pd	Ru
Monitoring	Ru	Pt	Pd
Spark number 1	83653	116059	53763
Spark number 2	47578	114573	45847
Spark number 3	53027	110407	36674
Spark number 4	52872	103172	36861
Spark number 5	52049	115718	34057

7.2 Calibration

The calibration graphs were established for the impurities in Ruthenium base. The elements were calibrated using the wavelength tables as in Table 7.6, 125. The conditions for calibration are recorded in Table in 7.5, 125. All the channels used were in the first order with the exception of Os 581.812, Pt 531.890, which were second order lines. All the wavelengths selected were atom lines.

Table 7.5 Conditions used for the calibration

Calibration Conditions								
	Time (s)	C (uF)	R (ohm)	L (uH)	Analytical Gap	Freq.(Hz)	Gate	Delay Time
Flush	5	0	0	0	4mm	300	64	144
SAFT	3x3	2.2	1	130	4mm	300	64	144

Table 7.6 Elements for analytical analysis and their selected wavelengths

Elements	Wavelength nm	Elements	Wavelength nm
Ag	338.289	Na	588.995
Al	396.153	Ni	361.939
As	234.984	Os	581.812
Au	267.595	Pb	405.782
Bi	306.772	Pb	283.307
Ca	422.673	Pd	340.458
Co	345.351	Rh	343.489
Cr	425.435	Sb	206.83
Cu	324.754	Si	288.16
Fe	371.994	Sn	317.502
Ir	351.364	Te	214.275
Mg	285.213	Ti	498.173
Mn	403.449	Zn	213.856
Mo	386.411	Pt	531.89

7.3 Comparison of samples analysed

Comparison of the round robin sample as analysed by the various techniques by different companies internationally. Discontinuity of the line indicates where companies did not report a result.

- A Spark Spectrometer Method to be evaluated
- B Spectrograph Company A South Africa
- C Inductively Coupled Plasma South Africa
- D Spectrograph Company B South Africa
- E Inductively Coupled Plasma Company C United Kingdom
- F Spectrograph Company D Russia
- G Spectrograph Company E United Kingdom

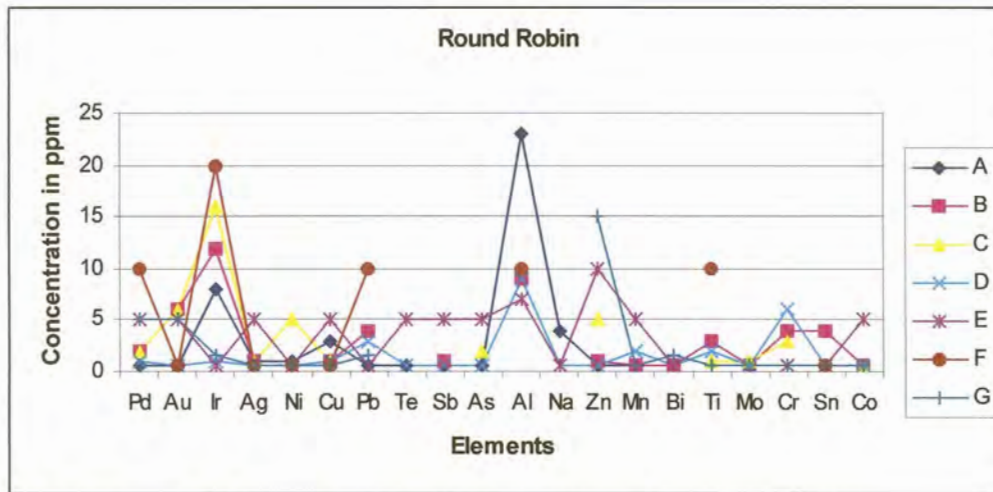


Fig 7.41 Round Robin sample analysed by seven different companies

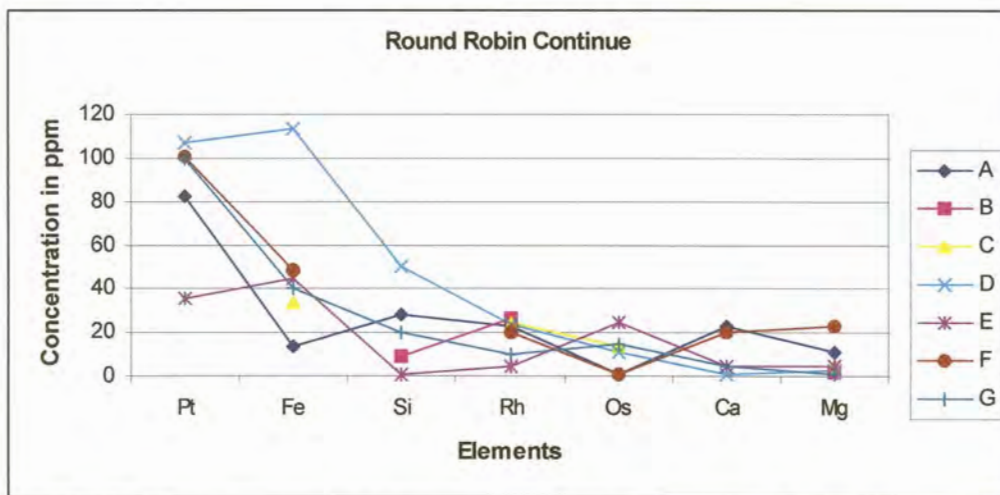


Fig 7.41 Continue. Round Robin sample analysed by seven different companies

The purpose of the analysis of ruthenium is to determine the percentage purity of the metal. The Spark spectrometer measures the concentrations of various impurities. These may vary in concentration at various positions in a single sample disc. The sum of the average of three analyses (expressed as a percentage) for all the impurities is taken. This sum is subtracted from 100 % to give the metal purity as a percentage.

The purities were compared for individual samples using the three techniques. The average is recorded and the variance of the sample s^2 used to calculate the standard deviation s .

$$\text{Sample standard deviation: } s = \sqrt{s^2}$$

The variance of the sample for n observations x_1, x_2, \dots, x_n having mean \bar{x} is defined as

$$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}$$

Table 7.7 % Purity of the Round Robin sample and the fourteen-interchange sample, including the average for each sample

	Spark	Spectrograph	ICP	Spectrograph	Spectrograph	Spectrograph	Spectrograph	
No.	A	B	C	D	E	F	G	Average
RR	99.9762	99.9912	99.9879	99.9660	99.9813	99.9724	99.9776	99.9789
1	99.9054		99.9129	99.8651				99.8945
2	99.9775		99.9791	99.9823				99.9796
3	99.9552	99.9817	99.9636	99.9581				99.9647
4	99.9855		99.9898	99.9884				99.9879
5	99.9842		99.9759	99.9730				99.9777
6	99.9792		99.9731	99.9735				99.9753
7	99.9660		99.9564	99.9268				99.9497
8	99.9748	99.9724	99.9719	99.9899				99.9773
9	99.9856	99.9865	99.9810	99.9881				99.9853
10	99.9712		99.9625	99.9722				99.9686
11	99.9852		99.9873	99.9898				99.9874
12	99.9842		99.9730	99.9759				99.9777
13	99.9792		99.9736	99.9732				99.9753
14	99.9649		99.9234	99.9580				99.9488

Table 7.8 Result of the spark analysis versus the average result from alternative techniques, the standard deviation and two sigma variance of the results

No	Spark	Average	Std. Dev.	+ 2s	- 2s	Maximum	Minimum
RR	99.9762	99.9789	0.0087	99.9963	99.9615	99.9912	99.966
1	99.9054	99.8945	0.0257	99.9459	99.8431	99.9129	99.8651
2	99.9775	99.9796	0.0024	99.9844	99.9748	99.9823	99.9775
3	99.9552	99.9647	0.0119	99.9885	99.9409	99.9817	99.9552
4	99.9855	99.9879	0.0022	99.9923	99.9835	99.9898	99.9855
5	99.9842	99.9777	0.0058	99.9893	99.9661	99.9842	99.973
6	99.9792	99.9753	0.0034	99.9821	99.9685	99.9792	99.9731
7	99.9660	99.9497	0.0204	99.9905	99.9089	99.9660	99.9268
8	99.9748	99.9773	0.0085	99.9943	99.9603	99.9899	99.9719
9	99.9856	99.9853	0.0030	99.9913	99.9793	99.9881	99.981
10	99.9712	99.9686	0.0053	99.9792	99.958	99.9722	99.9625
11	99.9852	99.9874	0.0023	99.992	99.9828	99.9898	99.9852
12	99.9842	99.9777	0.0058	99.9893	99.9661	99.9842	99.973
13	99.9792	99.9753	0.0034	99.9821	99.9685	99.9792	99.9732
14	99.9649	99.9488	0.0222	99.9932	99.9044	99.9649	99.9234

Comparison of interchange samples analysed by South African refineries using different techniques. Discontinuity of the line indicates where companies did not report a result. The graphs are split to accommodate the concentration variations.

- A Spark Spectrometer Method to be evaluated
- B Spectrograph Company A South Africa
- C Inductively Coupled Plasma South Africa
- D Spectrograph Company B South Africa

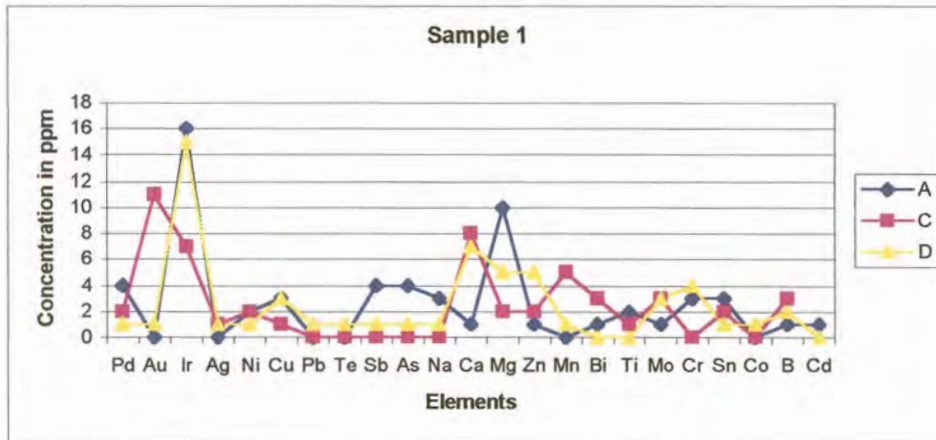


Fig. 7.42 Sample 1 analysed by three different companies

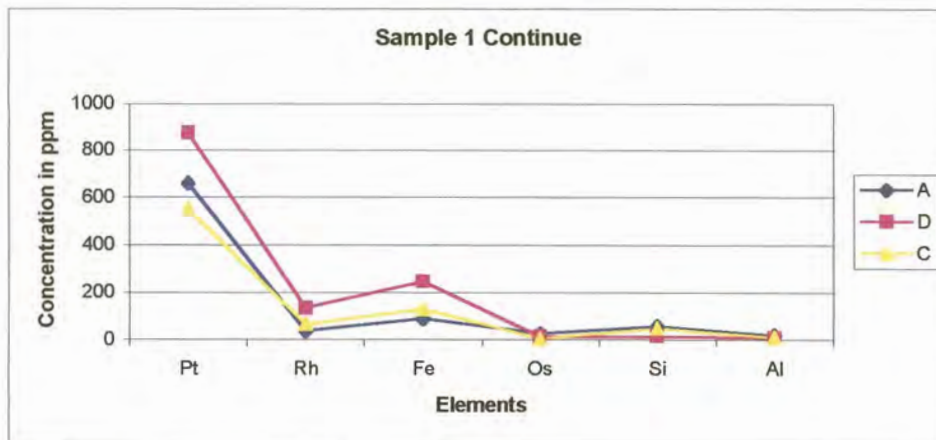


Fig. 7.42 Continued. Sample 1 analysed by three different companies

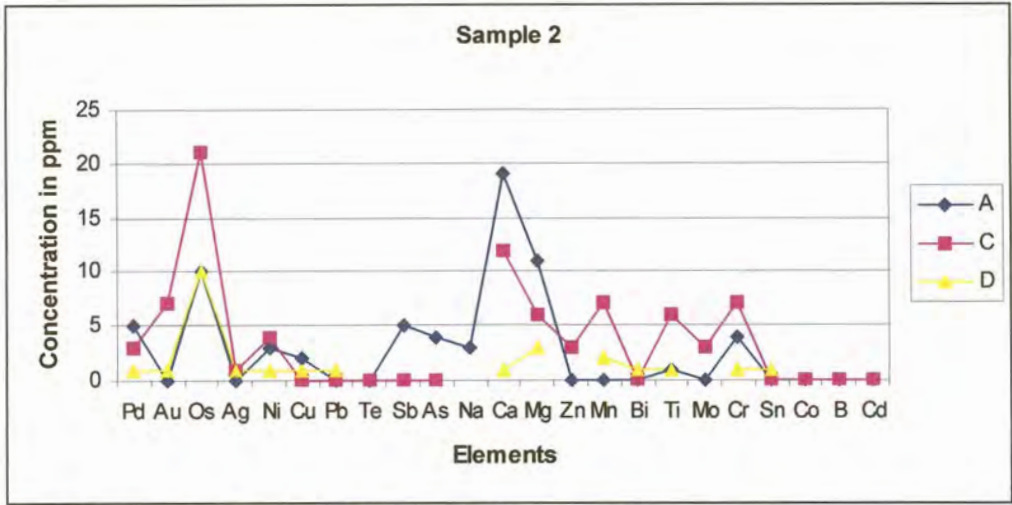


Fig. 7.43 Sample 2 analysed by three different companies

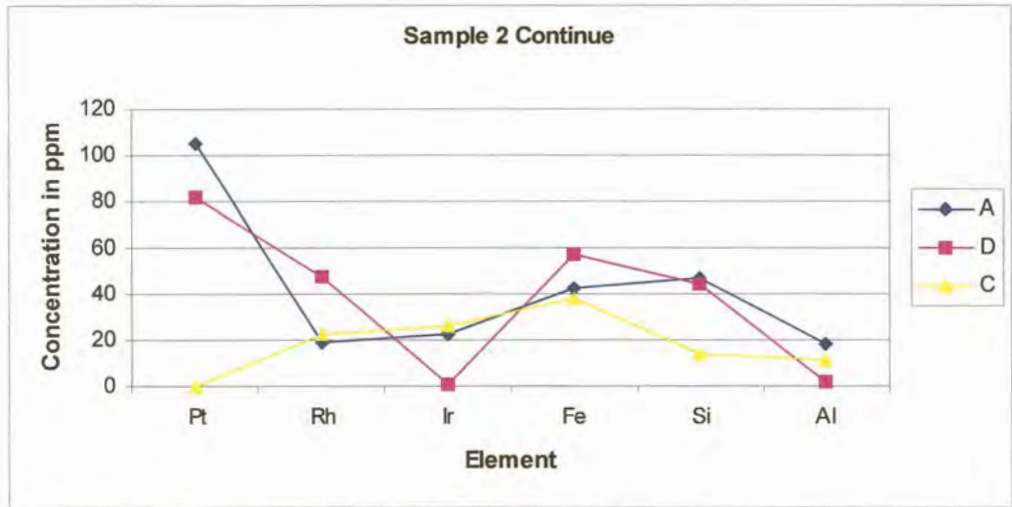


Fig. 7.43 Continued. Sample 2 analysed by three different companies

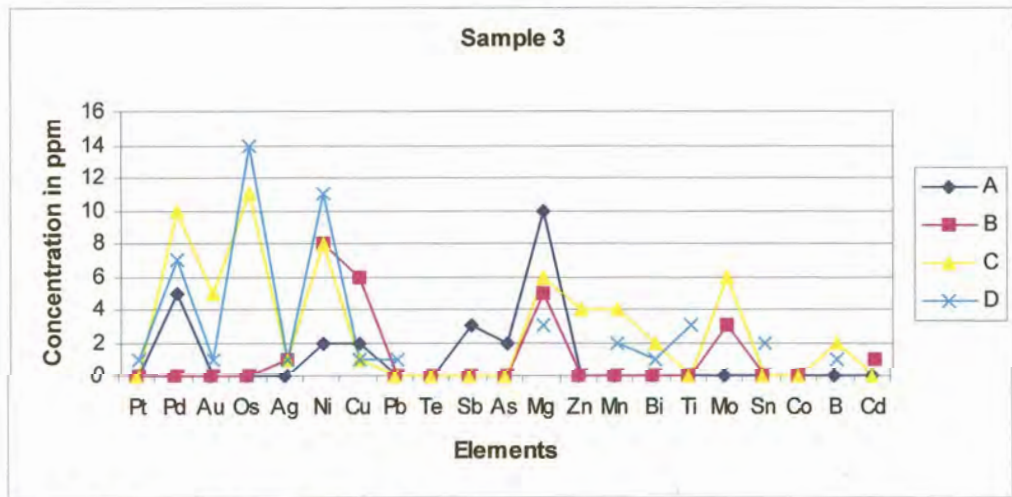


Fig. 7.44 Sample 3 analysed by four different companies

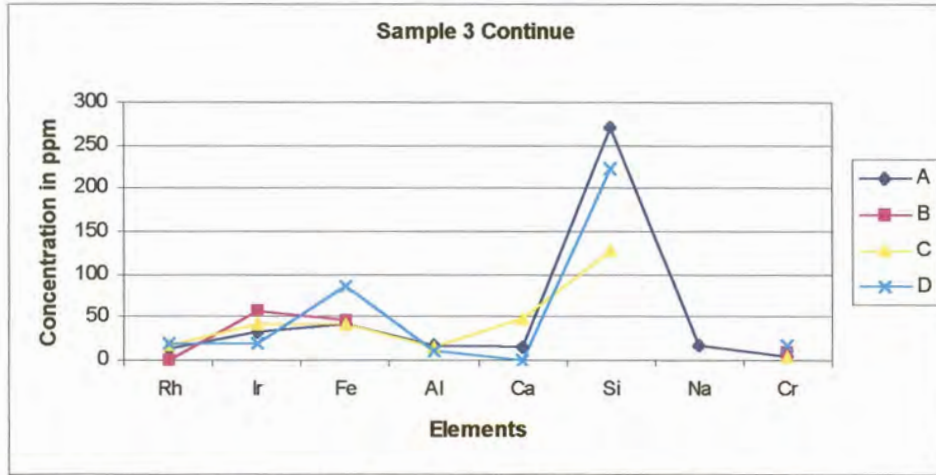


Fig. 7.44 Continued. Sample 3 analysed by three different companies

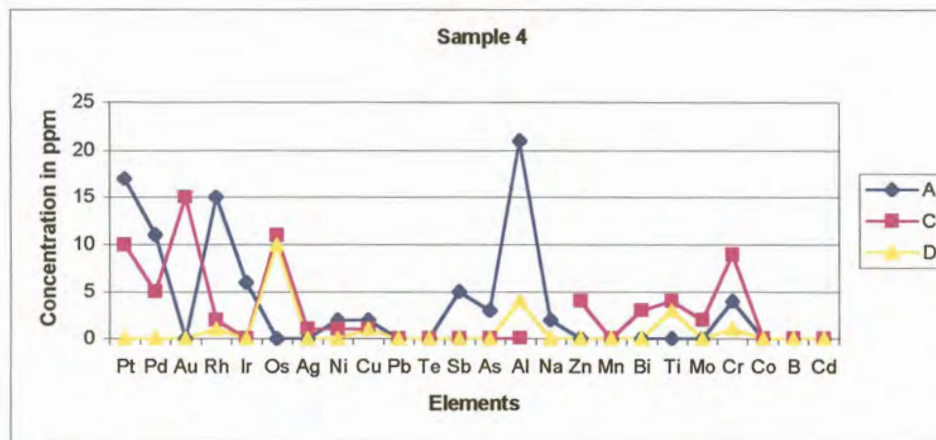


Fig. 7.45 Sample 4 analysed by three different companies

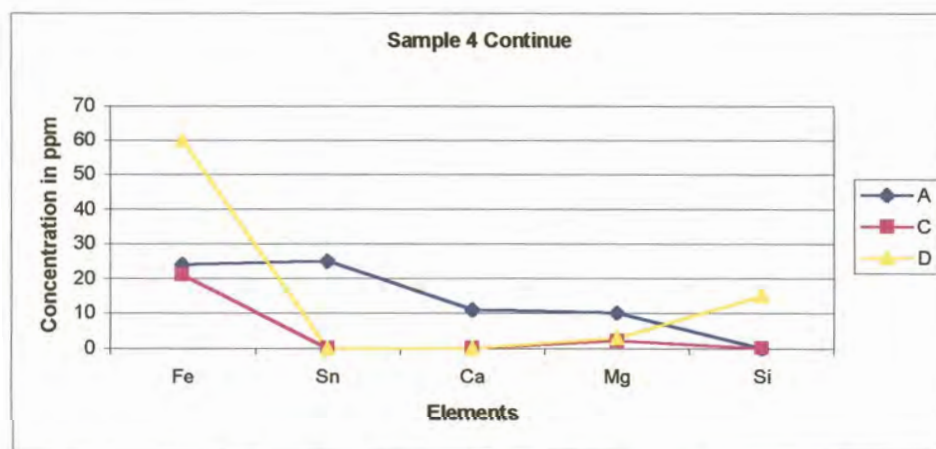


Fig. 7.45 Continued. Sample 4 analysed by three different companies

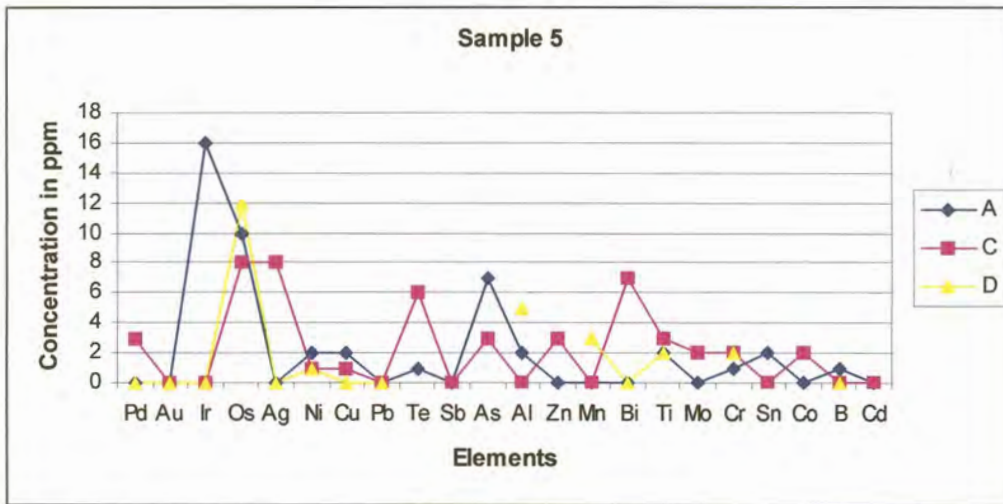


Fig. 7.46 Sample 5 analysed by three different companies

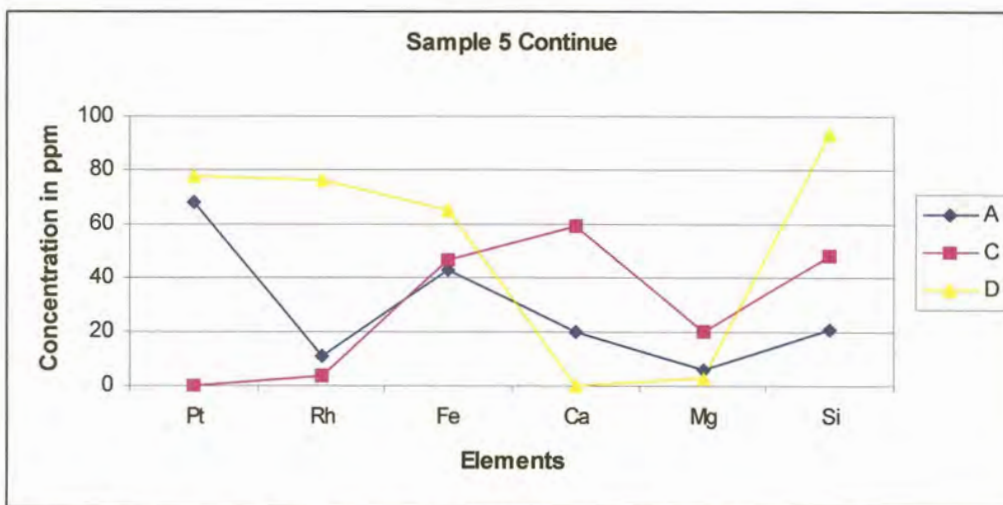


Fig. 7.46 Continued. Sample 5 analysed by three different companies

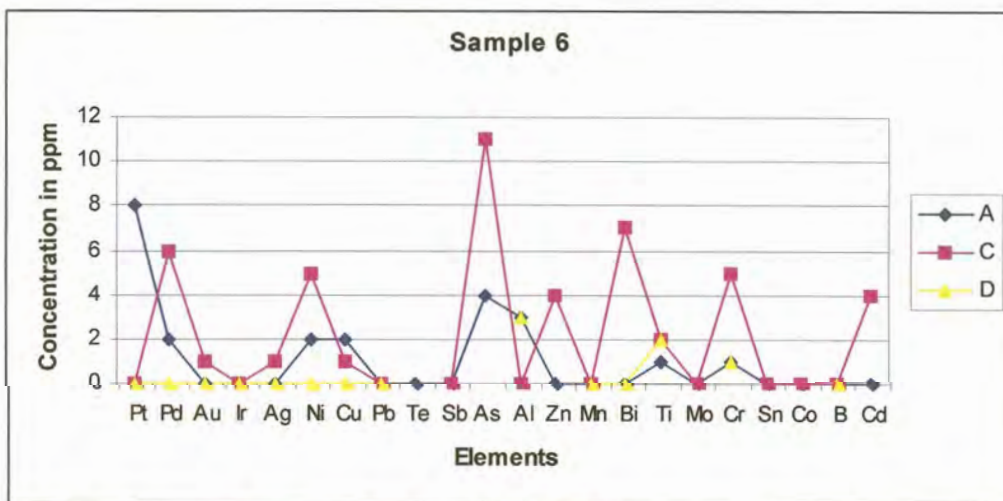


Fig. 7.47 Sample 6 analysed by three different companies

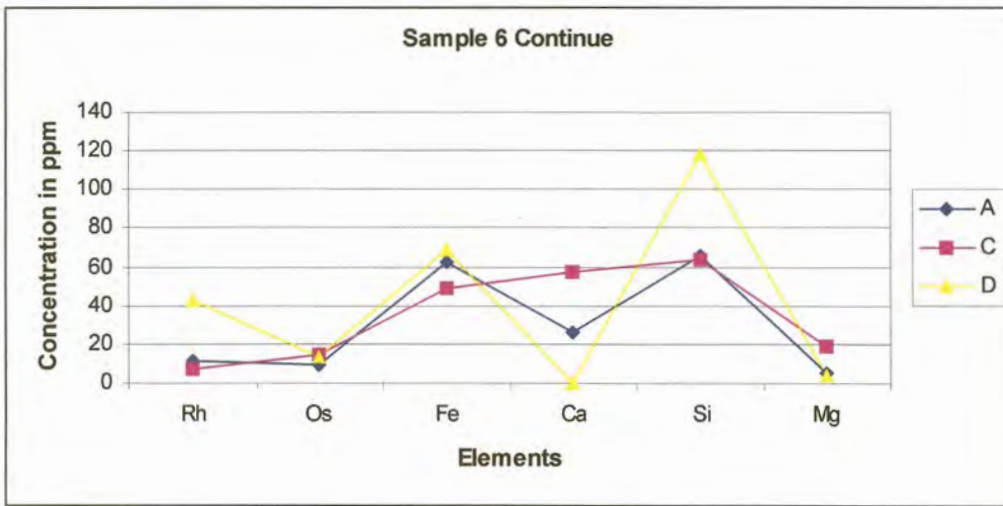


Fig. 7.47 Continued. Sample 6 analysed by three different companies

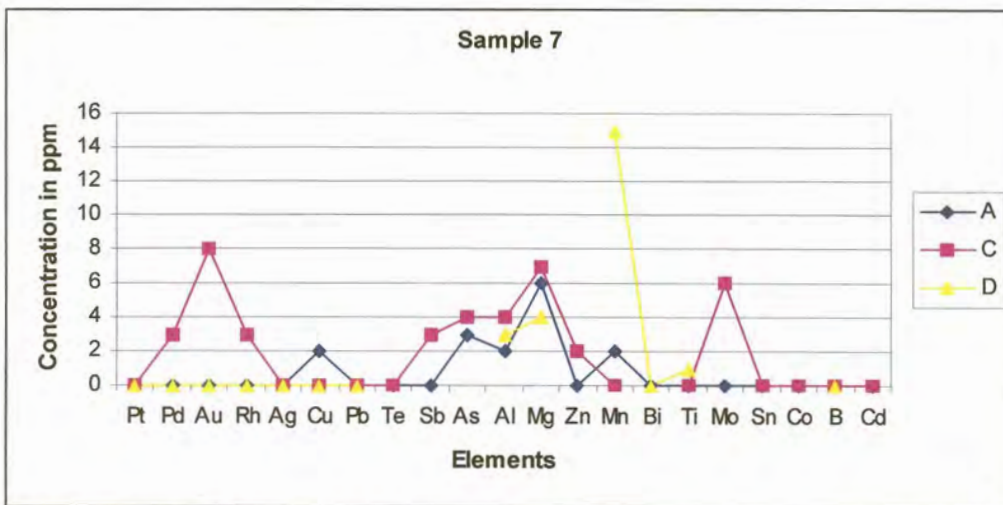


Fig. 7.48 Sample 7 analysed by three different companies

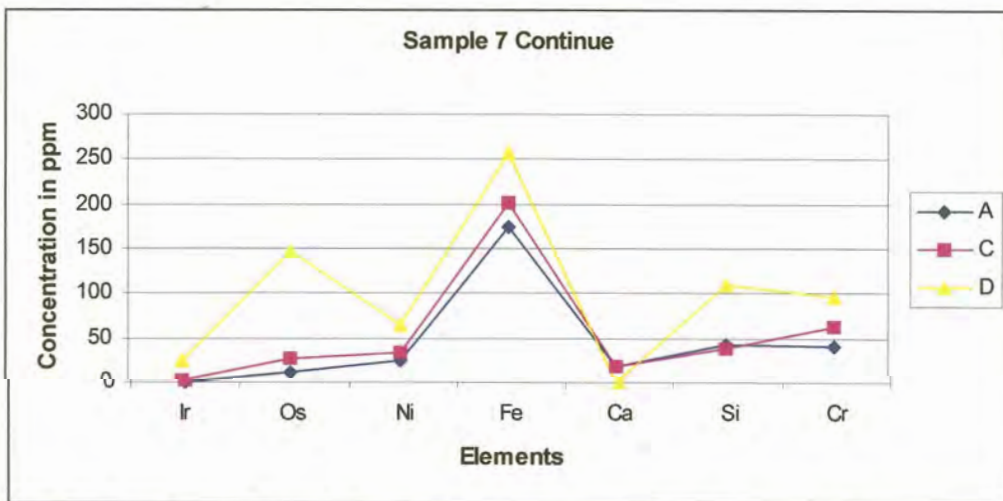


Fig. 7.48 Continued. Sample 7 analysed by three different companies

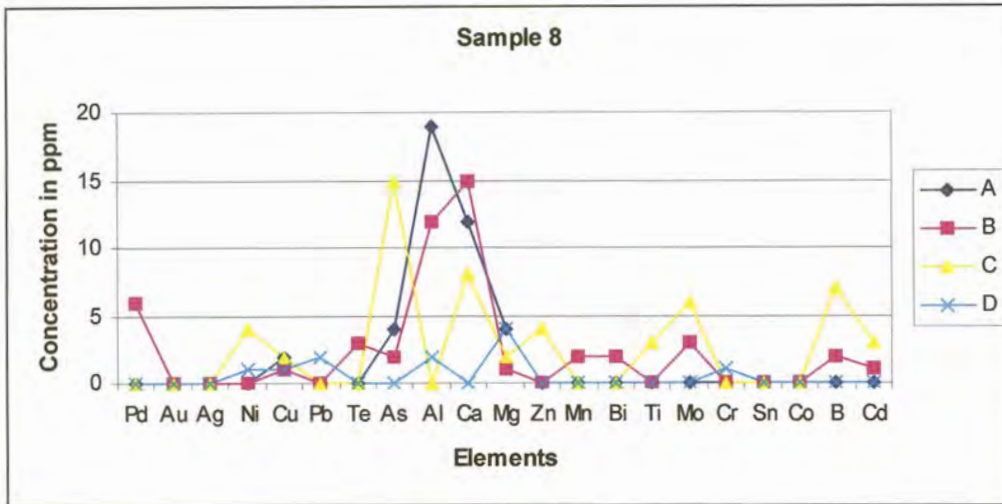


Fig. 7.49 Sample 8 analysed by four different companies

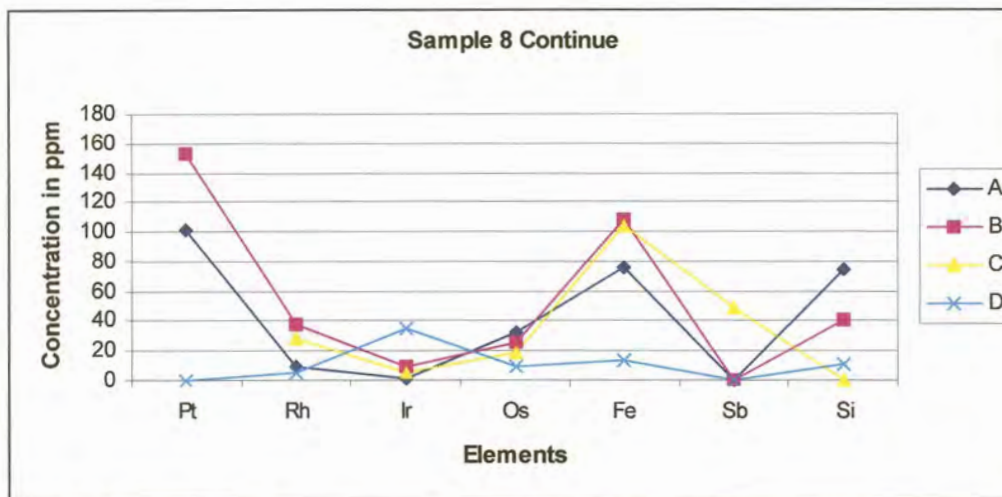


Fig. 7.49 Continued. Sample 8 analysed by four different companies

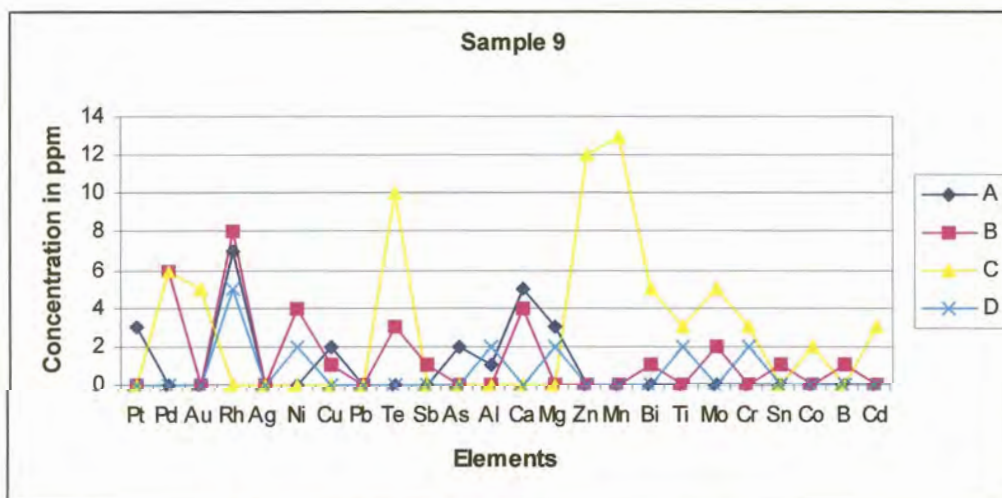


Fig. 7.50 Sample 9 analysed by four different companies

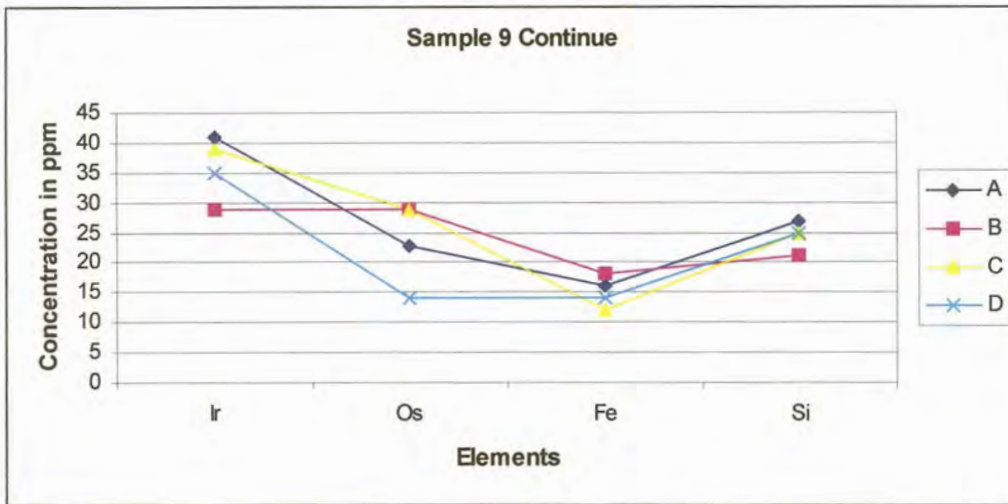


Fig. 7.50 Continued. Sample 9 analysed by four different companies

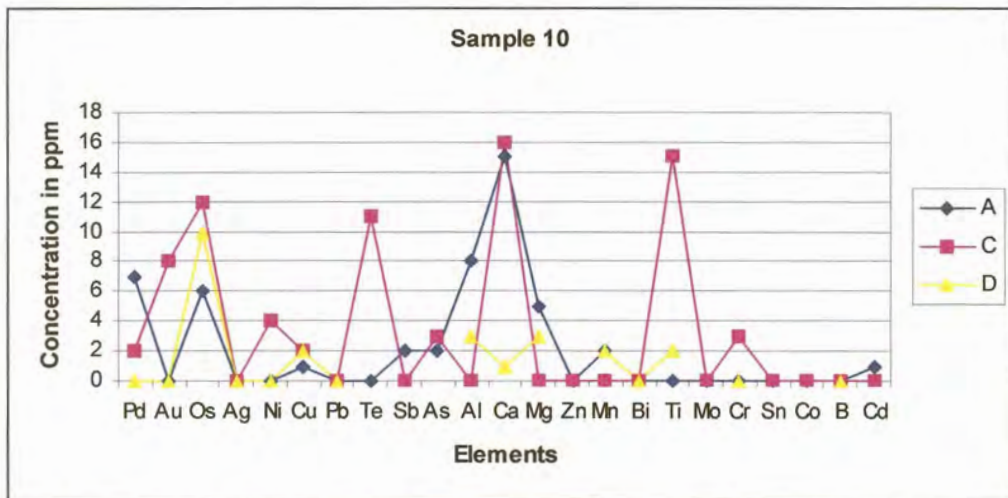


Fig 7.51 Sample 10 analysed by three different companies

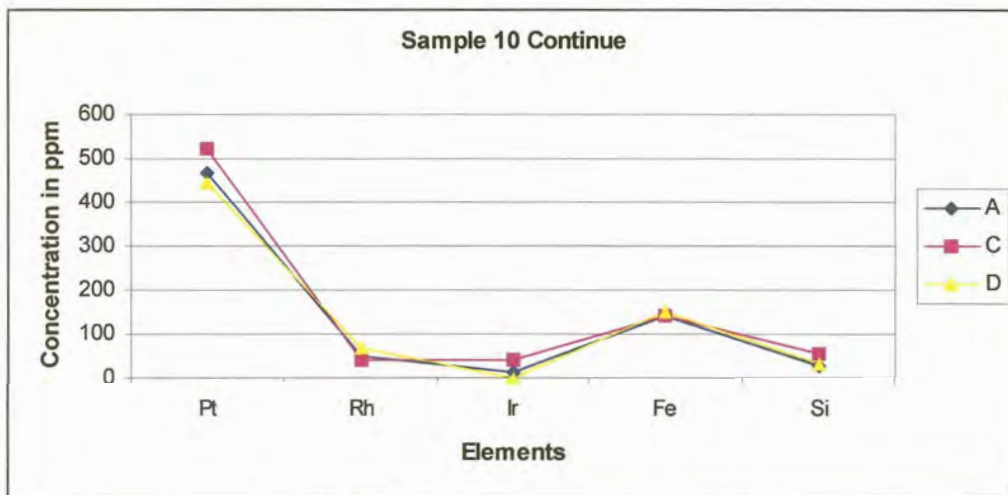


Fig 7.51 Continued. Sample 10 analysed by three different companies

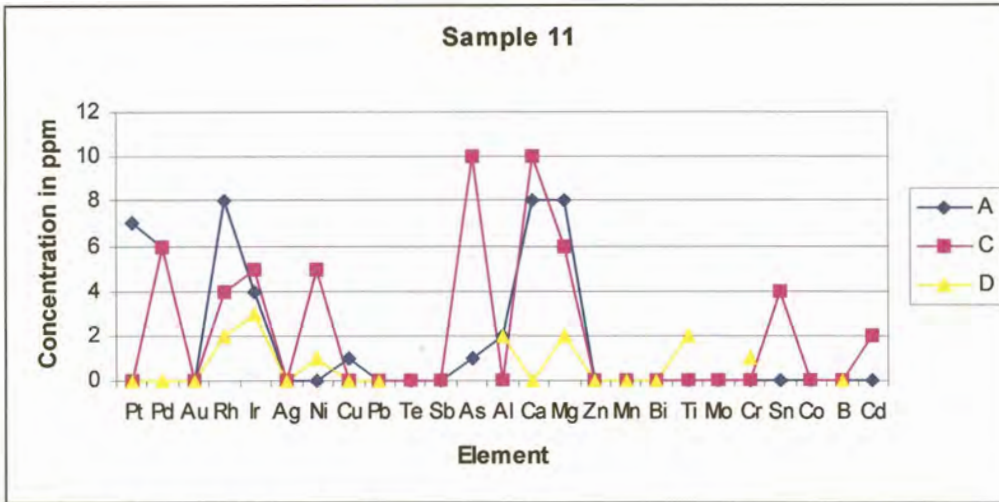


Fig. 7.52 Sample 11 analysed by three different companies

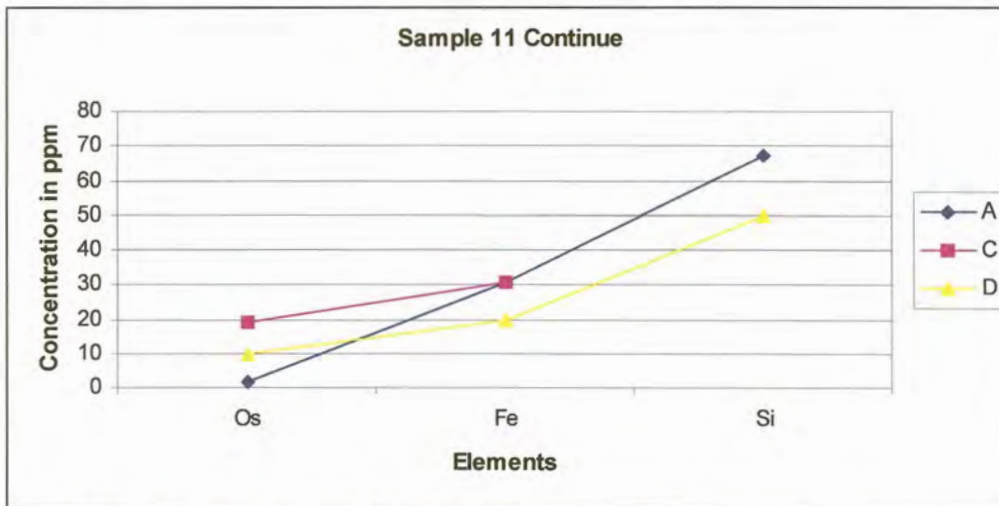


Fig. 7.52 Continued. Sample 11 analysed by three different companies

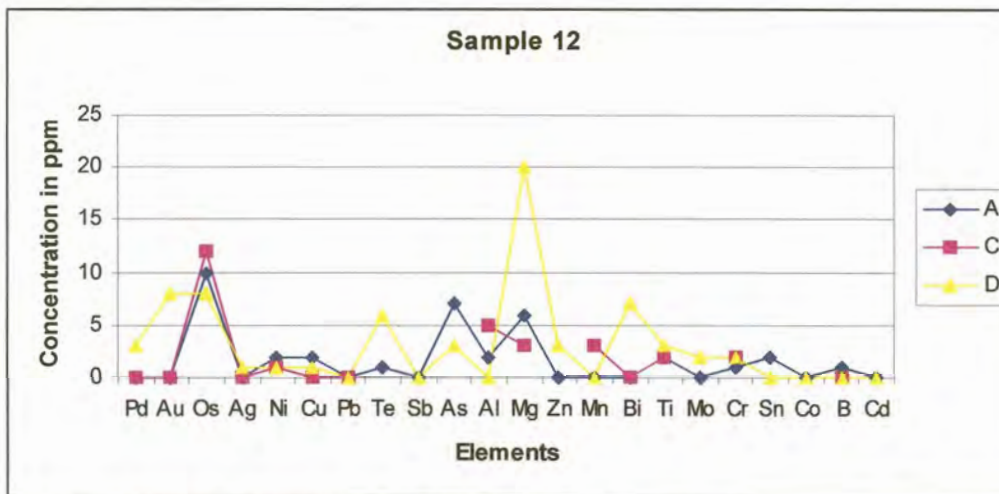


Fig. 7.53 Sample 12 analysed by three different companies

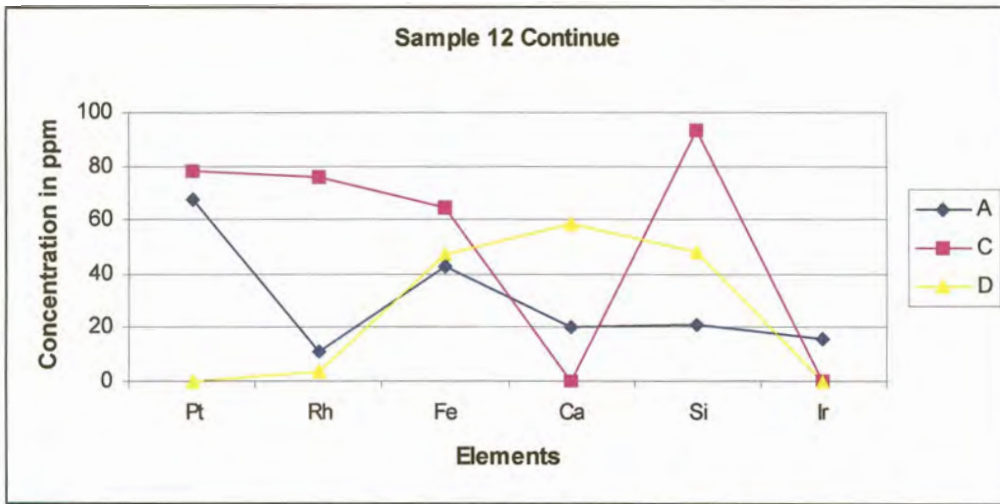


Fig. 7.53 Continued. Sample 12 analysed by three different companies

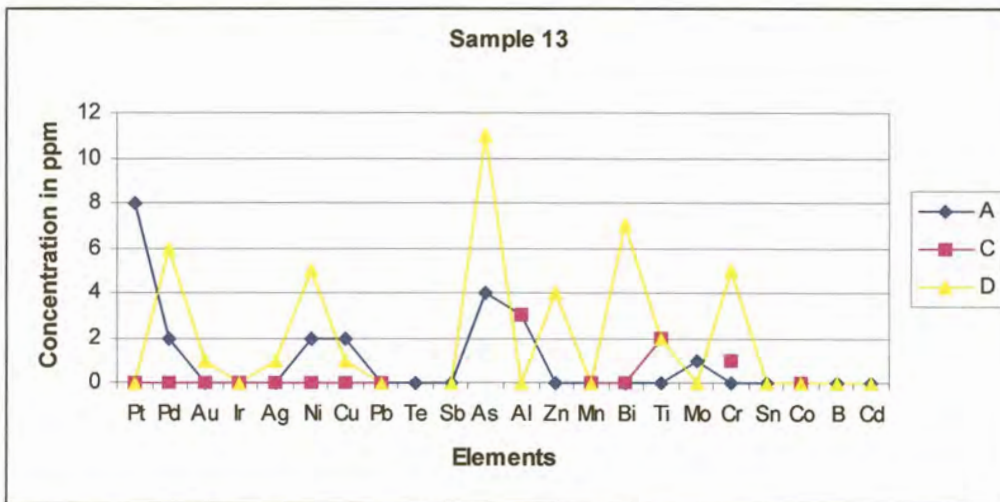


Fig. 7.54 Sample 13 analysed by three different companies

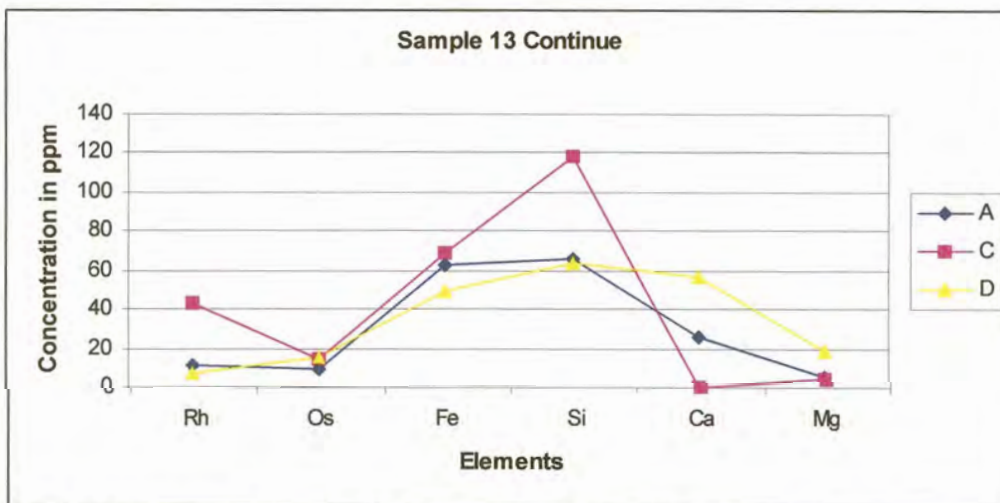


Fig. 7.54 Continued. Sample 13 analysed by three different companies

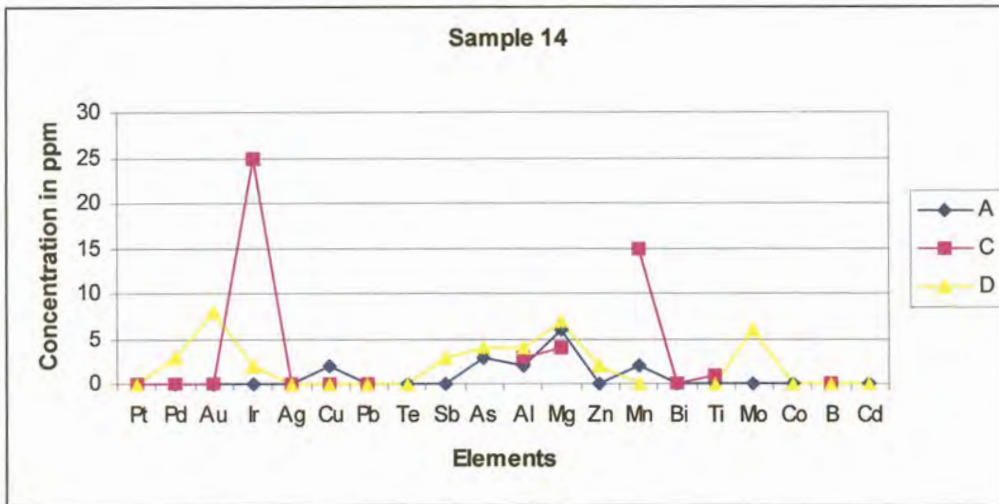


Fig. 7.55 Sample 14 analysed by three different companies

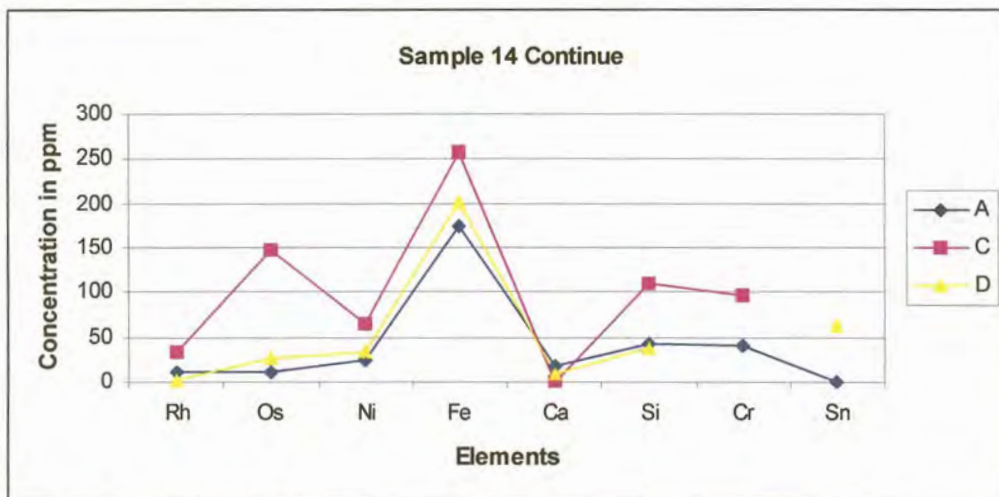


Fig. 7.55 Continued. Sample 14 analysed by three different companies

Chapter 8

Discussion of results and conclusion

8.1 Optimisation of parameters

8.1.1 High Energy Pre-spark

Two samples, 7 and 8, contained different elements in a Ru matrix. The samples were sparked using a high-energy spark. They were pressed and their surfaces disintegrated during sparking. To obtain a smooth surface for analysis, these samples had to be repressed during the process. The breaking up of the surface could cause a source error. When the spark was directed into an inclusion in the sample, it led to a diffuse discharge, caused by low plasma temperatures. Equilibrium should be reached after a certain period of sparking and this is referred to as the "steady state".

The intensity of the impurities in the base elements rose continuously and became steadier after 10 seconds of sparking time. The steady state was reached when all intensities of all elements became independent of sparking time. The curve became constant during the first 10 seconds of the spark and equilibrium was reached. With the sample disintegrating, 130 μH could be used which was then similar to that of the analytical spark. If this was used, the analytical spark was extended from 5 to 10 seconds sparking time to ensure a homogenous area for analysis.

Capacitance: When the capacitance was investigated, the necessity was borne in mind of selecting parameters that would be suitable for all the elements. Only one parameter could be selected for all elements. It was therefore necessary to consider compromising conditions in both instances. The trends of samples 7 and 9 were evaluated together. The highest intensities achieved for the majority of the elements for

integration gives lower relative standard deviations. The general sparking conditions for the calibration used will be three times 3-second integration time per spark. In general, three sparks are used but in industry samples are sparked between six to ten times to ensure the homogeneity of the samples.

8.1.3 Effect of different gating parameters

The aim was to optimise the delay conditions to reduce spectral interference from ion lines or to eliminate them so that the atom line of the element of interest appeared clearly above the background. The system had to be optimised to produce the best signal to background ratio. It was essential to investigate compromising conditions as only one parameter could be selected for all elements. The instrument made use of a 16-channel integrator board. As seen from Figure 7.19, 116 the delay times set up for the experiment were at intervals of 16 μs ranging from 16 μs (microseconds) to 176 μs . In each instance, the highest signal to background was considered as well as the time delay at 144 μs . and 160 μs . Table 8.1, 141 provides a summary of the best signal to background ratio position. The delay positions at 144 μs and 160 μs were evaluated as follows,

Yes: Indicated the position was similar (with in 10 % of the best position) and could be used.

No: Indicated this position was not suitable.

Possible: This position was a compromising position and could be used but was not optimal.

Table 8.1 Summary of best and compromised Signal to Background ratio position

Channel	Best S/B	Delay 144 μ s	Delay 160 μ s
Pt 1 Ω	160	Yes	Yes
Pt 15 Ω	144	Yes	Yes
Pd 1 Ω	144	Yes	No
Pd 15 Ω	176	Yes	No
Au 1 Ω	160	Yes	Yes
Au 15 Ω	176	Yes	Yes
Rh 1 Ω	160	Yes	Yes
Rh 15 Ω	176	Yes	Yes
Ir 1 Ω	160	Yes	Yes
Ir 15 Ω	144	Yes	Yes
Sb 1 Ω	144	Yes	Yes
Sb 15 Ω	144	Yes	Yes
Ag 1 Ω	144	Yes	Yes
Ag 15 Ω	144	Yes	Yes
Pb 1 Ω	144	Yes	Yes
Pb 15 Ω	144	Yes	Yes
Mn 1 Ω	160	Yes	Yes
Mn 15 Ω	160	Possible	Yes
Cr 1 Ω	160	Yes	Yes
Cr 15 Ω	160	Yes	Yes
Co 1 Ω	160	Yes	Yes
Co 15 Ω	176	Yes	Yes
Cu 1 Ω	144	Yes	Possible
Cu 15 Ω	144	Yes	Yes
Fe 1 Ω	144	Yes	Yes
Fe 15 Ω	160	Yes	Yes
Al 1 Ω	144	Yes	Yes
Al 15 Ω	144	Yes	Yes
Mo 1 Ω	160	Yes	Yes
Mo 15 Ω	176	Yes	Yes
Ni 1 Ω	176	Yes	Yes
Ni 15 Ω	160	Yes	Yes
Bi 1 Ω	144	Yes	Yes
Bi 15 Ω	160	Yes	Yes

Table 8.1 Continued. Summary of best and compromised Signal to Background ratio position

Channel	Best S/B	Delay 144 μ s	Delay 160 μ s
Mg 1 Ω	112	Yes	Yes
Mg 15 Ω	48	Yes	Yes
Na 1 Ω	80	No	No
Na 15 Ω	16	No	No
Ca 1 Ω	144	Yes	Yes
Ca 15 Ω	160	Yes	Yes
Si 1 Ω	144	Yes	Yes
Si 15 Ω	144	Yes	Yes
Sn 1 Ω	32	Yes	Yes
Sn 15 Ω	64	Yes	Yes
As 1 Ω	144	Yes	Yes
As 15 Ω	144	Yes	Yes

There was an insignificant difference between 144 μ s and 160 μ s for Pt.

Pd shows a significant difference between 144 μ s and 160 μ s. The "No" in Table 8.1, 141 does not mean it could not be analysed at that particular point. It is an indication that the S/B ratio for 144 μ s was significantly higher than at 160 μ s. Au had a slightly higher S/B ratio at 160 μ s, but was very similar to that of 144 μ s. Rh overall had a higher S/B ratio at all positions, the best at 160 μ s for 1 Ω and 176 μ s for 15 Ω , but acceptable at 144 μ s. Insignificant differences were found in the S/B ratio for Ir, Sb and Ag.

Mn, Cr and Co had their best S/B ratio at a delay time of 160 μ s. There was a significant difference between 144 μ s and 160 μ s, however, if compromising conditions of 144 μ s were to be used, the analysis could be done at 144 μ s since the S/B ratio at this position was still higher than the previous eight positions (from 16-128 μ s).

Cu seemed to peak at 64 μ s and then again at 144 μ s. There was a significant difference between 144 μ s and the 160 μ s position for Cu. Fe and Bi had their best S/B

ratio at 144 μs delay for 1 Ω and for 15 Ω at 160 μs . This was, however, very similar and the optimum condition was taken as 144 μs Al, Si and As had their best S/B ratio at 144 μs Mo and Ni tended to have increased S/B ratio's at the longer delay times of 160 μs and 176 μs . The difference between these and 144 μs . was insignificant. Na's best S/B ratio was confirmed to be at 80 μs delay time for 1 Ω and 16 μs . for 15 Ω . The "No" in the table showed a significant difference between the 80 μs and 16 μs delay position and 144 μs and 160 μs however, as compromising conditions had to be considered, there was an insignificant difference between 144 μs and 160 μs .

Ca had its highest S/B ratio at 144 μs for 1 Ω and 160 μs for 15 Ω , but both positions could be used for analysis. Sn had its best S/B ratio at 32 and 64 μs delay, however, this was an insignificant difference from the 144 and 160 μs delay. 144 μs will be used as the compromised conditions for the calibration.

Table 8.2, 144 is a summary of the channels at 1 Ω and 15 Ω to identify the highest signal to background (S/B) ratio. This table indicates the highest S/B ratio or similar if there was no significant difference. The signal to background ratio was evaluated at 144 μs delay time.

The highest S/B ratio gives an indication of the highest S/B at 1 Ω or 15 Ω and "similar" means they were similar in intensities. The "similar" column gives an indication of, the extent to which the S/B ratio differs at 1 Ω and 15 Ω . "Yes", means they are similar, "double" is an indication that the S/B ratio was double at the best position as indicated in the corresponding "Highest S/B ratio" column. In 16 instances, 1 Ω resistance gave the best S/B ratio. Rh, Ag, Mg, Ca, Mg, Si and As gave similar S/B ratios at 15 Ω resistance. The signal to background ratio was double at 1 Ω resistance than at the 15 Ω for Ag, Pb, Mn, Co, Bi, Fe, Al and Mo. Na was about ten times higher at 1 Ω resistance than at the 15 Ω . There was no significant difference for Pt, Au, Ir, Sb, Cr and Sn between the 1 Ω and 15 Ω resistance, their S/B ratios being very similar. The

resistance at 15 Ω gave better S/B ratio for Pd, Ni and Cu. The S/B ratio was similar for Pd and Ni but gave an approximately 40 % better S/B ratio for Cu. Therefore, we could use the 1 Ω resistance for the calibration of the impurities in Ru base.

Table 8.2 Summary of highest Signal to Background ratio between 1 and 15 resistance used

Channel	Highest S/B Ratio	Similar
Pt	Similar	Yes
Pd	15 Ω	Yes
Au	Similar	Yes
Rh	1 Ω	Yes
Ir	Similar	Yes
Sb	Similar	Yes
Ag	1 Ω	Yes
Pb	1 Ω	Yes
Mn	1 Ω	Double
Cs	Similar	Yes
Co	1 Ω	Double
Cu	15 Ω	40% higher
Fe	1 Ω	Double
Al	1 Ω	Double
Mo	1 Ω	Double
Ni	15 Ω	Yes
Bi	1 Ω	Double
Mg	1 Ω	Yes
Na	1 Ω	10 times
Ca	1 Ω	Yes
Si	1 Ω	Yes
Sn	Similar	Yes
As	1 Ω	Yes

8.1.4. Internal standardisation

Where the instrument was not equipped with a Ruthenium reference line in the optic, a background position was selected. There is a background position in the Ultra-violet

optic and the analytical line is ratioed to a background position. Reference lines were used in the air optics and used as the internal standard in the calibration.

8.1.5 Analytical gap

Overall there seemed to be no significant difference between the 3 mm and 4 mm analytical gap (distance between the sample and tungsten electrode), with the exception of Ag where the 4 mm gap gave an increased signal to background ratio (double that of the 3 mm gap). The signal to background ratio of Sn was double using the 3 mm gap and a higher S/B ratio was obtained for Cu at the 3 mm position. Since there was no significant difference and the suppliers installed the instrument with a 4 mm analytical gap, the calibration was performed using a 4 mm analytical gap.

8.1.6 Contamination from other base material

From Table 7.3, 124 it can be seen that when a Platinum (Pt) sample was sparked for analysis immediately after a Ruthenium (Ru) sample, contamination occurred. Ru was monitored as an impurity in the Pt sample. The sample was sparked in excess of ten times before a stable signal for Ru could be obtained. When a Palladium (Pd) sample was sparked immediately after the Platinum and Pt was monitored, the Pt signal only became stable after six sparks. When Ru sample was sparked and Pd monitored as an impurity in the Ru, the signal became stable only after ten sparks. It can therefore be concluded that there was cross contamination between the various bases when sparking pure samples. Between seven to ten sparks were required when changing to another base without changing the spark plate, electrode, electrode spring, glass ring and cleaning the spark chamber.

The results from Table 7.4, 124 indicated much less cross contamination between the samples when the spark stand chamber was cleaned and a Pt base plate, with electrode, electrode spring, and glass ring was used when analysing for impurities in a

pure Pt sample. After three sparks the results became constant. It was therefore standard procedure to clean the spark chamber, change the spark stand plate for the pure samples for analysis as well as all its accessories and to use these when analysing for different pure samples. Each base material (pure sample) must have its own equipment for analysis to avoid cross contamination.

8.2 Calibration

The calibration is performed using the optimal or compromised conditions as determined during the test work. Table 8.3, 147 provides a summary of the limits of detection obtained for the various wavelengths used to determine the impurities in pure Ru (> 99.9 %). This table also indicates typical LOD used for the traditional spectrograph analysis. Elements indicating ND (not detected) are generally too low to be analysed by the technique.

Table 8.3 Limits of detection (LOD) in parts per million (ppm) obtained from calibration graphs and traditional LOD

Elements	Wavelength (nm)	LOD in ppm SAFT	Traditional LOD
Ag	338.289	0.01	<1
Al	396.153	0.24	<10
As	234.984	0.26	ND
Au	267.595	0.15	<1
Bi	306.772	0.93	<1
Ca	422.673	0.31	<10
Cd	228.802	0.56	<10
Co	345.351	0.11	ND
Cr	425.435	0.04	ND
Cu	324.754	0.07	<1
Fe	371.994	0.93	<10
Ir	351.364	0.45	<10
Mg	285.213	0.12	<1
Mn	403.449	0.11	<1
Mo	386.411	0.72	ND
Na	588.995	0.27	<10
Ni	361.939	0.24	<1
Os	581.812	0.03	<10
Pb	283.307	1.30	<10
Pd	340.458	0.72	<10
Pt	531.89	0.13	<10
Rh	343.489	0.86	<10
Sb	206.83	0.85	<10
Si	288.16	2.00	<10
Sn	317.502	0.84	<1
Te	214.275	0.21	<10
Ti	498.173	0.67	<10
Zn	213.856	0.05	ND

8.3 Comparison of samples analysed

A sample, referred to as a "Round Robin", was analysed by seven different companies nationally and internationally, using different techniques. Due to the confidentiality of these results, they are displayed in a graphical format rather than in a table. The analysis as indicated in Fig. 7.41, 126 is a comparison of all the results.

“A” is the analysis of the spark emission using the time resolved spectroscopy, referred to as the SAFT (Spark Analysis for Traces) technique. Companies A and D did the analyses for all the elements, but the other companies did not, or did not report all the results.

The A analysis for Pt is 20 % lower than D and F, Fe was much lower than the average and Al higher than average. The Ca is higher than D and E but the same as F and Si is the closest to the average. The remaining elements all compared with the other methods, which were used. The results in Table 7.8, 127 show that the maxima and the minima values for each of the samples analysed by different techniques, all lie between +2 standard deviations and -2 standard deviations from the average. This means that, at 95 % confidence levels, there are no significant differences between the results. It is important to analyse as many elements as possible as the technique sums up all the impurities and subtracts this sum from 100 % to determine the purity of the metal. As indicated in Table 7.7, 127 the purity obtained using the SAFT technique compares well with the existing methods of analysis

The results of 14 other samples, which were analysed as interchange samples between Platinum Refineries in South Africa, were compared. The Spark Emission analysis, as indicated by A, is compared to traditional spectrographic analysis, B and D (same technique, different company), and inductively coupled plasma indicated by C.

The analysis of Fe, Ca and Si seems to have scattered values for most of the samples. In comparison to the other techniques, the results obtained for the spark emission technique making use of time resolved spectroscopy, compare very well with the established techniques. This technique takes only a fraction of the time for analysis and there is no dilution or dissolution involved. This technique has been introduced very successfully in the Precious Metals industry for the analysis of impurities in Pt, Pd, Au and Ag. Rh, Ru and Ir are much more complicated due to the lack of availability of reference materials and the high melting point of Ru and Ir.

Table 8.4 Comparison of interchange samples analysed by four different companies. A = Spark Emission (using time resolved spectroscopy), B = Spectrographic Analysis, Company A, C = Inductively coupled Plasma and D = Spectrographic Analysis, Company B

Sample	Variances between the different techniques		
	Higher Elements	Lower elements	Technique
1	Rh Fe	Si	D
1		Fe Rh	A
2		Pt Si	C
2	Rh Fe	Ir Ca Al	D
3	Ca	Si	C
3	Fe		D
4	Pt Pd Ir Al Sn		A
4	Au Cr		C
4	Fe Si	Pt Cd	D
5	Rh		A
5	Ca Si	Pt	C
5	Rh Fe Si	Ca	D
6	Ca	Fe	C
6	Rh Si	Ca	D
7	Os Fe Si Cr		D
8	Pt		B
8	Sb	Si	C
8	Ir	Pt Fe	D
9	Ni Fe		B
9	Au Te Mn Bi Ti Mo Cr Cd	Ca	C
10	Compares well		A D C
11	Si	Os	A
11	Os	As	C
11	Si Fe Ca		D
12	Ir	Si	A
12	Rh Si Fe	Ca	C
12	Ca	Pt	D
13	Rh Si	Ca	C
13	Ca		D
14		Cr	A
14	Rh Ir Os Fe Si Cr		C
14	Sn		D

8.4 Conclusion

The analysis for the determination of the purity of the precious metals was very important, as this has a direct impact on the price paid for the metal (Chapter 1, 1).