INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY:
ANALYTICAL METHODOLOGY AND CAPABILITY

A thesis submitted to
The University of Surrey for
the Degree of Doctor of Philosophy
in the Faculty of Biological
and Chemical Sciences

by

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The performance of the new analytical atomic techniques of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is assessed.

A detailed examination of ICP-MS instrumentation was carried out to derive data on performance criteria such as precision, resolution, dynamic range and limits of detection. For most elements, sub ng.mL\(^{-1}\) limits of detection can be achieved together with a linear dynamic range of 4-5 orders of magnitude.

Spectral simplicity is one of the attractions of ICP-MS; however, the technique is prone to spectral interference from polyatomic, analyte oxide and doubly charged ions. The significance of these species was studied together with methods for reducing their levels, in particular with use of a cooled spray chamber.

Plasma operating parameters were found to effect system performance so a detailed examination of the effects of varying plasma operating parameters was carried out and showed that for ICP-MS systems used in this study, optimisation for maximum elemental signal response resulted in near minimal levels of interference species.

Having assessed the optimum operating conditions and potential drawbacks of the technique, the final part of the study was devoted to elemental and isotope ratio
determinations using conventional and 'novel' sample introduction methods.

The study demonstrates that, apart from the interference problems identified, the technique of ICP-MS is a very useful addition to the field of analytical atomic spectrometry.
'Where sciences meet, their growth occurs. In scientific borderlands not only are facts gathered that are often new in kind, but it is in these regions that wholly new concepts arise.'

F. Gowland Hopkins 1938
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1.1 The Need for a New Analytical Technique

The elemental composition of a sample is perhaps one of the most common pieces of information that the analytical scientist is asked to provide. The instrumental determination of the elemental components of the bulk sample at major, minor, trace and ultra-trace levels has conventionally been carried out by optical and mass spectrometric techniques.

Atomic absorption and emission are the most widely used optical spectrometric methods for elemental determination, both offering low limits of detection and wide elemental coverage. Atomic absorption, in its currently marketed form, is primarily a single element technique, thus for multi-element analysis the use of an emission source for excitation combined with a scanning/sequential or simultaneous/direct-reading spectrometer is often used. Plasma emission spectrometry is proving invaluable as a multi-element technique offering good precision with high sensitivity. It is, however, limited in some cases by the inability of the optical spectrometers to resolve the complex spectra developed except where, more recently, expensive high resolution or Fourier transform spectrometers are employed.

Many of the most difficult problems that arise in trace analysis have been solved by resorting to mass spectrometry.
Atomic mass spectrometry is a very sensitive analytical tool, but from a multi-element point of view, with spark or secondary ion sources, it suffers from a number of disadvantages which have restricted its routine use. These techniques generally require samples to be in solid form, which can lead to problems in sample preparation, but does not prohibit their manufacture. The high degree of skill and intensive labour required to operate the equipment and interpret the data that are produced, together with the poor rate of analysis (typically 1-2 samples per day) and the extremely costly mass analysers that are compatible with these ion sources, are additional drawbacks to their use.

Investigating means of simplifying both sample introduction and analyser design, without losing the sensitivity of the mass spectrometer and the ability to carry out multi-element analysis, led to the development of atmospheric pressure electrically maintained plasmas as ion sources for mass spectrometry. The concept was first proposed by Gray (4) who wrote ".... the ease with which the sample may be introduced with little preparation and the simplicity of programming element selection with a quadrupole (mass analyser) suggest that this technique of Plasma Sampling Mass Analysis has a useful place in multi-element analysis."

Although the technique rapidly attracted widespread interest, the operational capabilities and limitations of the system had not been fully investigated. Many of the analytical capabilities of Inductively Coupled Plasma Mass
Spectrometry (ICP-MS) had been touched upon by the pioneers in the field (1, 4, 30), but no large scale examinations of performance as yet existed. Assessments of this type have now been carried out (41, 98, 116, 117) and some are reported on here together with demonstrations, using real sample analysis, of the practical capabilities and limitations of this new technique.

1.2 ICP-MS Development History

The development of ICP-MS has been very rapid. From the first demonstration of ion extraction from an ICP (1) to the realisation of ICP-MS as an analytically viable technique (45) and release of the first commercial systems took only three years. Before 1980, Gray had reported on work based solely on the Direct Current Plasma (DCP) system (2-7) which incorporated many of the ideas developed to investigate combustion processes in flames (8-14). Although laying the foundations for plasma source mass spectrometry, the DCP had too many drawbacks to be of analytical use.

After 1983, rapid progress was made in all areas of ICP-MS, due mainly to the increased number of workers in the field. Figure 1 shows the number of papers on ICP-MS that have been published since 1974. Subsequently some 130 papers have appeared which are split equally between applications and fundamentals studies. Up to 1982 nearly all the papers were on instrument design and development coming from the pioneers of ICP-MS. This is an indication of the speed of acceptance of ICP-MS in the analytical community, which is
Figure 1. PSMS Papers Published 1974 to 1987
further borne out by the many reviews and ICP-MS 'current status' reports (15-19).

In 1974 Gray (2) showed that ions could be extracted from an atmospheric DCP into the vacuum system of a mass spectrometer. Excellent limits of detection were obtained and useful isotope ratios could be determined. However the system did have its limitations, such as severe matrix and inter-element effects, mainly associated with the problems of introducing the sample into the core (temperature 5000K) of the DCP and poor sensitivity for elements with ionisation energies (IE) above about 8.5eV, due to the high level of undissociated NO⁺, (IE of 9.25eV). which effectively suppressed the ionisation of any element with an IE below its own (2-7).

Gray continued to report on the DCP-MS system until 1980 when Houk (1) and his colleagues, in association with Gray, showed that an Inductively Coupled Plasma (ICP) could be readily substituted for the DCP to overcome many of the matrix problems encountered in using the much cooler type of plasma. The work of Houk et al. clearly showed the tremendous potential of ICP-MS, such as very low limits of detection, direct determination of isotope ratios, long linear dynamic ranges (4 orders) and very simple spectra which allowed easy identification of interference ions. This initial work however did have some problems such as matrix effects, orifice clogging and ionisation type inter-element
effects associated with extracting the plasma through the cool (4000K) boundary layer that formed over the extraction orifice.

Orifice clogging occurred with solutions of above 150µg.mL⁻¹ concentration, due to the use of pin-hole sampling cone orifice (50-70µm). This led to the formation of a cool boundary layer over the sampling orifice, an aerodynamically stagnant layer of gas where ion-electron recombination, charge exchange, ion-neutral attachment and several other reactions could occur (20).

Work in the 'boundary layer' mode of operation, as it was named, continued for a short time giving low background, excellent limits of detection and good linear dynamic ranges. However very high levels of refractory oxides (MO⁺) and hydroxides (MOH⁺) were noted and susceptibility to cone blockage and ionisation suppression were evident (20-23). In the boundary layer mode, the metalloids could only be determined as the oxide, with M-O recombination occurring in the boundary layer.

Despite the drawbacks of boundary layer sampling, several pieces of analytical work were carried out successfully. Date and Gray (23) showed that useful isotope ratio measurements could be made with <1% precision (1σ relative standard deviation) on lead and zinc and <5% accuracy compared to the 'true' value. Houk et al. (24) analysed polar organic compounds to determine the fragmentation
products formed in the plasma. Houk and Thompson (25) used discrete volume nebulisation to determine magnesium and nickel isotope ratios to better than 3% precision.

It became clear that a representative portion of the extracted plasma gas containing the analyte species of interest was not reaching the mass spectrometer and that bulk or continuum sampling of the plasma was required to ensure that a representative sample of the plasma gas was being extracted. This could be achieved by increasing the sampling orifice diameter, thus breaking through the boundary layer.

The extraction aperture system used in both the USA (Houk) and UK (Gray) ICP-MS instruments, was based on the earlier work with the capillary arc. At the gas temperature of about 3500K at the aperture from the dc plasma, the small diameters used were just enough to prevent the formation of a boundary layer across the aperture. However, the same sizes were no longer adequate for the ICP where the gas temperature close to the torch exceeds 5000K. At these temperatures a minimum diameter of 100μm is needed to break through the boundary layer formed over the surface of the extraction cone. The diameter needs to be increased at higher temperatures, so that a minimum diameter of 100 times the mean free path (λ) in the gas in front of the aperture is achieved. Although both ICP-MS systems had adequate pumping capacity to use apertures up to 250μm diameter, as soon as the diameter exceeded about 120μm an intense
discharge or 'pinch' formed in the gas entering the aperture, which produced a large photon background. Difficulty was experienced in cooling apertures of 70\(\mu\)m and when these overheated at the lip and melted back they tended to stabilise at about 150\(\mu\)m with the same 'pinch' discharge formation.

The 'pinch' discharge appeared to be a product of two factors, the plasma potential and the rate of fall of pressure along the axis of the aperture. The formation of this discharge was overcome by controlling the vacuum behind the aperture (2-3 mbar) together with the use of an aperture length to diameter ratio of unity. A full explanation was given by Gray (18).

At the same time as this work was being carried out, Douglas and French (30) were applying their experience in molecular beam techniques to extracting ions from a Microwave Induced Plasma (MIP). In this work a large (0.41 mm) sampling orifice was used, with a smaller skimmer cone mounted directly behind the sampling cone forming a differentially pumped vacuum interface, or 'expansion stage' as it later became known. The expansion stage system was also adopted in the U.K. by Gray and Date at about the same time and later by Houk in the U.S.A.

The MIP system of Douglas and French exhibited similar interference problems to those experienced by Gray with the DCP, particularly NO\(^+\) suppression due to the low thermal temperature of the MIP, although there was no suppression
from 100μg.g−1 sodium on 200ng.g−1 Cd. The MIP was later replaced by an ICP to become the prototype for the Sciex ELAN ICP-MS instrument (31, 32). Research is still being undertaken by various workers to adapt MIP's as ion sources for mass spectrometry for specific tasks (33, 34).

The system described by Date and Gray (27, 28) for continuum or bulk sampling, using a three vacuum stage instrument with large sampling orifice diameters, became the basis for the second U.K. ICP-MS prototype instrument installed at the Institute of Geological Sciences (IGS), in London, (now the British Geological Survey, BGS). The PlasmaQuad marketed by VG Isotopes was based on the design of the IGS instrument.

The system exhibited many of the features required by a useful analytical tool. Minimal refractory oxides occurred and hydroxides were absent or very low. NO+ was greatly reduced compared to boundary layer sampling as well as other polyatomic ions such as 36ArO+ and 80ArAr+. Ions such as 81ArArH+ were absent in continuum sampling. Spectra were simple and clean above mass 80, with interference ions being readily predictable.

Limits of detection were not as good as in boundary layer mode, but were still superior to many of those exhibited by other atomic analytical techniques such as Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and
Flame Atomic Absorption Spectroscopy (FAAS). The linear dynamic range of five orders of magnitude was also superior to those of optical techniques. Easily ionisable element suppression was only significant above 200 μg.g⁻¹ for an element such as sodium. Ionisation temperature was measured as approximately 8000 K with all except three elements (He, Ne, F) of the periodic table being ionised and only some 26 elements exhibiting double ionisation. Ion energies were greater than in the boundary layer mode, a consequence of rupturing the boundary layer which shielded the rest of the system. from the high plasma potential that was present at that time.

1983 saw the market release of the two commercial instruments, the Sciex ELAN (35) and the VG Isotopes PlasmaQuad (36). This led to several evaluation studies of ICP-MS using the commercial systems. Gray had already pointed out the tremendous range of applications for the technique (17, 37, 38). Systems were shown to have very good detection limits and simple spectra, but were very prone to signal response drift (39, 40). Horlick et al. (41) carried out an extensive study of the effects of operating parameters (nebuliser flow, forward power, sampling distance etc.) on elemental ion signal rate and interference ion signal rate. This work, carried out on the ELAN, showed that the optimisation of operating parameters was critical.

Despite the initially rather cool reception, several pieces of applications work began to appear in the literature.
Reference Materials (RM) were studied to assess the accuracy of the technique (42) for environmental samples, geological samples (43) and marine samples (44). The spectral simplicity for all elements led to many workers investigating elements that were traditionally difficult to analyse by optical methods, such as the Rare Earth Elements (REE). Early work during the development of ICP-MS instrumentation had often pointed out the relative ease of REE analysis (16, 32, 45-47). Initial studies of REE showed that good accuracy was obtainable (40, 43). Possible errors arose from refractory oxides of the lighter REE whose masses coincided with those of the heavier elements.

Alternative methods of sample introduction began to emerge. Gale (48) illustrated the possibilities of using electrothermal vaporisation (ETV) for introducing a dry vapour into the plasma, following suggestions from Date and Gray (29) that dry sample introduction methods such as ETV, laser ablation or arc nebulisation could be an advantage where interferences from oxygen related species might be a problem. Both Gray (49) and Arrowsmith (50) later demonstrated the possibility of laser ablation. In addition to the initial studies in applications of ICP-MS, fundamental work was continuing on the nature of ion sampling of plasmas (51) and kinetic energy distributions.

By the time commercial systems had been available for 3-4 years, the number of papers published on ICP-MS had
increased greatly, as shown in figure 1. Applications greatly outnumbered fundamentals papers and covered a wide range of subjects. Conference proceedings also contained a large contribution from ICP-MS workers.

ICP-MS has now been applied to scientific study in the environmental and biological sciences, the earth sciences and in industrial and metallurgical fields.

Within these subject groups, both elemental analysis and isotope ratio determinations have been carried out (24, 55, 58, 61, 64, 65, 77, 90, 104, 108, 109, 110). The method of standard additions (44, 52) as well as internal standardisation (53-56, 89) and isotope dilution analysis (31, 44, 52, 54, 56-58, 61) have been employed for more accurate results and as methods of avoiding matrix effects.

As so many analytical applications of ICP-MS have been reported, it is beyond the scope of this text to comment on them all satisfactorily; comment on specific applications is made where relevant. The reader is directed to the literature, in particular the Annual Reports on Analytical Atomic Spectroscopy (ARAAS) which runs from Volume 1 (reviewing 1971) to 14 (1984) and is now incorporated in the bimonthly publication of the Journal of Analytical Atomic Spectrometry and renamed Atomic Spectroscopy Updates (ASU). This is an essential source of material reviewing all areas of atomic spectrometry. The impact of ICP-MS on the analytical community is such that a new section of ASU has been formed (X-Ray Florescence and Mass Spectrometry) which
incorporates a specific section on ICP-MS.

1.3 Aims of the Project

The project is a detailed study of the factors affecting the performance of ICP-MS as a multi-element trace analytical technique for the analysis of solutions and slurries and as a technique for the rapid determination of isotope ratios using a variety of sample introduction methods.

The study can be broken into six basic components:

i) An assessment of ICP-MS instrumentation currently commercially available and which was used in this study, together with quantitative data on factors affecting sensitivity, accuracy, precision, resolution and dynamic range.

ii) An examination of the spectral interference, from polyatomic, analyte oxide and doubly charged ions.

iii) An assessment of the effects of varying plasma operating parameters, such as power, gas flow etc., on system performance.

iv) Determination of trace impurities in pure and alloyed materials.

v) Determine ultra-trace levels of the nuclear decay product $^{99}\text{Tc}$.

vi) Development of procedures for solid sample introduction by slurry nebulisation.

The majority of the project has been dedicated to assessing and optimising the system with a view to improving performance and comparing this to the results reported by other workers on different systems. In addition to these fundamental studies, the analytical capabilities have been examined by performing analysis on several types of 'real' sample using a variety of sample introduction methods.
CHAPTER TWO

ICP-MS INSTRUMENTATION AND PRINCIPLES OF OPERATION
2.1 Introduction

As ICP-MS is a new technique and part of this project has been involved with system development, the details of the instrumentation and the principles of operation are reported below. The project was carried out using two ICP-MS systems:

i) The original U.K. prototype developed at the University of Surrey (22).


Each has advantages over the other for various aspects of the work described here and use of each instrument is detailed where relevant. In general the prototype was used for studies where significant instrument modifications were required or large amounts of data were not produced. Where large volumes of data requiring manipulation were involved, the PlasmaQuad was used, as it has more comprehensive computing and software facilities.

For a more complete picture of ICP-MS instrumentation, some details of the Perkin-Elmer Sciex ELAN (Thornhill, Ontario, Canada) ICP-MS system are given, as certain key parts of the instrument differ fundamentally from those of the PlasmaQuad and its prototypes and are reflected in the disparity of performance of the systems.
2.2 The Inductively Coupled Plasma

2.2.1 Development of the Inductively Coupled Plasma
The ICP has been traced back to 1884 by Eckert (132), when Hittorf (133) discovered the low-pressure electrodeless ring discharge in experiments on the conduction of electricity through rarefied gases. Babat (134) (credited as the inventor of the induction arc) discovered in 1942 that a ring discharge, once established, can be maintained while the pressure is raised up to atmospheric level. Major interest developed only after Reed (135), in 1961, had shown that with an open tube and streaming gas, one can produce an 'induction torch' where the plasma is directly observable and can be used as a heat source. The inductively coupled plasma torch (ICPT) described in Reed's paper operated at atmospheric pressure on argon (alone or mixed with other gases) powered by a 10kW high frequency heating unit operating at a frequency of 4MHz. The torch consisted of a quartz tube with a brass base, having a tangential gas entry, placed within the water cooled work coil (usually made of copper tubing) of the generator. A pilot plasma was first formed by the insertion of a carbon rod into the torch thus producing thermal electrons by the Joule heating effect of the alternating magnetic field. This provided the initial ionisation of the argon, enabling coupling to occur and a plasma to form. Reed thought that a tangential gas entry was necessary in order to create a vortex which would cause some of the plasma to flow counter current to the gas flow and so maintain the plasma. The equivalent circuit of this
discharge can be thought of as a transformer, with the secondary circuit closed by the gas discharge (138). In a subsequent paper (136) Reed described a torch with three concentric tubes with a centre powder feed which he used for growing crystals of refractory materials. Later (137) he described the physical properties of these plasmas and suggested possible application as spectral sources for solids. In 1963 patent applications were made (UK;139, US;140) by Greenfield and his colleagues for a torch similar to Reed’s, but adapted as a spectroscopic source and consisted of three concentric tubes. The two outer quartz tubes were used to contain the plasma and the inner borosilicate glass tube was used to inject an aerosol through the flattened base of the plasma, once this was formed. The plasma was started using the discharge from a Tesla coil or by using a graphite rod in the same way as Reed. This device was described in 1964 (141), which provides the first reference to the actual use of this type of cell with an annular plasma and the utilisation of the emission from the plasma. This original cell design was so successful that the same design is in use in modern instruments (Figure 2.1), with the laminar flow torch the only major alternative design to have emerged (142). The formation of the annular and stable plasma is a function of gas flows, tube geometry and operating frequency (138).

The very high temperatures of the ICP make it a remarkable vaporisation-atomisation-excitation-ionisation source for elemental analytes. The temperature distributions in the
Figure 2.1 The Greenfield and Scott-Fassel ICP Torches
ICP have been extensively studied; a suitable review can be found in Blades (143). Gas temperatures have been shown to be between 2000K and 8000K in the plasma. Fassel (144) shows the distribution of the temperature along the axial channel, the temperature within the fireball being about 8000K. Any sample contained in the centre channel is surrounded by the hotter (10,000K approx.) annular fireball. A combination of central channel gas velocity and the fireball length give sample residence times in the plasma of about 2ms. Samples introduced into the plasma via the injector tube as micro-particulates are subjected to rapid increases in temperature and begin to vaporise. As the carrier gas leaves the plasma energy addition region and enters the tail flame, the temperature starts to fall (Figure 2.2). It is important for analytical purposes that the residence time of the sample in the hottest region is sufficient for complete vaporisation and dissociation. In order that the matrix elements in a given sample are fully vaporised (for incomplete vaporisation may cause incomplete release of elements of interest from within the micro-particulates composed of matrix elements) and sufficient excitation of the elements of interest occurs, carrier gas flow rate has to be carefully optimised. However, the huge amount of literature reporting on the use of the ICP for optical emission trace analysis of samples shows the outstanding performance that can be obtained in terms of sensitivity, detection limits, dynamic range and freedom from matrix interferences. The advantages that the ICP
Figure 2.2 Temperature Profile in the ICP and Nomenclature System
offers as an ion source for mass spectrometry were summarised by Gray (145) and Gray and Date (22), thus:

a) High sample channel gas temperature of >5000K

b) Annular form which permits stable sample introduction to a region from which it cannot escape

c) Freedom from inter-element and matrix effects due to high gas temperature shown in use as an optical emission source

d) High electron population, which gives the plasma a high degree of stability

e) No electrodes in contact with the plasma to cause contamination

f) Much ICP experience world-wide as an emission source

g) Readily available commercial hardware

h) No organic ions will be produced from the molecules present from pump vapours and other organic materials present in the vacuum chamber, because the ion source is outside the vacuum envelope.

i) Simple spectra, few peaks at fractional masses, or peaks from molecular ions.
2.2.2 ICP Systems used in this Project

The ICP system operated on the Surrey research instrument has been described in detail elsewhere (45, 145). The version of PlasmaQuad used in this work, which was standard at the time of production, had a radio frequency (r.f.) generator and torch box (Radio Frequency Associates, Eastbourne, Sussex, U.K.), containing the automatic matching unit, horizontally mounted quartz torch, load coil and nebuliser system, as shown in Figure 3. Connection of the generator to the torch box is by high power rf cable. The generator is a crystal controlled r.f. generator producing 0-1500 Watt RMS (stabilised to 1%) power into a 50ohm output impedance, with an operating frequency of 27.12MHz. Gas supply to both instruments is normally provided from a liquid argon tank, although cylinders may also be used. Each instrument has a precision regulator to reduce the nominal 70-80 psig of argon to the operating pressures of 40 psig on the research instrument and 65 psig on the PlasmaQuad.

2.3 Sample Introduction

In ICP-AES, samples are often introduced from solution into the central carrier gas stream by means of a pneumatic nebuliser, although any method capable of producing a gas borne aerosol or vapour can also be used. Fassel (130) has summarised the various physical and chemical forms of the aerosols and gases that have been successfully injected into and analysed by ICP-AES systems. Both the systems used in this project originally used Jarrel-Ash fixed geometry cross
Figure 3 Left: PlasmaQuad expansion stage
Right: Torch box containing quartz torch, nebuliser system and load coil.
device, although the device had adjustable geometry. In this design, the argon flow from a capillary tube is directed across the mouth of a second capillary at right angles to it. The other end of this capillary is connected to fine bore plastic tubing which can either be directly dipped into the sample solution or fed via a peristaltic pump. In the work reported here, the solutions were always pumped to ensure a constant solution supply rate to the nebuliser so that was not dependent on suction created by the gas jet across the tip of the sample tube. The solution leaves the capillary in the path of the argon jet which disperses the sample in a fine spray. This type of nebuliser proved to be very robust for everyday usage, although occasional blockages occurred, caused by airborne dust particles, minute hairs settling in the solution or very fine particulates from incompletely dissolved samples, but these were very easily removed by applying back pressure to the uptake tube. This type of nebuliser was used for all solution work on the prototype instrument. Sample introduction was maintained at about 1.5mL.min⁻¹, the minimum flow rate that gave signal level close to maximum i.e. a plateau is achieved for signal response against increasing rate of sample introduction.

As the work reported here proceeded on the PlasmaQuad, a variety of pneumatic nebulisers were used. The Jarrel-Ash cross-flow, shown in Figure 4.1, was used for most solutions work, involving real sample analysis. A Meinhard type glass
Figure 4.1 Jarrel - Ash Cross Flow Nebuliser

Figure 4.2 Meinhard Glass Concentric Nebuliser
concentric nebuliser, shown in Figure 4.2, was used in the optimisation studies, in addition to a cross flow, to ensure that differences in nebuliser design did not play a part in system optimisation and to allow direct comparison with similar work carried out by other workers in the field who had used concentric nebulisers. Studies involving high dissolved solids or suspended solids (slurries) require the use of a Babington type V-groove nebuliser. For the slurries work reported here, either a PTFE Ebdon nebuliser (PS Analytical, Orpington, Kent, U.K.) or a De Galan nebuliser (Van der Plas products, The Netherlands) was used, (Figures 4.3 and 4.4 respectively). The De Galan nebuliser has subsequently proved very successful and is now used for all solutions and slurries work on the PlasmaQuad. All the nebulisers were operated with the single pass water cooled spray chamber described in chapter 4. This provided an indirect path to the plasma to allow larger drops to settle out and run into the drain.

The nebulisers described here are all very convenient to use. Although the cross flow and concentric nebulisers are self-aspirating, they were always pumped. The V-groove nebulisers have no self-aspirating ability and have to be pumped. This method of operation allows samples to be changed by merely transferring the uptake tube to a fresh container. Operation has also been successfully carried out on the PlasmaQuad with an automatic sample changer (Gilson model 221).
Figure 4.3 PTFE Ebdon V-groove Nebuliser.

Figure 4.4 De Galan V-groove Nebuliser.
The normal pneumatic nebuliser/spray chamber arrangement used for sample introduction into ICP's is very inefficient. For a pneumatic nebuliser operating at a normal gas pressure, most of the sample leaving the nebuliser is carried in droplets of about 30\(\mu\text{m}\) in diameter, which being too heavy to travel far in the gas stream, fall to the walls of the spray chamber. Droplets of <4\(\mu\text{m}\) in diameter are generally accepted as able to reach the plasma in the carrier gas and these constitute <2\% of the total sample volume (147).

2.4 Ion Extraction
The extraction of ions from chemical flames has been extensively investigated (8-14). The methods used in these techniques have been adapted for use with an ICP. As mass spectrometers are low pressure devices, their application to atmospheric pressure sources requires that the flame or plasma sample must be extracted and transferred to high vacuum for analysis, while retaining the chemical integrity of the sample. In the boundary layer sampling mode (1, 8, 29) where a layer of cooler gas forms over the extraction aperture, the residence time in an intermediate region of lower temperature (about 4000K) provides an opportunity for ion molecule reactions to change the composition of the sample. In order to avoid the formation of a boundary layer, large extraction apertures, with diameters exceeding 100 times the mean free path of atoms in the plasma, are required. With a mean free path of about
1.5μm (148), the minimum diameter is 150μm (0.15mm). In practice extraction cones with apertures of between 0.5 and 1mm are used to minimise problems of clogging caused by sample condensation around the aperture. As apertures of these sizes admit large volumes of gas, a very large pump would be required if the first stage behind the aperture were to operate at about 10⁻³ mbar, the usual pressure of a molecular beam stage, where ion lenses can operate effectively. This problem is avoided by using an initial 'expansion' stage or interface, which operates at about 2-3mbar as suggested by Douglas and French (30) in their MIP sampling work. This pressure can be readily achieved with a suitable rotary (mechanical) pump.

The arrangement of the ion extraction interface is very similar for all the current ICP-MS instruments, both commercial and 'home made', and have been described in detail elsewhere (45, 107, 119). For brevity, the interface that is used on the PlasmaQuad, which is based on the interface designed by Gray (45), will be described. Figure 5.1 shows the typical arrangement. A water cooled cone (extraction cone), Figure 5.2, with an aperture of 0.5-1mm and aperture diameter/length ratio of about 1, is inserted directly into the ICP, on axis with the central channel, with the base of the cone sealed to the vacuum system. Horizontal and vertical adjustment of the torch is provided to accommodate asymmetry in individual torches as well as axial positioning for extraction depth optimisation. The plasma jet encounters a sharp edge, to disrupt the gas
Figure 5.1 Arrangement of Ion Extraction Interface

Figure 5.2 L - R; Extraction cone, Wide skimmer, Narrow skimmer.
flow as little as possible. As the gas pressure in the expansion is about 2-3mbar, there is a steep pressure gradient (>100:1) along the length of the extraction aperture, which forms a jet of gas from the central channel of the plasma, (at a temperature of approximately 6000K), into the expansion stage. The directed jet formed by this expansion falls in temperature to about 200K within a few microseconds, thus effectively freezing any reactions between species that could occur in a slower expansion and distort the composition. Reactions that occur in less than a few microseconds, such as ion-molecule and attachment processes (103), result in the formation of polyatomic ions from species present in the ICP, such as argon gas and sample matrix ions. As ionic recombination is slow, the ionic composition of the sample is likely to be little changed.

Directly behind the extraction cone is a second sharper cone, (exterior angle of 57°), usually known as the skimmer. The skimmer, (the two types of which used in this project are shown in Figure 5.2), with an orifice of between 0.5 and 1mm, extracts from the core of the rapidly expanding jet of gas sampled from the ICP and passes it to the 2nd vacuum stage. The edges of this skimmer are generally as sharp as possible, to prevent formation of shock waves at the tip, although the tip does get hot enough to degrade the edge. The skimmer is carefully centred behind the extraction cone, with the tip inside the Mach disk (5). The pressure behind
the skimmer is usually less than $4 \times 10^{-4}$ torr and once in this region gas flow becomes molecular, making the use of electrostatic lenses necessary to separate the charged from neutral species. As these species pass through the skimmer aperture whose size is in the same order as the mean free path of these species, many collisions occur between the wall of the skimmer.

The extraction cone and skimmer are generally made of pure nickel, as it has a good thermal (and electrical) conductivity and chemical resistance, although many other materials have been explored for use (copper, aluminium, stainless steel, iron, graphite, ceramic etc.). The extraction cone surface slowly becomes pitted or roughened with use due to the high concentration of atomic oxygen in the plasma flame, forming a coating of nickel oxide. In addition, any matrix materials in the plasma such as sodium lead to faster degradation of the extraction cone, by chemical reaction, as do certain acids, such as sulphuric. Generally the lifetime of these two components is several months, with damage due to cleaning the more usual cause of failure. Some workers have reported the use of coatings, which are chemically exceedingly resistant, on their extraction cones such as titanium nitride or uniquely thorium oxide on platinum extraction cones, (Lichte et al., 73), who report unlimited life times.
Once separated from neutral species (which are pumped away), the ions are conducted by a series of electrostatic lenses to the spectrometer for mass analysis.

2.5 Ion Optics and Vacuum Systems

The design of the ion optics for ICP-MS instruments is very much dependent on the vacuum chamber arrangement. The vacuum system devised by Gray (45) which is used in the PlasmaQuad, as well as the majority of the 'homemade' instruments, (119) uses 3 discrete vacuum chambers. Figure 6 shows the basic layout, with the section between the extraction cone and skimmer, the expansion stage, forming the first section (2-3mbar), using a rotary pump to remove the gases. The section behind the skimmer, the intermediate stage which houses the extractor, collector and 2 other ion lenses, is evacuated using a diffusion pump, with rotary backing, with a pump speed of around 1200L.s⁻¹ and an operating pressure of around 4x10⁻⁴ mbar. The final or analyser stage, discrete from the intermediate stage except for a 2mm orifice (differential aperture) to allow ions through, houses a second set of lenses for ion collection and focusing into the entrance of the mass analyser. This stage is also pumped by a diffusion pump, of around 200L.s⁻¹ capacity, with an operating pressure of 10⁻⁶ to 10⁻⁷ mbar. The quadrupole mass filter can have potentials applied to the front plate, entrance rods and main rods (and in some cases exit plate and/or rods), although it is often found unnecessary and these potentials remain at ground. In order that photons from the plasma cannot reach the ion detector,
Figure 6 Schematic of VG PlasmaQuad ICP—MS Instrument

Figure 7 Schematic of Sciex ELAN ICP—MS Instrument
a 'photon stop' (of about 4mm) is placed in direct line of sight of the plasma to detector. This is placed in the intermediate stage, at about the position of the first lens after the collector, although it could be placed elsewhere.

In the vacuum system devised by Douglas and French (30) and used in the Sciex ELAN system, there are only 2 vacuum stages (Figure 7). The first is an expansion stage similar in many ways to that of Gray's design, but with generally larger orifice diameters. The second stage houses both ion optics and the mass analyser and is pumped by a single cryogenic pump. The reported pump capacity is around $2 \times 10^5 \text{L.s}^{-1}$ and operating pressure of around $10^{-3}\text{mbar}$. The most recent design of ion optics for the ELAN use a series of 4 ion optic elements to focus the ions into a Bessel box, which acts both as a lens system and a photon stop. As there is no differential aperture to assist in photon blockage, the photon stop in this device is somewhat larger (a disk of about 10mm in diameter). An additional photon stop behind the first lens has also recently been added. The ions are guided around the disk and focused into the quadrupole by applying small dc potentials to the various elements of the Bessel box and the disk. The ion lens systems used are simple arrangements of electrically biased cylinders, which collect ions emerging from the skimmer and focus them into a circular beam for entry into the mass analyser. The ions enter the analyser at low energy, (required for best resolution), which gives a long dwell time in the mass analyser. Excessive ion energy can be
offset by applying a small dc potential to the main rods of the quadrupole.

2.6 The Mass Analyser

2.6.1 Principles of the Quadrupole Mass Analyser

A quadrupole mass analyser is used in all current ICP-MS instruments for several reasons, including convenience and cost. From a practical point of view, most peaks occur at whole mass numbers, thus only relatively low mass resolution is required, which is readily satisfied by the quadrupole type analyser.

In the quadrupole analyser (mass filter), developed by Paul and co-workers (148), mass separation is achieved solely with electric fields. It is a path stability spectrometer where the parameter determining the stability of the ion paths is the specific charge (149). The analyser consists of a set of 4 parallel rods, usually of circular section, manufactured from stainless steel or molybdenum and mounted to very close tolerances in precision ground ceramics.

Opposing rods are connected together and to each pair a potential \((U + V \cos wt)\) with opposite polarities is applied; \(U\) is a fixed dc potential and \(V\) is the amplitude for an r.f. potential of frequency \(f = \omega/2\pi\). Ions are injected into the rod assembly along the axis and the system operates as a mass band pass filter, only ions within a limited range about a mean mass/charge ratio (m/z) being transmitted;
\[ m/z = \frac{C \cdot V}{f^2 r_o^2} \]

where 

- \( C \) = constant
- \( r_o \) = radius of the cylinder defined by the inner surface of the rods

The resolving power of the analyser \((M/\Delta M)\) where \( M \) is the mass transmitted in \( m/z \) is controlled by the \( U/V \) ratio, which can be electrically controlled. The mass transmitted is varied by changing the rf amplitude, \( V \), whilst maintaining the \( U/V \) ratio. This ensures that the relative peak width \((\Delta M)\) may be kept constant over the operating mass range. Figure 8 shows a schematic of the quadrupole mass filter.

2.6.2 Resolution

The resolving power or resolution of a mass analyser is a measure of its ability to separate (and identify) ions of (slightly) different masses (149). There are two commonly used determinations of resolution. The valley definition, which expresses resolution in terms of the highest mass at which two adjacent peaks of equal height, differing in mass by one unit exhibit a valley between the peaks not greater than a certain percentage (10%) of the peak height. The second definition is more useful in practice as it uses an isolated peak in the mass spectrum and can be defined as \( M/\Delta M \);
Figure 8. Schematic of a Quadrupole Mass Filter
where \( M \) = mass of the peak (in u)  
\( \Delta M \) = is the peak width at 5% or 50% (u)  
(5% peak width = 10% valley definition)

The mass resolution of \( M/\Delta M \) for a quadrupole is not constant, as with magnetic instruments, but the ratio of peak width to the separation between adjacent peak centres is usually constant and the resolution is often expressed as \( 1/\Delta M \). At any particular mass the usual \( M/\Delta M \) resolution may thus be obtained by multiplying the \( 1/\Delta M \) value by \( M \). The resolution of a quadrupole is thus often quoted as a multiple of \( M \).

For the peak shape produced by the quadrupole mass filter, unit mass resolution (1M) at 5% is approximately equal to 2M defined at 50% peak height. However in practical quadrupoles, there is some departure from truly triangular shape, the peaks are said to have "tails". This can be a problem if a small peak must be determined next to a large one. The ability of a mass spectrometer to separate the tail of one (large) peak from another (small) peak is termed abundance sensitivity. A number of factors contribute to tailing including imperfections in rod geometry, the limited number of r.f. cycles occurring during the ion flight and the energy and energy spread of the ions entering the quadrupole. Resolution cannot be increased indefinitely. Precision in the assembly of the rods, entrance aperture diameter, ion path angle and ion velocity all contribute towards finite resolution.
2.6.3 Instrument Quadrupoles

The quadrupole used in both instruments in the Surrey laboratory is a V.G. Analytical type 12-12S analyser with main analysing rods of 12mm diameter, 220mm long. A set of short rods, 25mm long is mounted at each end of the main rods on the same axis, which act as entrance and exit filters. These rods are fed with only the a.c. potential so that their main effect is to control the fringe fields which otherwise occur at the field discontinuities at the ends of the analysing rods. The normal scanning range of the analyser in the research instrument is 0-800u, although only 0-300u is used, but only 0-300u on the PlasmaQuad. They are normally operated at a resolution of 1.6M, which achieves background counts in the valley between two adjacent peaks. Operation at higher resolutions such as 2.3M, is possible, although ion transmission losses of some 50% occur. The quoted abundance sensitivity is between $10^{-5}$ and $10^{-6}$ of the peak height.

Ions are admitted to the rod systems through a 5mm circular aperture in the entrance plate. A pole bias facility is available which enables the mean dc rod potential with respect to earth be varied. This is normally set to about +6V during solution analysis to reduce ion energy, (mean ~12eV).
2.7 Ion Detectors and Signal Handling
To date, most ICP-MS instruments have a channel electron multiplier (CEM), shown in Figure 9, as an ion detector, in the pulse counting mode, although the use of other types of detectors have been reported (104, 128). The CEM, unlike other types of electron multiplier, can tolerate a relatively poor vacuum and can be repeatedly exposed to the atmosphere, a situation that sometimes arises.

Ions striking the mouth of the detector release electrons that are attracted along the conducting inside surface of the tube by the high electric field (a typical EHT of 3-3.5kV is applied to the CEM). Each time they strike the wall they release further electrons, so that an observed gain of about $10^8$ is achieved. Pulses from the ion detector are fed by coaxial cable to a pulse amplifier and discriminator (to reject electrical and r.f. noise) which produce a standard output pulse for every input pulse which exceeds the discriminator threshold. The output is sent to a multichannel analyser and a rate meter in parallel in the Surrey based instruments. The ratemeter allows rapid visual count rates (counts/s) to be obtained for a specific mass set by the quadrupole.

2.8 Data Accumulation
In principle, quantitative measurements could be made by tuning the quadrupole mass analyser manually to the peaks of interest and integrating the signal pulses obtained. Looked at simply, this is not a very practical method of data
Figure 9 Galileo Channel Electron Multiplier, Model 4870.

Figure 10 Tracor Northern Model 7200 Multi Channel Analyser used on the PlasmaQuad.
acquisition, requiring a high degree of peak stability and operator patience. This is however, the principle upon which computer controlled 'peak hopping' is based. As a direct pulse output is available from the preamplifier, the rate of which is proportional to the rate of ion arrival at the detector, digital storage of the incoming data is straightforward.

In the Surrey type systems, the pulse output is fed into a Multichannel Analyser (MCA), a fast digital buffer store, in Multichannel Scaler mode. Use of high speed scanning gives some degree of immunity from plasma noise. Figure 10 shows the Tracor Northern model 7200 MCA used on the PlasmaQuad. Models differ, but in principle they have a number of memory channels (Research Inst., 4096; PlasmaQuad, 2048 or 4096) each capable of storing around $10^6$ counts. The total memory can be divided to 2 or 4. The channel dwell time can be set from a few microseconds up to several seconds. For data acquisition, the MCA completes one sweep of its memory channels, as the mass analyser completes one sweep of the preset mass range. As the two are synchronised, the time for one sweep is controlled by the channel dwell time set in the MCA. For example, if 1024 channels are selected with a dwell time of 100μs, one sweep would take 0.1024s. Preselecting 600 (repetitive) sweeps or scans would give an integrating time for any given spectrum of just over one minute, regardless of the mass range covered. Once accumulated in active memory, a spectrum can
be downloaded to a storage medium, such as floppy disk, via a computer. On the Surrey research instrument, the mass range is manually preset on the quadrupole control unit with the MCA used to initiate the mass scan via an interface. Once accumulated, the spectrum is usually down-loaded to an IBM PC portable computer, via a serial (RS232) interface, for storage on floppy disk. Data collection software was provided by Canberra Packard, Pangbourne, Berks, U.K. All software for spectrum display, manipulation and integration was written by the author.

The PlasmaQuad is completely under computer control for all data accumulation and manipulation. The software prompts the operator for mass range, number of sweeps, dwell time and number of channels, or can be automatically selected from an operator defined set of elements and isotopes. This information is sent to an 'onboard' hard wired computer which is responsible for all MCA and quadrupole control. Computer control has the advantage of allowing specific regions of the mass spectrum to be 'skipped'. For example, with this feature, if a mass region contains ions of an excessively high count rate ('gas' or 'water' peaks) the quadrupole and MCA can be instructed to scan across this region at their maximum rate, thus minimising the number of ions striking the detector. The benefits of computer control are paid for with a certain loss of flexibility and control over the MCA during data acquisition. The Sciex ELAN system has no MCA data buffer, amplified detector pulses are fed directly into a fast computer. With this arrangement,
scanning rate, (which is slower than the MCA controlled systems) is controlled by the processor speed of the computer.

2.9 Data Acquisition

There are two basic modes of data acquisition on the current ICP-MS systems; (i) scanning mode and (ii) peak hopping mode, each with its own method of acquiring data over the mass range of interest. Data acquisition was carried out in scanning mode throughout this project.

2.9.1 Scanning Mode

As described above, scanning involves setting the quadrupole to scan across a selected mass range, synchronised to the MCA. Apart from the physical resolution set by the mass spectrometer, peak profile in the MCA can be optimised. If a scan range of 100u is chosen, with 1024 channels of the MCA, each peak would occupy 10 channels. This provides good peak profile on screen and for subsequent peak integration, whereas a scan of 250u would only provide 4 channels per peak. A scan of this width would therefore require 2048, or even 4096 channels which would give 8 or 16 channels per peak respectively.

In a scan when 10 channels are available for each span of 1u, the total integrating time on any single isotope peak is only 0.6 seconds for a total time of 61.44 seconds for 600 sweeps and 100μs dwell time. This emphasises the problem of time sharing across the spectrum in a scanning based system. This affects the total integrated count for each
peak and therefore its statistical precision. Qualitatively, there is no effect; a peak does not increase its visibility above its surroundings, as peak height in the display is not increased if more channels are devoted to it, only its width, which improves the statistics for that peak.

A scan of 0 to 250u is useful for assessing unknowns before carrying out detailed analysis and quantification. There are several options available for improving the precision. The most obvious and straightforward method is to narrow the scan width, set by the mass analyser, over isotopes of interest, so long as they are adjacent. In addition, the dwell time and number of sweeps could be increased for improved counts and precision. Narrowing the mass width may not be an acceptable method of improving peak integrals if isotopes of interest are several mass units apart. For example, investigations into the rare earth elements often involves Sc (45u) and Y (89u) as well as the REE's (130-175u approx.). This involves a scan width of some 130u, of which 81u (46-88u and 90-129u), over half the mass range, are of no interest and waste scan time. This problem can be overcome in the PlasmaQuad computer controlled system, where skip scan regions can be implemented. The quadrupole and MCA can be instructed to scan as rapidly as possible over specific mass ranges, in this case 46-88u and 90-129u. Assuming 100μs dwell time, 2048 channels and 300 sweeps (61.44s total integration time), therefore approximately 16 channels per peak, the dwell time for each peak would be 0.48s. Skipping a total of 81 mass units would save
approximately 38s of a 1 minute scan. This 'saved' time can then be used by increasing the dwell time which would only be spent on the regions of interest: increasing the dwell time to 200μs would increase the dwell time for each mass of interest to just under 1 second and give a total integration time of a little over 45 seconds. Increasing the number of sweeps would have a similar effect, except that this would also increase the number of times the skipped regions are covered, which would waste some time.

This method does lead to a certain degree of 'blindness'; important potential matrix and interfering elements may be skipped over and thus missed. However, providing that full range qualitative scans are carried out before quantitation, this should not happen.

2.9.2 Peak Hopping Mode

Peak hopping is in reality an extreme skip scan and can only be carried out under microprocessor control. Simply, it involves making the quadrupole transmit predetermined masses to the detector and maintaining that mass transmission for a preset dwell time before 'hopping' to the next mass of interest.
Under computer control several parameters can be set up:

a) Masses of interest
b) Number of points per peak
c) Digital to Analogue Converter (DAC) stepping
d) Dwell time for points at a specific mass. Each mass can have a different dwell time.
e) Number of passes across selected mass range.

For each mass of interest (a), a number of points across the peak can be specified (b), as shown in Figure 11. A minimum of three points is recommended as peak shape is not stable, only one point per peak may miss the nominal top or centre of the peak. The distance between the points across the peak can be set by the number of DAC steps (c) between each point on the peak. Each digital value corresponds to a voltage which corresponds to a mass point. For each peak specified, a dwell time (d) can be set up for the points on each peak. The advantage of peak hopping over skip scan is that individual dwell times can be set on different isotopes, particularly useful in isotope ratio determinations where a very small isotope can have a much longer dwell time to increase its integrated counts and improve its precision. This would allow any non-random noise to be spread out across the range, rather than concentrated in a particular mass.

Peak hopping offers several advantages in its economy of analysis time since only the masses of interest are dwelt
Figure 11  Idealised Peak Hopping Arrangement
3 Points/peak, DAC Step=50, 0.25 μ spacing
upon and isotopes of very low abundance can be more efficiently counted by significantly increasing the amount of dwell time spent on it. The major disadvantage of peak hopping is its 'blindness'. There is no spectral information available following an acquisition, so that problems arising from isotopic overlaps, interference ions, lack of resolution or even contamination cannot be identified at a later date when a data error is suspected. This 'blindness' eliminates one of the major advantages of ICP-MS, the ability to check back over acquired spectra for problem solving or information on elements that were not originally selected for attention.

2.10 Data Acquisition and Display
Although the MCA is an excellent means of data acquisition, the facilities available to the operator are dependent on the sophistication of the equipment. The MCAs on the two instruments used in this project serve essentially the same role - data acquisition. On the PlasmaQuad this is entirely true, with all control of the MCA and handling of the acquired data carried out by a small IBM PC XT computer. Initially on the research instrument, the MCA was used to control data acquisition, spectral identification, manual peak integration, data storage to tape and spectrum dumping to serial plotter. With the addition of a small PC portable computer and relevant software, many of these tasks are now carried out "off line", with data being directly transferred to the computer for storage onto floppy disk which allows
subsequent spectral manipulation, automatic full mass integration and spectrum dumping to printer or plotter. Data acquisition is still carried out under the control of the MCA.

Once acquired, the level of sophistication of data manipulation depends on the available software, but can be split into 4 basic categories:

1) Qualitative
2) Semi-quantitative
3) Quantitative
4) Isotope ratios

The categories have other features such as the use of dilution or standard additions. On the research instrument current software allows 1) to be carried out, with 2)-4) being carried out by third party software, such as commercially available spreadsheet packages. The software available for the PlasmaQuad allows all these procedures to be carried out, on line.

2.10.1 Qualitative Analysis
In simplistic terms, qualitative scanning is a visual interpretation of any acquired sample spectrum by the operator. This can either be carried out on the MCA or via the appropriate piece of software. In reality this is one of the more powerful features of ICP-MS. Spectral interferences can be rapidly identified; isotopic overlaps,
polyatomic or other interference ions can be identified; unknown matrix elements can be located and the possible interference repercussions sought. Date al. (43, 71) pointed out the importance of spectral examination for possible interference identification.

Figure 12 shows a spectrum recorded of a solution containing 1% sulphuric acid with 10ng.mL⁻¹ of Co, over the mass range of 45-80u. In practice this could be a sample of sulphur containing compounds e.g. cadmium sulphate, or the result of a sample digestion involving sulphur based acids, of which the operator is unaware. Sulphur based polyatomic peaks occur at several masses from 48 to 66u. These could interfere with Ti(48-50), V(51), Cr(52), Zn(64,66) and Cu(65). Straight forward calibration against a standard would result in serious inaccuracies in the determined elemental concentrations of the sample. An examination of a complete spectrum would quickly show up any such peaks and incorrect isotope relationships. Carrying out qualitative scans and spectral interpretation can avoid possible problems at a later stage and enable peaks free from interferences to be chosen for analysis, or if none are available, corrections to be made.

So long as samples are acquired in scanning mode, spectra can always be examined at a later date. If an analysis has been carried out on a series of samples and the results do not appear to be correct, the spectra can be examined for evidence of interference problems. Other isotopes of the
Figure 12  Spectrum of 1% Sulphuric Acid and 10ng.ml\textsuperscript{-1} Co.
elements of interest may then have to be selected for the calibration.

Survey scans of a qualitative nature can very rapidly tell the analyst which elements are present in a totally unknown sample, a feature that has considerable value in many branches of science.

2.10.2 Semi-Quantitative Analysis

Following on from 'What is in my sample?', the next question is often 'How much is in there?'. Normally this would require standards to be made up for all the elements of interest, which can be a time consuming operation. If only an estimate of the concentration of the elements in the sample is required, to within an order of magnitude, semi-quantitative analysis is an ideal method for determining these values.

All elements with an ionisation potential below 8eV will exhibit 100%, or close to, ionisation and should therefore give the same signal response for 100% isotopic abundance. In practice a curve similar to that shown in Figure 13 is obtained. The curvature is due to mass bias effects in the interface, quadrupole, detector and probably discrimination against ions with masses below 40 (argon). There only remains the response level of this curve to be determined, which can be obtained from the integral of one element in the centre of the mass range. All elements, corrected to 100% isotopic abundance, can be calibrated against this
Figure 13  Signal Response Curve for Selected Elements across the Mass Range. Responses Corrected to 100% Abundance
curve for semi-quantitative analysis, except those with significantly lower degrees of ionisation (e.g. Br, 1st ionisation potential, 11.85eV; degree of ionisation 4.5%). For these elements an additional correction for degree of ionisation adjusts their response closer to the mass response curve.

2.10.3 Quantitative Analysis
Multi-element quantitative analysis at the very basic level requires the peak integrals of elements of interest in a spectrum of an unknown sample to be compared to those from a sample containing these elements at a known concentration. In practice, real analysis requires several other "samples" to be taken into account in the final calculations, such as instrument and sample blanks, drift standards, ranges of standards (composition and concentration), internal standards. These refinements are quite apart from the analytical precautions such as matrix matching of blank samples and standards.

An initial blank, usually of deionised water or a suitable acid (usually 1% nitric), is analysed to obtain levels of the background species that may be important in a particular analysis (e.g. polyatomic ions such as ArO or ArAr) or general full mass random background. This is followed by the first of a series of sensitivity standards or drift monitors. This is a standard containing all or most of the elements of interest and is analysed at intervals throughout
the analysis procedure. Multi-element drift from monitor to monitor can be calculated and applied to the standards and samples accordingly. Calibration standards follow, containing the elements of interest at a variety of concentrations. The samples and sample blanks can follow this, interspersed with the sensitivity standard drift monitors.

Internal standardisation is a possible alternative or addition to sensitivity standardisation. It has been shown however, (89) that internal standards have to be used with caution in ICP-MS, taking factors such as the mass and ionisation energy of the internal standard into account as well as the elements that it is standardising. Generally one internal standard cannot be used for all elements in the mass range.

2.10.4 Isotope Ratio Analysis

ICP-MS offers the ability to carry out rapid isotope ratio determinations directly on sample solutions. Analytical precision can be determined from replicate analysis of the sample and the accuracy of the determinations can be assessed with solutions containing elements with a certified isotopic composition. These certified solutions can also be used to assess and correct for mass bias in sample analysis. At high count rates, counting loss in the ion detection and pulse counting system is caused by dead time. This would appear as a mass bias, if isotopes of very different abundances were compared.
CHAPTER THREE

ASSESSMENT OF ICP-MS PERFORMANCE
3.1 Introduction

For a new analytical technique to be of practical use to the scientist, it must possess the performance qualities that he has come to expect from other systems. In analytical atomic spectrometry the four deciding factors for the usefulness of an instrument are probably accuracy, precision, limits of detection and sensitivity. Additional criteria such as linear dynamic range and resolution are often also very important to the analyst. These have to bear some relationship to reasonable analysis times, sample preparation methods and cost of maintenance and operation of the instrument. The use of an instrument with excellent precision and accuracy might be impractical if the analysis time is prohibitive, or sample preparation so complex that errors are introduced in the form of contamination.

Factors affecting the criteria mentioned above have been investigated for ICP-MS by several workers and have been reviewed elsewhere (15, 17). However, for completeness, the factors are discussed here with qualitative data derived from the instruments used in this project.

3.2 Sensitivity

The sensitivity for a given element can be determined by aspirating a solution of that element at a given concentration or molarity and determining the count rate.
The count rate could be determined with the mass spectrometer set to transmit ions of only one mass and monitoring the count rate. This is impracticable if several elements are to be determined. A more straightforward method is to run a multi-element solution, with a set of elements ranging in mass and ionisation energy and measure the integral over each peak of interest in the mass spectrum.

Table 1 shows the sensitivities obtained on the PlasmaQuad for a series of elements run in a multi-element solution, each at 1µg.mL⁻¹, together with their ionisation energies. These sensitivities were determined with the ion optics adjusted to give level response across the mass range. Response across the mass range is dependent on other factors, as described in chapter 5 and these were optimised to give level response.

The resolution on the mass spectrometer was set to give unit resolution at 1µg.mL⁻¹ i.e. down to background counts in the valley between peaks at M ± 0.5u. An example is shown in Figure 14, a section of a multi-element spectrum showing Ag, Cd, In, Sn, Sb, and Te. Sensitivity is directly affected by changes in mass resolution as this affects ion transmission through the quadrupole. Under normal circumstances resolution is never changed once set up. Figure 15 shows the effect of increasing resolution on the signal obtained from 1µg.mL⁻¹ Ce.
Table 1.

Signal Response for Several Elements across the Mass Range

<table>
<thead>
<tr>
<th>Element</th>
<th>Response</th>
<th>I.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>79842</td>
<td>5.39</td>
</tr>
<tr>
<td>Mg</td>
<td>60041</td>
<td>7.65</td>
</tr>
<tr>
<td>Al</td>
<td>72828</td>
<td>5.99</td>
</tr>
<tr>
<td>Co</td>
<td>186987</td>
<td>7.87</td>
</tr>
<tr>
<td>Rb</td>
<td>81739</td>
<td>4.18</td>
</tr>
<tr>
<td>In</td>
<td>161798</td>
<td>5.79</td>
</tr>
<tr>
<td>Ba</td>
<td>118148</td>
<td>5.21</td>
</tr>
<tr>
<td>Ce</td>
<td>151690</td>
<td>5.57</td>
</tr>
<tr>
<td>W</td>
<td>422817</td>
<td>7.98</td>
</tr>
<tr>
<td>Pb</td>
<td>260092</td>
<td>7.42</td>
</tr>
<tr>
<td>Bi</td>
<td>203199</td>
<td>7.29</td>
</tr>
<tr>
<td>U</td>
<td>250587</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Forward power 1300W, Meinhard nebuliser flow 0.73L.min⁻¹
Elemental responses corrected for isotopic abundance
Responses in Area counts.sec⁻¹
Area counts.sec⁻¹ = Peak area (in counts)/total peak dwell time (in secs.)
I.E. = 1st Ionisation Energy (eV)
Figure 14 Part of a Spectrum of a 1μg.ml⁻¹ Multi-Element Standard

Xe is a contaminant in the Ar support gas.
Integral at 115μ is 83,000.

Figure 15 Dependence of Signal Response on Resolution
Elements which are less than 100% ionised will show lower sensitivities. The degree of ionisation for a plasma in Local Thermal Equilibrium (LTE) may be calculated from the Saha equation, if values are known for the ionisation temperature \( T_i \), ion and atom partition functions and electron concentration \( N_e \). For typical values in an argon ICP of \( T_i = 8000K \) and \( N_e = 2.5 \times 10^{15} \text{ cm}^{-3} \), the degree of ionisation for all elements \( V = 15.76 \text{ eV} \) is shown in Figure 16, plotted against ionisation energy.

Sensitivity is also determined by factors other than degree of ionisation, such as: abundance of each elemental isotope, mass discrimination throughout the system (including ion extraction and expansion process), ion transmission of the mass analyser and mass dependent response of the ion detector. As will be shown later, the sensitivity of individual elements also varies with changes in operating parameters.

3.3 Linear Dynamic Range and Dead time
The linear dynamic range in atomic spectrometry can be expressed as the part of a calibration curve where change in signal response is directly proportional to change in the concentration of the element(s) of interest, i.e. the relationship between response and elemental concentration satisfy the equation for a straight line. The dynamic range of the PlasmaQuad was determined by running a series of Ni solutions of 1, 2, 5, 10, 20 and 50\( \mu \text{g.mL}^{-1} \). Ni has five isotopes, ranging from 0.95% to 67.8% abundance. This
Figure 16  Degree of Ionisation against First Ionisation Potential assuming $T_i = 8000K$ and $N_e = 2.5 \times 10^{15} cm^{-3}$
provides an effective concentration range of 9.5ng.mL\(^{-1}\) to 33.9\(\mu g.mL^{-1}\) from the six solutions. The lower limit of this range was approaching zero. Figure 17 shows the signal response curve for this range. At concentrations above 1.5\(\mu g.mL^{-1}\), where the signal was over 1.2x10\(^6\) counts.sec\(^{-1}\), deviation from linearity begins.

The channel electron multiplier detector and pulse counting system begin to count fewer events than actually occur at high ion count rates due to their dead time. Dead time (\(\tau\), in nanoseconds), is the inability of a detector and its associated electronics to resolve successive pulses which occur at less than a given interval. However, a dead time correction can be applied which compensates to some extent for deviations from linearity. If the true count rate, \(n\), is much less than \(1/\tau\) then:

\[
m = n (1-n\tau)\]

where \(m\) is the observed rate.

Applying a dead time correction of 110ns, with the detector used at the time, linearised the upper part of the calibration curve as shown in Figure 17. An alternative way of dealing with high counts is by detuning the ion optics for the higher concentrations. This is acceptable for demonstrating dynamic ranges, but impractical for real analysis, where solutions will contain elements at a whole range of concentrations. In this case, dead time correction is the only acceptable way of maintaining linearity. Figure 17 also shows the effect of over correction using
Figure 17  Signal Response against Ni Concentration
With and Without Dead Time Correction
dead time compensation methods. Use of 150ns dead time correction with the data for this calibration curve causes the latter part of the curve to become over corrected and deviate from linearity. This shows the importance of determining and using the correct dead time value.

When count rates in excess of about $8 \times 10^6$ counts/sec$^{-1}$ in pulse counting mode are expected, the CEM can be used in the less sensitive mean current mode of operation. Here ion currents are detected by the CEM and electronically converted to pulses for the purposes of counting.

It is particularly important for isotope ratio determinations to use the correct dead time value, especially where the two isotopes under investigation may have a difference in abundance of 3 orders of magnitude and the concentration of solution has to be high enough to detect the minor isotope but pushes the major isotope above the uncorrected linear range of the calibration curve. Under these circumstances dead time should be assessed accurately.

A convenient method of doing this is to analyse a series of solutions of the element(s) of interest at a range of concentrations. By integrating the raw data several times, each time with a different dead time correction value, then by calculating the isotope ratio of isotopes offering the greatest difference in abundance, the optimum dead time can be determined. Figure 18 shows the results from the measurement of $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratio for 3 elemental
Figure 18  Lead 208/204 Ratio against Dead Time, for 3 Lead Solutions
concentrations following peak integration with several different values of dead time. The convergence point indicates that a dead time correction of 90ns is required to obtain maximum linearity from the detection system. Detector dead time should be regularly checked, as it changes with the age of the device, particularly if high ion count rates are normally observed.

On the PlasmaQuad, dead time correction is automatically applied to each channel of data during peak integration, using the operator input dead time, by the on-line computer. Data acquired with the research instrument can be corrected using commercial software packages.

The wide dynamic response and the high throughput of the technique are of little value if the linear range is subject to memory effects. This is one of the drawbacks of a system with good sensitivity and low limits of detection; lower levels of memory can be detected. This is a particular problem in isotope ratio determinations. Certain elements are very troublesome, particularly those which are volatile, such as Br. Lithium and Hg are retained on the glassware, especially on the injector tip of the torch, for a long period of time, even if they are introduced at low levels (approx. 10-100ng.mL⁻¹) making isotope ratio determination almost impossible. Most elements however, have more realistic washout times. In designing the water cooled spray chamber (described in detail in Chapter 4), short washout times were one of the criteria considered. The
response for 1µg.mL⁻¹ ⁴⁹Co solution was monitored at a fixed mass setting. One second per channel dwell time was set on the multichannel analyser so that it plotted a continuous series of 1 second count integrals. The sensitivity was about 5x10⁵ counts.sec⁻¹/µg.mL⁻¹. After a steady signal rate was obtained, the uptake tube was placed in deionised water. The decay curve can be seen in Figure 19. After about 10 seconds, the signal had dropped to 1% of the original and 0.1% after about 50 seconds. After 90 seconds the signal was very close to the original background (5x10¹ counts.sec⁻¹), about 10⁻⁴ of the original signal.

3.4 Accuracy and Precision

Accuracy is a measure of how close the results of analysis are to the 'true' composition of the sample. The accuracy of an analytical technique is perhaps best assessed using RM's. Such materials are available in a whole range of matrices. In this work some references will be made to analysis of RM's for specific matrices under investigation. RM's have now been analysed using ICP-MS in many different scientific disciplines. In general the agreement with the certified value has been very good (±1-2 sigma).

As with other atomic analytical techniques, the accuracy of a determination relies on the accuracy of the standards and the type of standardisation, such as standard addition, isotope dilution or substitution. In addition, sample matrix related problems will affect accuracy. In ICP-MS, errors from both spectroscopic (polyatomic ions, analyte oxide ions
Figure 19  Single ion monitor of Co$^{+}$ ion for Spray Chamber Washout
and doubly charged ions) and physical effects (analyte signal suppression or enhancement, cone blockage) of the matrix elements affect accuracy. Nebuliser and spray chamber effects caused by differences in sample viscosity, changes in spray chamber temperature, fluctuations in nebuliser gas flow and sample uptake flow will affect the accuracy. Many of these factors will be discussed in detail later.

Many users quote the precision of a technique as a rather optimistic indication of "accuracy." Precision is a measure of the analytical reproducibility of a measurement. The major factors affecting precision are probably instrument 'noise' (e.g. electronic) and instrument instability or drift.

3.5 Background Noise Signals
The causes of random background, which is present right across the mass range, consist of a number of possible components (145):

a) Random electrical noise radiated externally or introduced on supply lines.

b) Radio frequency noise from the plasma system and from the quadrupole r.f. generator

c) Pulse amplifier noise

d) Random detector pulses (dark noise)

e) Direct plasma photons

f) Photons from decaying excited states of atoms and ions within the system after the photon stop.
All of these were observed at various times on both the PlasmaQuad and the research instrument. Careful grounding and, on the research instrument, filtered mains unit supplies, were the only solutions to (a). Attention to screening and grounding (and cable routing for the research instrument) holds (b) at negligible levels which can easily be rejected by the discriminator system of the amplifier.

Amplifier and detector background (c, d) were normally found to be very low. Several channeltron type detectors have been used in both instruments, all giving background counts of less than 1 count per second whilst operated without any ion introduction and all (unessential) electrical devices switched off. By use of the photon stop on the lens stack, between the collector and differential aperture, direct photons (e), are completely rejected; no counts were observed with all lens potentials and quadrupole switched off, but with the plasma in normal sampling position and slide valve open. The remaining source of random background is contributed by excited state decay. Total random background in normal operation of the PlasmaQuad is typically less than 10 counts per second. This rate has been observed to be dependent on the type of skimmer employed, in particular the diameter of the back of the skimmer. The internal angle of the skimmer base has an affect on the levels of random background.
There is a non-random element to noise from sources such as the peristaltic pump feeding the nebuliser. The ion source itself can be considered 'noisy', (caused by turbulence in the gas flows) as the plasma operates from tangentially introduced coolant argon, through which the sample is 'punched'. The ions are therefore extracted from a constantly fluctuating source. All these factors will affect the precision of the technique and ultimately the detection limits, as the standard deviation (σ) of the peak signal will determine whether it can be observed above the background level.

One of the advantages of ICP-MS over other mass spectrometry techniques for determining isotope ratios is the short analysis time. The precision of the isotope ratios will be affected by the factors already mentioned. Some work on isotope ratio determinations using ICP-MS, as well as the use of isotope dilution analysis and internal standardisation, has been published (67, 104, 108). Precisions of 0.3% have been reported. Factors affecting precision in isotope ratio determinations will be discussed, along with a description of isotope ratio determinations using sample introduction by both conventional nebulisation and electrothermal vaporisation (ETV) for elements affected by polyatomic ions, present at high levels in normal solutions analysis.
3.6 Limits of Detection

Although sensitivity is a useful indication of the performance of a system, it does not show the ability to detect an element. For a system with a random background, the lowest concentration at which an element can be detected above this background (limits of detection), is a more useful indication of system performance than sensitivity. In atomic emission and absorption spectrometry, the practice has become established of quoting a detection limit in terms of the concentration equivalent to the smallest statistically significant change in blank level. This is generally taken to be three times (sometimes two) the standard deviation of the blank level which is usually determined from a series of blank runs, normally ten or more. In ICP-MS, limits of detection can be obtained by two methods, single ion monitor or scanning mode.

In single ion monitor mode an individual mass is selected on the mass spectrometer and the multichannel analyser set up to have long dwell times per channel (0.1 or 1 second). Ten or more successive 'channels' are then taken to determine the limit of detection for that element. This method represents the best possible conditions for determining limits of detection, but is only realistic for analyses that are carried out in peak hopping mode. Perhaps a more true to life method of determining limits of detection is in the scanning mode, where a blank solution is repeatedly analysed by scanning across the masses of interest. Dwell times per mass are then far more representative of those that will be
Table 2
Comparison of Detection Limits (3σ blank, ng.mL⁻¹)

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-MS</th>
<th>ICP-AES*</th>
<th>F-AAS*</th>
<th>XRF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.29</td>
<td>22.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>3.78</td>
<td>4.8</td>
<td>1050</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>3.44</td>
<td>29</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.94</td>
<td>30</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.97</td>
<td>23</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>33.2</td>
<td>12</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>3.81</td>
<td>6000</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>10.2</td>
<td>10</td>
<td>1.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.06</td>
<td>1.5</td>
<td>75</td>
<td>2</td>
</tr>
<tr>
<td>Titanium</td>
<td>2.43</td>
<td>3.8</td>
<td>75</td>
<td>2</td>
</tr>
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<td>Vanadium</td>
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<td>Manganese</td>
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<td>Iron</td>
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<td>6.2</td>
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<tr>
<td>Cobalt</td>
<td>0.34</td>
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<tr>
<td>Nickel</td>
<td>3.24</td>
<td>15</td>
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<td>3</td>
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<tr>
<td>Copper</td>
<td>0.23</td>
<td>5.4</td>
<td>4.5</td>
<td>3</td>
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<td>Zinc</td>
<td>0.59</td>
<td>1.8</td>
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<td>Arsenic</td>
<td>2.84</td>
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<td>5</td>
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<td>Selenium</td>
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<td>Rubidium</td>
<td>0.36</td>
<td>37000</td>
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<td>Strontium</td>
<td>0.10</td>
<td>0.42</td>
<td>7.5</td>
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<tr>
<td>Niobium</td>
<td>0.11</td>
<td>36</td>
<td>3000</td>
<td>3</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.70</td>
<td>7.9</td>
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<tr>
<td>Silver</td>
<td>0.32</td>
<td>7</td>
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<td>Cadmium</td>
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<td>0.43</td>
<td>45</td>
<td>150</td>
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<td>Antimony</td>
<td>0.28</td>
<td>32</td>
<td>60</td>
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<td>Tellurium</td>
<td>3.06</td>
<td>41</td>
<td>70</td>
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<td>Iodine</td>
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<td>Barium</td>
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<td>1.3</td>
<td>30</td>
<td>12</td>
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<td>Lanthanum</td>
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<td>3000</td>
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<td>1800</td>
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<tr>
<td>Gold</td>
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<td>15</td>
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<td>Mercury</td>
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<td>Thallium</td>
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<td>Lead</td>
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<tr>
<td>Bismuth</td>
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</tr>
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<td>Thorium</td>
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<td></td>
<td>9</td>
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<td>Uranium</td>
<td>0.02</td>
<td>250</td>
<td></td>
<td>45000</td>
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</table>

*From ref. 150
encountered in real analysis. Table 2 lists the limits of detection in scanning mode for most elements for the PlasmaQuad and compares them to those obtained for ICP-AES, FAAS and XRF (150).

3.7 Resolution and Abundance Sensitivity

3.7.1 Introduction

Resolution or resolving power in mass spectrometry has already been discussed (section 2.6). In ICP-MS, only quadrupole mass analysers have been used to date. On the PlasmaQuad and the Surrey research instrument, both high and low mass resolution controls are provided, each having its main effect over different parts of the spectrum. As has been shown, the resolution setting affects the ion transmission (sensitivity) of the quadrupole and could be used to balance the response across the mass range. This is not their true function and they are normally set to give uniform resolution at the necessary level. Obtaining the required level of resolution is achieved using a multi-element solution containing elements with several adjacent isotopes, setting the low mass control first, then adjusting the high resolution to match.

3.7.2 Measurement of Resolution and Abundance Sensitivity

The VG 12-12S quadrupole is used in both the PlasmaQuad and Surrey research instruments and has a specified resolution of 2.5M (50% peak width), but is usually operated at almost 1.6M. Figure 20 shows a part of a full mass spectrum, with 1µg.mL⁻¹ of Al and Figure 21 shows a similar spectrum at Ce,
Figure 20 Part of the full range spectrum on a multielement standard at 1μg/ml showing the response obtained with normal resolution settings for quantitative analysis.

Figure 21 As Figure 20 but for region of spectrum around $^{140}\text{Ce}^+$. 
greatly expanded to show the small peak of La at 0.22ng.mL\(^{-1}\) in the Ce (specpure grade) at 1ug.mL\(^{-1}\). Greater resolution is available if necessary, at the cost of lost sensitivity, but it is rarely required. The resolution controls are not normally adjusted. As there is sufficient sensitivity (0.5-1x10^6 counts.sec\(^{-1}\)) at these settings, relaxation of the resolution is not necessary.

The peaks obtained in scanning mode tend to have fringes on the edges, which if sufficiently long, could interfere with the adjacent peaks. The amount of overlap between peaks is known as the abundance sensitivity and is defined as the ratio of the signal at mass M-1 or M+1 to the signal at mass M. Typically, quadrupole peaks tail on the low mass side. There is always the possibility of contamination in the solution, which can contribute to the intensity at the masses M-1 and M+1. Figure 22 is an effective illustration of abundance sensitivity, where the response to a solution containing 10ng.mL\(^{-1}\) of Mn in a matrix of 0.1% Fe is shown. The \(^{55}\)Mn peak is completely resolved from the large peaks of \(^{54}\)Fe and \(^{56}\)Fe. Even with the extended tailing on the low mass side, the response falls to zero between \(^{55}\)Mn and \(^{56}\)Fe, leaving the Mn peak completely free from overlap. Taking into account the difference in concentration of the two elements (10^3) and the abundance of \(^{56}\)Fe, the top of the Mn peak represents an abundance sensitivity of 1.09x10^5. Most of the area between \(^{54}\)Fe and \(^{56}\)Fe is well below the 10^-6 level and the area response for Mn is thus free
Figure 22 Spectrum obtained with increased resolution on a solution of 1000 ug/mL Fe and 10 ng/mL Mn. Sensitivity of Mn$^{+}$ ion $5 \times 10^5$ counts/sec per ug/mL.
from Fe interference. These levels compare favourably with those of Date and Gray (21) who obtained an abundant sensitivity <10⁻⁶ with boundary layer sampling. Douglas and Houk (15) showed levels of 10⁻⁴ to 10⁻³ on the low mass side and 10⁻⁷ on the high mass side on the Sciex ELAN for Pb isotopes. Russ and Bazan (104) showed an abundant sensitivity of about 8x10⁻⁴ with U on a PlasmaQuad. The 'home made' instrument of Wilson et al. (105) exhibited 1.6x10⁶ abundant sensitivity on the low mass side of Na.

3.7.3 Effect of Ion Kinetic Energy on Resolution

Ion kinetic energy is an important factor affecting resolution in a quadrupole mass filter. The mass resolution is set electronically by the ratio of the r.f. to d.c. voltages. Although in theory this can be infinite, in practice resolution is limited by the number of r.f. cycles the ions experience. Douglas and Houk (15) point out that if ions of too high energy enter the quadrupole, the number of cycles is reduced and the resolution degrades, which in practice appears as asymmetrical peaks and long tailing. Compared to other mass analysers, the quadrupole can tolerate quite large energy spreads. Gray and Williams (117) indicated that the final energy of ions is of little importance, as excess energy can be offset by the pole bias of the analyser rods. More significant is the spread of ion energies across the mass range. The performance of the ion optics is dependent on this energy spread. Systems with a larger energy spread have a tendency to exhibit mass
dependent tuning. Ion energy effects will be dealt with in
detail in Chapter 5. The ion stopping potential of the
PlasmaQuad, which is closely related to mean ion energy, is
9±1V for all elements at the operating conditions used.
Douglas and Houk (15) report different ion energies and
spreads for several ICP-MS systems, but point out that in
all cases unit resolution is easily achieved throughout the
mass range.
CHAPTER FOUR
SPECTRAL INTERFERENCES
Spectral Interferences

4.1 Introduction
ICP-MS has, in principle, superior detection limits to many other atomic analytical techniques. It is becoming appreciated, however, that the detection limits obtainable using laboratory standards and single ion monitor mode are often considerably better than those obtainable in high levels of matrix. The primary cause of this degradation is spectroscopic interferences with the isotope(s) of interest, which cannot usually be resolved by the quadrupole mass analyser. These interferences are distinct from other types found in ICP-MS, such as analyte signal suppression in the presence of matrix elements, or extraction cone blockage caused by the introduction of solutions containing matrix elements, in particular those that are highly refractory in nature. Spectral interferences arise from three main sources:

i) Polyatomic ions, resulting from ion-molecule reactions between major species in the plasma which occur during the extraction process or expansion stage.

ii) Analyte oxide ions, resulting from incomplete dissociation in the plasma, recombination in the boundary layer or ion molecule reactions during ion extraction.

iii) Doubly charged ions of analyte or matrix species.
The most serious of these problems for solution analysis generally occur below mass 80, as the major plasma ions (Ar, O, H, N) have masses of 40 or less and are dependent on several factors, including extraction geometry, plasma and nebuliser operating parameters and the type of matrix.

4.2 Ion Extraction Interface

The interface regions of the systems used in this study are essentially identical, with the version in the PlasmaQuad based on the one designed by Gray and described in some detail elsewhere (45). Figure 23 is a diagram of the interface showing extraction cones, plasma torch and load coil. The normal configuration at the start of this work employed a skimmer cone with 1.0mm orifice and an extraction cone with 0.7mm orifice. However, as will be shown, it became clear that alternative configurations offer some advantages. A 3 turn coil, grounded at the interface end, is used on the PlasmaQuad and a type B coil (a 2 turn coil equivalent, described in reference 96) is employed on the research instrument. Apart from its horizontal configuration the torch is a standard 'Fassel' type, extending 6mm from the end of the load coil. The injector tube of the torch is normally aligned with the extraction cone aperture to give a spacing from extraction cone tip to load coil outer end of 10 mm. The 'normal' operating conditions of the plasma are power 1300W, coolant flow 12-14L.min⁻¹, no auxiliary flow and 0.75L.min⁻¹ carrier flow.
Figure 23 Arrangement of Ion Extraction Interface
4.3 Polyatomic Ions

4.3.1 Occurrence of Polyatomic Species

Of the three types of interfering ion observed, polyatomic ions are often the least obvious cause of interference because they mostly occur at very low levels and make determination of elements at trace and ultra-trace levels more difficult. A blank spectrum up to mass 80 is shown in Figure 24, which illustrates the major polyatomic ions. Two groups of peaks, one the oxygen and hydrogen (or 'water') group between masses 14 and 19, the other at 40 and 41 due to $^{40}\text{Ar}^+$ and $^{41}\text{ArH}^+$ (the 'gas' group), are fully saturated in the counting system but coincide with very few wanted elements. Various combinations of Ar, O, H and N occur in the blank aqueous spectrum and the more significant ions are shown in Table 3 together with the ions with which they interfere. Ions such as ArO$^+$ occur at several masses according to the isotopes actually in combination ($^{36}\text{Ar}^+$ to $^{40}\text{Ar}^+$ with $^{16}\text{O}^+$ to $^{18}\text{O}^+$). In practice $^{40}\text{Ar}^{16}\text{O}^+$ (on $^{56}\text{Fe}^+$) is the major interference, the other isotopes having much lower abundances means that interferences are far less likely to occur. Apart from coincidences where the removal of water would remove the offending interference, very little can be done about the major ions. Large O$_2^+$, N$_2^+$ and Ar$_2^+$ arise from condensation reactions during the expansion process and are well known in molecular beam work (111, 112, 113). In addition to the condensation reactions, the formation of species such as Ar$_2^+$ is affected by the degree
Figure 24 Blank spectrum of 1% HNO₃ showing 'water' and 'gas' peaks and associated polyatomic ions. 36Ar⁺ has an integral of 1.4 x 10⁶.
### Table 3
Polyatomic Ion Interferences from Water

<table>
<thead>
<tr>
<th>Mass (u)</th>
<th>Probable ion</th>
<th>Ion affected</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>( ^{14}N_2^+ )</td>
<td>( ^{28}Si^+ )</td>
</tr>
<tr>
<td>29</td>
<td>( ^{14}N^2H^+ )</td>
<td>( ^{29}Si^+ )</td>
</tr>
<tr>
<td>30</td>
<td>( ^{14}N^1O^+ )</td>
<td>( ^{30}S^+ )</td>
</tr>
<tr>
<td>31</td>
<td>( ^{14}N^1OH^+ )</td>
<td>( ^{31}P^+ )</td>
</tr>
<tr>
<td>32</td>
<td>( ^{14}O^+ )</td>
<td>( ^{32}S^+ )</td>
</tr>
<tr>
<td>33</td>
<td>( ^{16}OH^+ )</td>
<td>( ^{33}S^+ )</td>
</tr>
<tr>
<td>34</td>
<td>( ^{16}O^2O^+ )</td>
<td>( ^{34}S^+ )</td>
</tr>
<tr>
<td>35</td>
<td>( ^{16}O^1OH^+ )</td>
<td>( ^{35}Cl^+ )</td>
</tr>
<tr>
<td>36</td>
<td>( ^{16}Ar^+ )</td>
<td>( ^{36}S^+ )</td>
</tr>
<tr>
<td>37</td>
<td>( ^{36}ArH^+ )</td>
<td>( ^{37}Cl^+ )</td>
</tr>
<tr>
<td>39</td>
<td>( ^{38}ArH^+ )</td>
<td>( ^{39}K^+ )</td>
</tr>
<tr>
<td>40</td>
<td>( ^{40}Ar^+ )</td>
<td>( ^{40}Ca^+ )</td>
</tr>
<tr>
<td>41</td>
<td>( ^{40}ArH^+ )</td>
<td>( ^{41}K^+ )</td>
</tr>
<tr>
<td>42</td>
<td>( ^{40}Ar^2H^+ )</td>
<td>( ^{42}Ca^+ )</td>
</tr>
<tr>
<td>52</td>
<td>( ^{40}ArC^+ ) or ( ^{36}Ar^16O^+ )</td>
<td>( ^{52}Cr^+ )</td>
</tr>
<tr>
<td>54</td>
<td>( ^{40}Ar^14N^+ )</td>
<td>( ^{54}Fe^+ )</td>
</tr>
<tr>
<td>56</td>
<td>( ^{40}Ar^16O^+ )</td>
<td>( ^{56}Fe^+ )</td>
</tr>
<tr>
<td>76</td>
<td>( ^{36}Ar^40Ar^+ )</td>
<td>( ^{76}Se^+ )</td>
</tr>
<tr>
<td>78</td>
<td>( ^{38}Ar^40Ar^+ )</td>
<td>( ^{78}Se^+ )</td>
</tr>
<tr>
<td>79</td>
<td>( ^{38}Ar^40ArH^+ )</td>
<td>( ^{79}Br^+ )</td>
</tr>
<tr>
<td>80</td>
<td>( ^{40}Ar^40Ar^+ )</td>
<td>( ^{80}Se^+ )</td>
</tr>
<tr>
<td>81</td>
<td>( ^{40}Ar^40ArH^+ )</td>
<td>( ^{81}Br^+ )</td>
</tr>
</tbody>
</table>

### Table 4
Effect of Blunt Skimmer Tip on Formation of some Polyatomic Ions

<table>
<thead>
<tr>
<th>Skimmer Type</th>
<th>Integrals</th>
<th>Equivalent Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Ce</td>
<td>ArO</td>
</tr>
<tr>
<td>Blunt</td>
<td>18112</td>
<td>978</td>
</tr>
<tr>
<td>Sharp</td>
<td>139937</td>
<td>10815</td>
</tr>
</tbody>
</table>

Total Ce = Ce\(^+\) + CeO\(^+\) + Ce\(^2+\), Abundance Corrected Equivalent Conc., (μg.mL\(^-1\)), is compared with Ce at 1μg.mL\(^-1\)
of disruption of the gas jet after entering the expansion chamber, or shock wave effect.

The skimmer should be kept sharp to prevent formation of a shock wave at its tip, but this allows the tip to get hot enough to degrade at its very thin edge. Table 4 shows the effect of substituting a normal sharp tipped skimmer for one with a deliberately blunt tip. The signal responses of both total Ce and ArO⁺ using a blunt skimmer are lower by about 1 order of magnitude when compared to the signal responses obtained with a standard sharp skimmer. The signal response of Ar²⁺ with the blunt skimmer is only half of that obtained with the sharp skimmer; relative to Ce⁺, the Ar²⁺ response is over 3.5 times higher when a blunt skimmer is used instead of a sharp one. It is interesting to note that ArO⁺ showed little difference in relative intensity with the two skimmer types, suggesting that its formation is independent of shock effects at the skimmer entrance.

Other ion clusters such as OH⁺, NO⁺ and ArH⁺ as well as larger ones such as OH₂⁺ occur as the result of ion-molecule reactions in the interface. Generally there are few overlaps between these ions and elemental ion of interest. The formation of these ions during the extraction process has been discussed (113). All ICP-MS workers have reported the major water and gas peaks (O, H, Ar, N) which, in spite of their size, cause very few analytical problems. Tan and Horlick (114) identified a polyatomic ion for nearly every mass up to 84u. In reality, most of these ions probably
occur, but at levels that are too low to be detected.

4.3.2 Role of Water in Polyatomic Ion Formation

From very early on in the development of ICP-MS, water was identified as a major source of ions for polyatomic species. The advantages of carrying out analysis in the absence of water, with techniques such as laser ablation, electrothermal vaporisation or arc nebulisation, were reported \( (29, 45, 48, 49, 103) \). Gray \( (103) \) calculated the population levels of \( \text{H}^+ \), \( \text{O}^+ \) and \( \text{Ar}^+ \) in the plasma, from the Saha equation, along with those for \( \text{N}^+ \), \( \text{S}^+ \) and \( \text{Cl}^+ \) from common mineral acids in a 1\% solution and suggested that only very low reaction rates are needed to form polyatomic ions of the major species. Figures 25-28 show the 45-80u region of the mass spectrum for deionised water, nitric, hydrochloric and sulphuric acids (at 1\%) on the PlasmaQuad. Table 5.1 indicates the concentrations of some polyatomic ions from the acids compared with Co (at 1\( \mu \text{g.mL}^{-1} \)). This is a convenient form to express their levels, as it gives a realistic measure of the level of interference compared with analyte ions of interest. This level of interference would of course be much worse if the elements of interest had high ionisation energies with a correspondingly poorer signal response, compared with Co\(^+\). If the amount of water or solvent introduced into the plasma could be reduced, the level of polyatomic ions should be reduced. In addition, the level of any given polyatomic ion should be more stable, assuming that residual water that was introduced was stable. Figure 29 shows a single ion
Figures 25 and 26. Polyatomic peaks from deionised water and 1% HNO₃. ArO integral is 4,000. Ni response either from sampling cone or contamination. Cu from contamination.
Polyatomic species from 1% HCl and 1% H$_2$SO$_4$.
Table 5.1
Relative Concentration of some Mineral Acid Polyatomic ions

### 1% Nitric Acid

<table>
<thead>
<tr>
<th>Polyatomic ion</th>
<th>Mass (u)</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArN</td>
<td>54</td>
<td>23.1</td>
</tr>
<tr>
<td>ArO</td>
<td>56</td>
<td>232</td>
</tr>
<tr>
<td>ArAr</td>
<td>80</td>
<td>2580</td>
</tr>
</tbody>
</table>

### 1% Hydrochloric Acid

<table>
<thead>
<tr>
<th>Polyatomic ion</th>
<th>Mass (u)</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO</td>
<td>51</td>
<td>1500</td>
</tr>
<tr>
<td>ClO or ClOH</td>
<td>52</td>
<td>24.5</td>
</tr>
<tr>
<td>ClO</td>
<td>53</td>
<td>497</td>
</tr>
<tr>
<td>ArN</td>
<td>54</td>
<td>52.5</td>
</tr>
<tr>
<td>ArO</td>
<td>56</td>
<td>365</td>
</tr>
<tr>
<td>ArCl</td>
<td>75</td>
<td>58.5</td>
</tr>
<tr>
<td>ArAr</td>
<td>80</td>
<td>4840</td>
</tr>
</tbody>
</table>

### 1% Sulphuric Acid

<table>
<thead>
<tr>
<th>Polyatomic ion</th>
<th>Mass (u)</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO</td>
<td>48</td>
<td>4750</td>
</tr>
<tr>
<td>SO or SOH</td>
<td>49</td>
<td>65.1</td>
</tr>
<tr>
<td>SO or SOH</td>
<td>50</td>
<td>258</td>
</tr>
<tr>
<td>SO or SOH</td>
<td>52</td>
<td>3.38</td>
</tr>
<tr>
<td>ArN</td>
<td>54</td>
<td>23.8</td>
</tr>
<tr>
<td>ArO</td>
<td>56</td>
<td>265</td>
</tr>
<tr>
<td>S₂ or SO₂</td>
<td>64</td>
<td>1130</td>
</tr>
<tr>
<td>S₂ or SO₂</td>
<td>65</td>
<td>59.4</td>
</tr>
<tr>
<td>S₂ or SO₂</td>
<td>66</td>
<td>56.4</td>
</tr>
<tr>
<td>ArAr</td>
<td>80</td>
<td>2800</td>
</tr>
</tbody>
</table>

Equivalent concentrations, ng.mL⁻¹ (ref. 1μg.mL⁻¹ ^59^Co)
Extraction cone 0.7mm, Skimmer 1mm.
Figure 29  Variation of ArO\(^+\) Response with Time and Spray Chamber Temperature. Spray Chamber at 25\(^\circ\)C at 0 minutes and 35\(^\circ\)C after 18 minutes.
response of $^{36}$ArO$^+$ recorded from startup over a period of some 20 minutes. Over this period the $^{36}$ArO$^+$ intensity almost doubles. In addition, the temperature in the torch box area of the PlasmaQuad increased from 25°C at startup to 35°C. This suggests that the amount of water entering the plasma is a temperature dependent process and points to water evaporation as a possible reason. Figure 30 shows the total amount of water from both vapour and aerosol entering the plasma in the carrier gas, based on data from Saturated Water Vapour Tables (115) and an assumed 1% aerosol transport efficiency. At the temperatures at which the PlasmaQuad was operating, more water entered the plasma as vapour than in the form of aerosol.

4.3.3 Development of the Water Cooled Spray Chamber

Cooling the spray chamber caused much of the vapour to condense on its walls, significantly reducing the water input to the plasma. A water cooled spray chamber was designed (Figure 31) and built to directly replace the model supplied. Certain modifications were made to the design of the double pass style supplied in addition to a water jacket. The double pass inner tube was removed, as the majority of its length constitutes dead space and a large surface area exposed to sample solution. This leads to greater washout times as a result of increased sample "memory" (material remaining on the glass surfaces), which is slowly removed by the aerosol. A short lip or baffle was placed directly below the outlet to prevent any large
Figure 30 Mass of Water entering Plasma for 5 Carrier Gas Flows. Straight Lines represent Aerosol (at 1% with no temperature effect) Component and Curves represent Vapour Component.

Figure 31 Water Cooled Single Pass Spray Chamber
droplets escaping. A drip line path was provided from this lip to the waste outlet to prevent pulsing from excess solution running to waste from the lip. Finally a large aerosol outlet was provided, for it had been observed that the smaller outlet (on the model supplied) became obstructed by condensation droplets after a period of time.

With the water cooled spray chamber (WCSC) in place, a series of tests was carried out to assess its performance. Firstly a single ion monitoring run was carried out on $^{35}\text{ArO}^+$. The instrument was allowed to warm up, until the torch box temperature reached 35°C. The very rapid effect of switching on the tap water (cooling the WCSC to a final temperature of 11°C), on the $^{36}\text{ArO}^+$ response can be seen in Figure 32. Figures 33 and 34 show the 45-80u mass region of 1% HNO$_3$ with 1µg.mL$^{-1}$ Co, before and after cooling the spray chamber. Compared to $^{59}\text{Co}^+$, nearly all polyatomic ions show a marked decrease in response. Table 5.2 shows the equivalent concentrations of three of the most troublesome polyatomic ions, namely $^{34}\text{ArN}$, $^{36}\text{ArO}$ and $^{80}\text{ArAr}$, with the interface configuration used to obtain the spectra shown in Figures 33 and 34, together with results for two other interface configurations. Gray (103) had already pointed out the possible advantages of using extraction cones with larger orifice sizes. Operating the interface with a 0.7mm skimmer and a 1.0mm extraction cone, in conjunction with the WCSC, gave the lowest levels of polyatomic ions. Hutton and Eaton (118) carried out a
Figure 32 Variation of ArO$^+$ Response with Decreasing Spray Chamber Temperature v Time. Temperature Stabilised at 35°C before beginning Cooling of the Spray Chamber to 11°C
Integrals
Co  62,000
ArO  10,000
ArAr  120,000

Figure 33  Part of spectrum for 1% nitric acid, with 1ug.ml⁻¹ Co, without cooling of the spray chamber

Integrals
Co  40,000
ArO  2,500
ArAr  35,000

Figure 34  As Figure 33, with cooling of the spray chamber.
Table 5.2
Responses of some common Polyatomic Ions from 1% HNO₃ without and with a Cooled Spray Chamber and Modified Interface Configuration

<table>
<thead>
<tr>
<th>Polyatomic Ion</th>
<th>Interface 1</th>
<th>Interface 2</th>
<th>Interface 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UC</td>
<td>C</td>
<td>UC</td>
</tr>
<tr>
<td>$^{34}$ArN</td>
<td>23.1</td>
<td>20.1</td>
<td>121</td>
</tr>
<tr>
<td>$^{36}$ArO</td>
<td>232</td>
<td>141</td>
<td>3390</td>
</tr>
<tr>
<td>$^{80}$ArAr</td>
<td>2580</td>
<td>1440</td>
<td>7130</td>
</tr>
</tbody>
</table>

Equivalent concentrations in ng.mL⁻¹ (ref. 1μg.mL⁻¹ $^{59}$Co)
Interface 1 - Extraction Cone 0.7mm, Skimmer Cone 1mm
Interface 2 - Extraction Cone 1mm, Skimmer Cone 1mm
Interface 3 - Extraction Cone 1mm, Skimmer Cone 0.7mm
UC - Uncooled Spray Chamber
C - Cooled Spray Chamber

Table 6
Effect of Cooling Nebuliser Spray Chamber on Oxygen Containing Polyatomic Ion Peaks

<table>
<thead>
<tr>
<th>Mass (u)</th>
<th>1% HNO₃</th>
<th>1% HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncooled</td>
<td>Cooled</td>
</tr>
<tr>
<td>31</td>
<td>20.0</td>
<td>9.78</td>
</tr>
<tr>
<td>32</td>
<td>8030</td>
<td>2560</td>
</tr>
<tr>
<td>48</td>
<td>1.40</td>
<td>0.64</td>
</tr>
<tr>
<td>49</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>50</td>
<td>0.21</td>
<td>0.12</td>
</tr>
<tr>
<td>51</td>
<td>0.17</td>
<td>0.13</td>
</tr>
<tr>
<td>52</td>
<td>0.90</td>
<td>0.49</td>
</tr>
<tr>
<td>53</td>
<td>0.22</td>
<td>0.08</td>
</tr>
<tr>
<td>56</td>
<td>64.4</td>
<td>16.9</td>
</tr>
<tr>
<td>64</td>
<td>1.60</td>
<td>0.51</td>
</tr>
<tr>
<td>65</td>
<td>1.70</td>
<td>1.30</td>
</tr>
<tr>
<td>66</td>
<td>0.25</td>
<td>0.17</td>
</tr>
<tr>
<td>67</td>
<td>0.27</td>
<td>0.08</td>
</tr>
<tr>
<td>69</td>
<td>0.49</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Equivalent concentrations ng.mL⁻¹ (ref. 10ng.mL⁻¹ $^{59}$Co)
similar study using a water cooled double pass spray chamber and also showed attenuation of the major polyatomic ions when cooling the spray chamber.

4.3.4 Polyatomic Ions Arising from Matrix Elements

Water cooling of the spray chamber can also influence the formation of polyatomic ions from a matrix. One percent solutions of nitric and hydrochloric acids were analysed, with and without water cooling of the spray chamber. Table 6 summarises the effects of the WCSC on equivalent concentrations of some of the oxygen containing polyatomic ions. The improvements for the interferences range from about 10% to about 60%. Mineral acids are important solvents to consider for they are likely to be used in many sample preparation procedures. Several workers have pointed out the problems involved in analysing samples in the presence of chlorides, sulphates, phosphates and other major radicals (103, 114, 117).

Hydrochloric acid and other mineral acids such as sulphuric and phosphoric, or matrices that contain high levels of these elements (e.g. sea water) cause the most serious interferences. 1% HCl produces interfering peaks from clusters of chlorine with oxygen or argon, which occur at masses 51(V), 53(Cr), 75(As) and 77(Se), shown in Figure 35. Arsenic is monoisotopic and vanadium effectively so, but Cr and Se have other isotopes that could be used. In real sample analysis, isotope ratios may have to be examined to ascertain whether any interference is present or not. Tan
Figure 35 Polyatomic ions arising from introduction of 1% HCl. Co at 10ng.ml\(^{-1}\) added as reference, peak integral of 3250. Ni and Cu present as contamination in the acid.
and Horlick (114) state that V cannot be determined in the presence of a chlorine matrix. This is not entirely true, as mathematical correction procedures can be successfully applied to determine V in a chloride matrix, but the analysis of vanadium at low levels in the presence of chlorine does, at first sight, seems impossible. Table 7 shows the peak integrals for 100ng.mL⁻¹ of ⁵¹V⁺, ⁵²Cr⁺ and ⁵³Cr⁺ with and without a chlorine matrix provided by 1% HCl. Clearly polyatomic ions containing chlorine are interfering with ⁵¹V⁺ and ⁵₃Cr⁺ (³⁵Cl¹⁶O⁺ and ³⁷Cl¹⁶O⁺ respectively).

With the correction procedure described in Table 8, correction to within 10% of the true value was achieved for ⁵³Cr and to approximately 2% for ⁵¹V. The accuracy of the correction will depend on several factors, including:

i) the concentration of the element of interest
ii) the concentration of the interference element(s)
iii) the abundance of the isotope(s) of interest
iv) whether any other polyatomic ions are present but masked by the major interferences

This correction method was applied to the analysis of marine reference material TORT-1, a lobster hepatopancreatic material, for Cr and V. Table 9 shows the chromium values together with the uncorrected and corrected vanadium values.

Comparing the results with the certified values suggests that the ⁵¹V peak suffers from the addition of ³⁵Cl¹⁶O at an unknown concentration. By using the correction method
Table 7

Peak Integrals for 100ng.mL⁻¹ V and Cr with and without a chlorine matrix

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Cl Matrix</th>
<th>Non-Cl Matrix</th>
<th>Corrected Cl Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁵¹V</td>
<td>14216</td>
<td>5603</td>
<td>5464</td>
</tr>
<tr>
<td>⁵²Cr</td>
<td>5548</td>
<td>5652</td>
<td>-</td>
</tr>
<tr>
<td>⁵⁹Cr</td>
<td>3474</td>
<td>699</td>
<td>632</td>
</tr>
</tbody>
</table>

Table 8

Correction Method for Vanadium in the presence of Cl and Cr
(In the absence of significant carbon content, leading to ⁴⁰Ar¹²C formation)

1. Correct ⁵³u, to remove contribution from ⁵³Cr

\[
A = \frac{⁵²Cr \times 9.55 \text{ (abundance of } ⁵³Cr)}{83.76 \text{ (abundance of } ⁵²Cr)}
\]

\[
B - A = C
\]

where

- A = ⁵³Cr contribution
- B = total ⁵³u
- C = ³⁷Cl¹⁶O contribution

continued
2. Take ratio of $^{33}\text{Cl}:^{37}\text{Cl}$ from Cl abundances

\[ C \times D = E \]

where \[ D = ^{33}\text{Cl}:^{37}\text{Cl} \text{ ratio (3.08)} \]

\[ E = ^{33}\text{Cl}^{16}\text{O} \text{ contribution at 51u} \]

3. Correct for $^{51}\text{V}$

\[ F - E = G \]

where \[ F = \text{total 51u} \]

\[ G = \text{corrected value for } ^{51}\text{V} \]

Table 9
Corrected values for TORT-1

<table>
<thead>
<tr>
<th>Element</th>
<th>Uncorrected</th>
<th>Corrected</th>
<th>Certified</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{51}\text{V}$</td>
<td>3.58</td>
<td>1.40</td>
<td>1.40±0.30</td>
</tr>
<tr>
<td>$^{52}\text{Cr}$</td>
<td>2.09</td>
<td>-</td>
<td>2.40±0.60</td>
</tr>
</tbody>
</table>

All values in $\mu g.mL^{-1}$
described, the $^{51}$V value shows good agreement with the certified value. The $^{52}\text{Cr}$ value is in good agreement with the certified value, which suggests that a negligible amount of $^{40}\text{Ar}^{12}\text{C}$ polyatomic ion has been formed, from organic carbon.

Sulphur has a relatively low ionisation energy (10.36eV) which produces a relatively high $S^+$ population. This gives a large peak at mass 48 from $\text{SO}^+$. The effects of a WCSC on this peak are minimal. This is probably because sulphuric acid has a lower vapour pressure than water, therefore a change of spray chamber temperature of some 25° will have little effect on the amount of acid vapour produced. An interference at this mass seriously interferes with $^{48}\text{Ti}^+$, the main isotope of Ti. Mass 64 suffers from an appreciable peak due to $^{32}\text{S}^{16}\text{O}_2$, $^{32}\text{S}_2$ or most likely a combination of both (shown in Figure 36), which interferes with $^{64}\text{Zn}^+$. Fortunately for these elements other isotopes are available for quantitation, although at lower abundance.

The practice has been adopted for this work of using 1% nitric acid wherever possible and arranging digestion procedures so that in the final solution only nitric acid remains with the sample. Prior to the use of a WCSC, determination of iron was complicated by large and unstable peaks of $^{40}\text{Ar}^{14}\text{N}^+$ superimposed on $^{54}\text{Fe}^+$, $^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$ and $^{40}\text{Ar}^{17}\text{O}^+$ ($^{40}\text{Ar}^{16}\text{OH}^+$) on $^{57}\text{Fe}^+$. Although the interference at mass 57 was only small, the abundance of $^{57}\text{Fe}$ is also only 2.14%. The possibility of instability is
Figure 36  Polyatomic ions arising from introduction of 100 \text{mg} \text{ml}^{-1} \text{H}_2\text{SO}_4. 
Co at 100\text{mg} \text{ml}^{-1} added as reference, peak integral of 2638. Ni present as contamination in the acid.
clearly seen from Figures 29 and 30 where changes in spray chamber temperature are shown to greatly affect water vapour levels. The use of a WCSC has gone a long way to improving the stability and size of the interferences on iron. However, a dry sample introduction method, such as electrothermal vaporisation, is a good alternative for the determination of iron as it greatly reduces the levels of polyatomic ions. This is particularly useful for isotope ratio determinations using isotopes that are normally subject to interference from water based polyatomic ions.

Gray stated (103) that 'a major step forward would be made if a continuous method of introducing the sample aerosol without the large amount of accompanying water produced by pneumatic nebulisers was made available'. It would appear that the WCSC has gone some way to achieving this step forward. The WCSC reported on here has been used continually and successfully in several projects (92, 116, 117) for nearly 2 years. Although cooling is normally achieved with tap water, a closed loop water chiller system could just as easily be used, but it has been shown (118) that reducing spray chamber temperature below 10°C provides little additional benefit from further reductions in polyatomic ion levels. This is evident from the water vapour pressure graph, Figure 30, which shows that below 10°C, little further reduction of vapour level is produced.
4.3.5 Nickel Levels from Extraction Cone Degradation

The blank ICP-MS spectrum normally displays small peaks of the cone material, usually nickel. In early reports, it was thought that ion bombardment from high plasma potential led to 'sputtering' of the cone surface. Use of the WCSC actually reduced the level of cone material in the spectrum by a factor of 10, from 66ng.mL⁻¹ to 6.4ng.mL⁻¹, equivalent concentration. This indicates that water is playing a part in the removal of Ni from the extraction cone, possibly as part of an oxidation/dissociation reaction at the back of the cone. Removing much of the oxygen available for this reaction has drastically reduced the level of Ni in the spectrum. Hutton and Eaton (118) showed a similar effect in their study, with the residual Ni level reduced to <1ng.mL⁻¹, when the spray chamber was cooled below 20°C. Gray (personal communication) has added evidence to this hypothesis by showing that increasing the plasma forward power, which reduces plasma potential, leads to greater cone degradation.

4.4 Analyte Oxide Ions

4.4.1 Occurrence of Analyte Oxide Species

Analyte oxide ions may arise from incomplete dissociation in the plasma, recombination in the boundary layer or ion-molecule reactions during ion extraction. The level of these oxides depends on several factors. One of the most important, plasma operating parameters, will be discussed in Chapter 5.
Figure 37 Spectrum showing response of CeO when Ce introduced in solution. 
$^{140}\text{Ce}$ integral of 600,000, $^{156}\text{CeO}$ integral of 14,000 gives 2.3% CeO.

Figure 38 As Figure 37, but sample introduced by laser ablation. $^{140}\text{Ce}$ integral of 30,000, $^{156}\text{CeO}$ integral of 56 gives 0.2% CeO.
The level of these oxide species also appears to depend on the amount of water introduced into the plasma with the sample. Figures 37 and 38 show comparative levels of Ce by different sample introduction methods. Normal aqueous introduction of a standard containing Ce (with a WCSC) produces oxide levels of around 2% ($\text{CeO}^+/\text{Ce}^+$), as shown in Figure 37. If a ceramic material containing Ce is introduced without accompanying water, for example by laser ablation, an oxide level of about 0.2% is found, Figure 38, nearly an order of magnitude lower. The much lower levels in the absence of water suggest that the oxide level residual in the plasma is low but some reformation of oxides during ion extraction occurs when there is a great excess of oxygen in the plasma.

For solution analysis the WCSC should offer some improvement in the levels of analyte oxides. Table 10 shows relative levels ($\text{MO}/\text{M}$) of the Rare Earth Elements (REE) with and without cooling of the spray chamber, with 0.7mm extraction cone and 1mm skimmer cone. The REE's have some of the highest M-O bond strengths (600-800 kJ.mol$^{-1}$) and as such are likely to cause the greatest oxide problems. The reduction in oxide level is between 20 and 25% with the WCSC. The REE standards were individual elemental standards, not a multi-element standard, because interferences such as $^{172}\text{GdO}$ on $^{172}\text{Yb}$ would make determination of the elemental level more difficult.
Table 10
Effect of Cooled Spray Chamber on Refractory Oxide Species of some Rare Earth Elements

<table>
<thead>
<tr>
<th>Rare Earth Isotope</th>
<th>M-O Bond Strength (kJ.mol⁻¹)</th>
<th>Oxide (MO/M%)</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uncooled</td>
<td>Cooled</td>
</tr>
<tr>
<td>²⁵²Sm</td>
<td>619</td>
<td>0.24</td>
<td>0.18</td>
</tr>
<tr>
<td>²⁴²Nd</td>
<td>703</td>
<td>1.04</td>
<td>0.86</td>
</tr>
<tr>
<td>²⁶⁸Tb</td>
<td>707</td>
<td>0.58</td>
<td>0.48</td>
</tr>
<tr>
<td>²⁴⁸Gd</td>
<td>716</td>
<td>0.68</td>
<td>0.51</td>
</tr>
<tr>
<td>²¹⁴Pr</td>
<td>753</td>
<td>1.21</td>
<td>0.97</td>
</tr>
<tr>
<td>²⁴⁰Ce</td>
<td>795</td>
<td>1.20</td>
<td>0.94</td>
</tr>
<tr>
<td>²⁴⁹La</td>
<td>799</td>
<td>1.07</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 11
MO/M Response and Oxide Bond Strength (ref.116)

<table>
<thead>
<tr>
<th>Element</th>
<th>M-O Bond Strength (kJ.mol⁻¹)</th>
<th>Oxide (MO/M%)</th>
<th>This Work</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>255</td>
<td>5.5x10⁻⁵</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cs</td>
<td>297</td>
<td>2.8x10⁻⁶</td>
<td>1.1x10⁻¹⁺</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>368</td>
<td>1.7x10⁻³</td>
<td>1.2x10⁻¹⁺</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>378</td>
<td>1.2x10⁻³</td>
<td>7.1x10⁻²⁺</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>409</td>
<td>1.1x10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>427</td>
<td>3.6x10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>512</td>
<td>1.1x10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>563</td>
<td>8.3x10⁻²</td>
<td>4.8x10⁻²⁺</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>597</td>
<td>3.7x10⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>607</td>
<td>9.5x10⁻²</td>
<td>1.8x10⁻¹⁺</td>
<td>-</td>
</tr>
<tr>
<td>Sm</td>
<td>619</td>
<td>2.3x10⁻¹</td>
<td>7.1x10⁻¹⁺</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>662</td>
<td>1.8x10⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>760</td>
<td>4.7x10⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ce</td>
<td>795</td>
<td>1.3x10⁰</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Long and Brown. (97)
+ McLeod et al. (80)
4.4.2 Reported Levels of Oxide Species

Mcleod *et al.* (80) illustrated the severe limitations of refractory oxides in the determination of Ga, As, Se, Ag, Cd and Te in nickel base alloys. Date (71) *et al.* showed that these kinds of interferences limited analysis of geological samples in the same way, but that correction procedures could be applied. However, in order to enable corrections to be made, more peaks needed to be measured than just those of elements of interest. This could readily be done with wide mass coverage scans, with the data subsequently available for correction of both suspected and unsuspected interference of elemental peaks. This work reinforced the desirability of making full range multi-element scans of unknown samples, before any quantitation is attempted, to identify and correct possible interferences.

Long and Brown (96), using a PlasmaQuad with 0.45mm extraction cone orifice and no WCSC, investigated spectral interferences and showed levels of about 0.1% for all the elements studied, regardless of M-O bond strength. For example, BaO/Ba was 0.04% (563kJ.mol\(^{-1}\)) but CsO/Cs was 0.11% (297kJ.mol\(^{-1}\)). Mcleod *et al.* (80) using the BGS instrument with 0.5mm extraction cone orifice also showed very similar oxide levels for Co and Mo (0.12% and 0.18% respectively), despite having M-O bond strengths of half an order of magnitude difference. Vaughan and Horlick (98), using an ELAN with 0.037inch (0.94mm) extraction cone orifice diameter, investigated interferences for a number of
different operating conditions. They reported lowest MO/M levels of about 2% for Ba and >2% for Ce and, in a companion paper, reported 1% for Mo, 2% for W (41). For most of the elements studied, the operating conditions at which minimum MO/M ratios were achieved did not correspond to the maximum elemental ion signal. For Mo, with a forward power of 1300W, a signal loss of over 60% was necessary to reach minimum oxide levels.

McLaren et al. (75) studied the behaviour of Ti⁺ and TiO⁺ species as a function of nebuliser gas flow rate. The study showed that at a flow rate of 0.7L.min⁻¹ no TiO⁺ peaks were distinguishable above the background, but also that the sensitivity for Ti was more than 100 times lower than that observed at 0.9L.min⁻¹. In addition, at a flow rate of 1.1L.min⁻¹, the TiO⁺ peaks were larger than the Ti⁺ peaks. At flow rates between the two extremes, a reasonable compromise between high sensitivity and low oxides could be made, but the minimal measurable TiO⁺/Ti⁺ ratio (0.009) could only be achieved by sacrificing about an order of magnitude in sensitivity.

4.4.3 Assessment of Levels of Oxide Species

Clearly, there is some disagreement between the levels of analyte oxides observed by different users. Having shown that a 1mm extraction cone and a 0.7mm skimmer cone together with the WCSC offer the best performance in terms of polyatomic ion interference levels, a set of analyte oxide values was determined on the PlasmaQuad. The instrument was
set up for normal multi-element analysis on a 1µg.mL⁻¹ solution of Al, Co, In, Ce and Bi. The elemental signal response obtained was approximately uniform across the mass range. The response was calibrated for the elements examined by running multi-element solutions as necessary at 1µg.mL⁻¹. Oxide ion response was measured using 100 and 1000µg.mL⁻¹ solutions. These of course saturated (beyond linear range) at the M⁺ peak but to calculate the response ratio, MO/M⁺, 1µg.mL⁻¹ values were used for the same elements, extrapolated as necessary. High concentrations were used because:-

i) They more closely represent the analytical situation where MO⁺ response from matrix elements cause interferences.

ii) Despite having very low background levels, (1-5 c.s⁻¹), some MO⁺ responses had small polyatomic peaks beneath them and although a blank was subtracted in each instance, it was desirable to minimise blank subtraction errors as far as possible.

The oxide responses for the set of elements studied is shown in Table 11. MO⁺/M⁺ ratios range from 2.8x10⁻⁶% to 1.3% and occur roughly in the order of bond strength. If these values are compared with those of the published (80, 96) values for the PlasmaQuad type instruments, it can be seen that for the high bond strength elements the agreement is within a factor of 2-3. However, for the lower bond strength elements there are several orders of magnitude difference (depending on element), the previously published
values being much higher. Ion-molecule reactions may be responsible for this (much like the formation of ArO⁺) in the previous work, which were avoided in this study by using high concentrations of the elements of interest.

Oxides of elements with low bond strengths would not be present in the plasma or possibly in the boundary layer around the extraction orifice. The oxide levels reported here are generally much lower than those reported for the ELAN. Doherty and VanderVoet (40) report on REE oxide levels, including SmO⁺ (0.9%) and CeO⁺ (5.3%). Longerich and coworkers (74) also investigated REE oxides, with 4% SmO⁺ and >10% CeO⁺. These are in agreement with the levels reported by Horlick et al. (41, 98). These values are significantly higher than those found in this study (Table 11) with 0.23% SmO⁺ and 1.3% CeO⁺. It has been postulated (15) that the residual discharge said to exist at the extraction cone of the PlasmaQuad type instruments is responsible for additional dissociation of oxide species in the extracted plasma gas, thus resulting in lower detected oxide levels. Although analyte oxide ions do occur, they are not prohibitive to sample analysis as has been implied. There are occasions where their appearance makes elemental determination less than straightforward (80), but these occasions are few.
4.5 Doubly Charged Ions

4.5.1 Occurrence of Doubly Charged Species

Doubly charged ions tend to be a minor cause of spectroscopic interference, with only some 30 elements with sufficiently low 2nd ionisation energies (E_{i''}) to form these species. The highest levels of M^{2+} ions are expected for Ba (2nd I.E. 10.00eV). Elements with M^{2+} energies comparable to Pb (2nd I.E. 15.03eV) form negligible levels of M^{2+} ions.

Elements with second ionisation energies below the first ionisation energy of argon (the main plasma gas) will suffer some degree of double ionisation. The degree of secondary ionisation can be predicted with the Saha equation, upon making assumptions (16, 107, 116) of ionisation temperature, T_i, electron density, N_e and that the plasma is in Local Thermal Equilibrium (LTE).

Levels of M^{2+} ions are also dependent on instrumental parameters such as extraction orifice diameter, carrier gas flow through the plasma and water content of the carrier gas. These parameters affect the magnitude of the plasma potential in the PlasmaQuad type instruments, which is thought to be responsible for additional M^{2+} formation. Many of these factors will be discussed in detail later. Table 12 shows the doubly charged ion response for eight elements of increasing second ionisation energy, E_{i''}, on the PlasmaQuad optimised for maximum ion signal and using a WCSC. For Cs^{2+} and Rb^{2+} the response occurred at a half mass position 66.5u and 43.5u, respectively. Each of these partly overlaps...
Table 12

$M^2+ / M^+$ Response and Ionisation Energy (ref.116)

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_1''$ (eV)</th>
<th>$M^2+ / M^+$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>This Work</td>
</tr>
<tr>
<td>Ba</td>
<td>10.00</td>
<td>2.0x10^1</td>
</tr>
<tr>
<td>Ce</td>
<td>10.85</td>
<td>5.4x10^0</td>
</tr>
<tr>
<td>Sm</td>
<td>11.07</td>
<td>3.8x10^0</td>
</tr>
<tr>
<td>Zr</td>
<td>13.13</td>
<td>1.6x10^-1</td>
</tr>
<tr>
<td>Ti</td>
<td>13.64</td>
<td>7.2x10^-2</td>
</tr>
<tr>
<td>Pb</td>
<td>15.03</td>
<td>8.4x10^-2</td>
</tr>
<tr>
<td>Cs</td>
<td>25.08</td>
<td>1.5x10^-9</td>
</tr>
<tr>
<td>Rb</td>
<td>27.5</td>
<td>3.5x10^-11</td>
</tr>
</tbody>
</table>

* Long and Brown. 97
+ Assuming $T_1 = 7,500$ K, $N_e = 3x10^{15}$ cm$^{-3}$

Table 13

Levels of Doubly Charged Species for some Rare Earth Elements using a 0.7mm extraction cone and 1mm skimmer

<table>
<thead>
<tr>
<th>Rare Earth Isotope</th>
<th>$E_1''$ (eV)</th>
<th>$M^2+ / M^+$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{144}$Pr</td>
<td>10.55</td>
<td>1.33</td>
</tr>
<tr>
<td>$^{142}$Nd</td>
<td>10.73</td>
<td>1.63</td>
</tr>
<tr>
<td>$^{140}$Ce</td>
<td>10.85</td>
<td>1.38</td>
</tr>
<tr>
<td>$^{139}$La</td>
<td>11.06</td>
<td>1.80</td>
</tr>
<tr>
<td>$^{152}$Sm</td>
<td>11.07</td>
<td>1.49</td>
</tr>
<tr>
<td>$^{158}$Gd</td>
<td>12.1</td>
<td>0.76</td>
</tr>
</tbody>
</table>
a minor background peak, possibly from zinc memory or \( ^{14}\text{CO}_2 \). As responses were of a very low value, the mass analyser resolution was increased for these measurements so that these peaks at half mass unit intervals were resolved down to the base line, enabling a unique integral to be obtained for each. This resulted in a reduction of the ion transmission by a factor of two, which still left ample sensitivity for the analysis.

4.5.2 Assessment of Levels of Doubly Charged Species

Reasonable agreement is found with the values of Long and Brown, except for \( \text{Cs}^2^+ \). The calculated values of \( \text{M}^2^+ \) ions are derived from the Saha equation, which assumes that thermal equilibrium exists in the plasma. In addition, the assumption is made that no further ionisation occurs beyond the point at which \( T_i \) drops below the assumed 7,500K. The experimental results suggest that the Saha model is not being followed. Ba and Ce appear less doubly ionised than would be expected for the values of \( T_i \) and \( N_e \) assumed and the elements with \( E_{i^+} > 14\text{eV} \) are over ionised. Although using a lower value for \( T_i \) than is generally assumed would reduce the levels for Ba and Ce, it would not correct the response at the other end of the range. However this behaviour is consistent with faster recombination occurring for \( \text{M}^2^+ \) ions than for \( \text{M}^+ \) ions during ion extraction from the plasma, together with an additional mechanism for ionisation after extraction at a relatively low rate that does not follow the Saha relationship with \( E_{i^+} \) (116). Several possible
mechanisms can be suggested for this, but the most likely seems to be that of collisional ionisation in the plasma expanding beyond the orifice, involving the small proportion (< 1%) of ions in the tail of the ion-energy distribution (99, 116). At the carrier gas flow rate used, the mean ion energy of $^{59}$Co ions was 12eV. At this ion energy ions may have energies >25eV. This would seem to account for the apparent flattening of the $M^{2+}/M^+$ response to a level of ca. $10^{-6}$, above $E_i > 27.5$eV. Rubidium was studied as it has an $E_i$ similar to that of argon. $^{40}$Ar$^{2+}$ is very difficult to determine, in spite of the high population of $^{40}$Ar ions, because it coincides with $^{18}$OH$^+$. Calculation of the intensity of the $^{18}$OH$^+$ from $^{16}$OH$^+$ cannot be carried out because the latter peak is saturated and would itself suffer from interference from $^{18}$O$^+$ and $^{17}$OH$^+$. In addition, determination of the very small $^{40}$Ar$^{2+}$ peak after such a correction would be very prone to error. Even in the dry plasma, with very small oxygen related peaks, mass 20 is completely accounted for by $^{18}$OH$^+$, calculated from $^{16}$OH$^+$.

Table 13 shows the levels of doubly charged ions of some REE's, found when using a 0.7mm extraction cone and 1mm skimmer in the interface. The use of 1mm extraction cone and 0.7mm skimmer arrangement in conjunction with the WCSC has already been described. Comparison of the common elements (Ce and Sm) in Tables 12 and 13 shows that the larger extraction cone gave the lowest levels of $M^{2+}$ ions. The use of a larger extraction cone orifice diameter results in a reduced secondary discharge at the orifice. As this
discharge probably plays a part in $M^{2+}$ formation, it follows that a larger orifice diameter will produce lower levels of doubly charged ions.

Hutton and Eaton (118) showed that reducing the spray chamber temperature from 30°C to 0°C resulted in a reduction of $\text{Ba}^{2+}$ from 1.5 to 0.5%. Coincidentally, ion kinetic energies were seen to fall from 10-12eV across the mass range, to 4-5eV, at the lower spray chamber temperature.

These observations are consistent with those made by Gray and Williams in collaboration with Houk (99). In this work a floating Langmuir probe was used to measure the apparent d.c. potential in an ICP whilst the latter was used as an ion source for mass spectrometry. It was shown that as the potential increased, due to increasing aerosol gas flow rate or decreasing forward r.f. power, ion kinetic energies and doubly charged ion levels also increased. This is consistent with the hypothesis that at higher energies additional double ionisation is produced in species such as Ba, with low second ionisation energies, inside the expansion chamber.

From this, it can be concluded that the water content of an ICP generated with an asymmetrical load coil plays an active role in determining the overall electrical and chemical characteristics of the plasma when the latter is used as an ion source.
4.6 Computer Prediction of Interference Ions

The qualitative prediction of the occurrence of interference ions in ICP-MS is relatively straightforward, involving the major plasma ions (Ar, H, O and N) and any introduced matrix and lends itself very well to computer prediction. However quantitative prediction or correction for all interference ions in a mass spectrum is a very complex task. Date et al. (71) suggested that a library of possible interferences be generated, similar to those used in organic mass spectrometry for compound identification, as well as a real time correction for any interference. The library approach is probably unnecessary, as there are a limited number of possible combinations for interference ions in ICP-MS, unlike the much greater number of daughter ions that occur from large molecules in, for example, organic mass spectrometry. The possible combinations of interferences could be rapidly determined by a computer, given certain criteria. Real time correction for any interferant is already available on one of the commercial systems, but is generally too slow (7 minutes for a 300u spectrum) and easily mislead, to be of any practical use. Vaughan and Horlick (106) produced a 'Computerised Reference Manual for Spectral Data and Interferences' which showed any likely elemental overlaps (isobaric) together with possible oxide, hydroxide and doubly charged ion overlaps for a given mass.

A more detailed program was written by this author (listing Appendix 1) in Microsoft compiled BASIC, making the program
Figure 39

************************** ICP-MS INTERFERENCE DATA **************************

(1) ISOTOPIC ABUNDANCES FOR A GIVEN ELEMENT (SCREEN DISPLAY)

(2) ISOTOPIC SPECIES FOR GIVEN MASS NUMBERS (PRINTER OR SCREEN DISPLAY)

(3) MASS NUMBERS FOR ISOTOPES, MO, MOH, M2+, MH, MO2, MO2H
AND MAR FOR AN ELEMENT (PRINTER DISPLAY)

(4) SPECIES M, MO, MOH, MH, MO2, MO2H, MAR AND M2+
FOR A GIVEN MASS NUMBER (PRINTER DISPLAY)

(5) MASS RANGE SEARCH (PRINTER DISPLAY)

(0) END

INPUT REQUIRED ROUTINE

Figure 40

ISOTOPIC ABUNDANCES FOR Sn

<table>
<thead>
<tr>
<th>MASS</th>
<th>ISOTOPE</th>
<th>ABUNDANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>Sn</td>
<td>.96</td>
</tr>
<tr>
<td>114</td>
<td>Sn</td>
<td>.66</td>
</tr>
<tr>
<td>115</td>
<td>Sn</td>
<td>.35</td>
</tr>
<tr>
<td>116</td>
<td>Sn</td>
<td>14.3</td>
</tr>
<tr>
<td>117</td>
<td>Sn</td>
<td>7.61</td>
</tr>
<tr>
<td>118</td>
<td>Sn</td>
<td>24.03</td>
</tr>
<tr>
<td>119</td>
<td>Sn</td>
<td>8.58</td>
</tr>
<tr>
<td>120</td>
<td>Sn *</td>
<td>32.85</td>
</tr>
<tr>
<td>122</td>
<td>Sn</td>
<td>4.72</td>
</tr>
<tr>
<td>124</td>
<td>Sn</td>
<td>5.94</td>
</tr>
</tbody>
</table>

* - ISOTOPE OF GREATEST ABUNDANCE

ANOTHER ELEMENT....Y/N
### Figure 41

**MASS SEARCH**

<table>
<thead>
<tr>
<th>MASS</th>
<th>ISOTOPE</th>
<th>ABUNDANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>Ar</td>
<td>.06</td>
</tr>
<tr>
<td>39</td>
<td>K</td>
<td>93.1</td>
</tr>
<tr>
<td>40</td>
<td>Ar</td>
<td>99.6</td>
</tr>
<tr>
<td>40</td>
<td>K</td>
<td>.02</td>
</tr>
<tr>
<td>40</td>
<td>Ca</td>
<td>96.97</td>
</tr>
<tr>
<td>41</td>
<td>K</td>
<td>6.88</td>
</tr>
<tr>
<td>42</td>
<td>Ca</td>
<td>.64</td>
</tr>
</tbody>
</table>

### Figure 42

**ISOTOPES..MO..MOH..M2+..FOR Cl**

<table>
<thead>
<tr>
<th>ISOTOPE MASS</th>
<th>%</th>
<th>MO MASS</th>
<th>MOH MASS</th>
<th>M2+ MASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Cl 35</td>
<td>75.53</td>
<td>*ClO</td>
<td>51</td>
<td>*ClOH</td>
</tr>
<tr>
<td>Cl 37</td>
<td>24.47</td>
<td>ClO</td>
<td>53</td>
<td>ClOH</td>
</tr>
</tbody>
</table>

**ISOTOPES..MH..MO2..MO2H..FOR Cl**

<table>
<thead>
<tr>
<th>ISOTOPE MASS</th>
<th>%</th>
<th>MH MASS</th>
<th>MO2 MASS</th>
<th>MO2H MASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Cl 35</td>
<td>75.53</td>
<td>*ClH</td>
<td>36</td>
<td>*ClO2H</td>
</tr>
<tr>
<td>Cl 37</td>
<td>24.47</td>
<td>ClH</td>
<td>38</td>
<td>ClO2H</td>
</tr>
</tbody>
</table>

**ISOTOPES AND MAR FOR Cl**

<table>
<thead>
<tr>
<th>ISOTOPE MASS</th>
<th>%</th>
<th>MAR</th>
<th>ARGON MASS (ABUNDANCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Cl 35</td>
<td>75.53</td>
<td>*ClAr</td>
<td>36 (0.34)</td>
</tr>
<tr>
<td>Cl 37</td>
<td>24.47</td>
<td>ClAr</td>
<td>38 (0.07)</td>
</tr>
</tbody>
</table>

* - PRINCIPAL ISO TOPE
both very fast and freestanding (no BASIC interpreter required) so that it could be run on any IBM PC/XT or compatible clone. Figure 39 shows the opening menu. Option (1) produces a list as shown in Figure 40, on entering a 'natural' element, showing the masses and natural abundances for the chosen element and indicates the most abundant. Option (2) displays a list of all the elements, isotopes and their abundances for a given mass number or range of mass numbers, as in Figure 41. This allows isobaric overlaps to be quickly assessed. Option (3), after entry of an element of interest, suggests a series of interference ions based on the entered element and their mass shown in Figure 42. The abundance (indicated by %) merely represents the abundance of the isotopes of the matrix element under investigation. The principle isotope is indicated, showing which masses are likely to show the biggest peaks. Many of the suggestions are unlikely (for example Cl₂⁺ cannot occur in an argon plasma) and will never occur, but some combinations have been reported and are included in the list. The list is not comprehensive, MN ions are not included as they are rarely seen, but could be included if necessary. This option would be useful if a sample had a known matrix; the analyst could get an indication of the masses that might be affected. Options (4) and (5) produce a list(s) of possibilities for a given mass(es). Figure 43 shows the listing for the entered mass, 56. First the elemental isotopes occupying that mass are listed, with their abundances, in this case only the main isotope of Fe occupies mass 56. Next are the oxides,
**Figure 43**

**SPECIES CORRESPONDING TO MASS NUMBER 56**

<table>
<thead>
<tr>
<th>MASS (M)</th>
<th>SPECIES</th>
<th>ISOTOPIC ABUNDANCE (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISOTOPIC SPECIES (ELEMENTS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>Fe</td>
<td>91.66</td>
</tr>
<tr>
<td>MO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>ArO</td>
<td>99.6</td>
</tr>
<tr>
<td>40</td>
<td>KO</td>
<td>.02</td>
</tr>
<tr>
<td>40</td>
<td>CaO</td>
<td>96.97</td>
</tr>
<tr>
<td>MOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>KOH</td>
<td>93.1</td>
</tr>
<tr>
<td>MH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>MnH</td>
<td>100</td>
</tr>
<tr>
<td>MO2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>MgO2</td>
<td>78.7</td>
</tr>
<tr>
<td>MO2H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>NaO2H</td>
<td>100</td>
</tr>
<tr>
<td>MAr (40...99.6%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>OAr</td>
<td>99.75</td>
</tr>
<tr>
<td>MAr (36...0.33%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>NeAr</td>
<td>90.92</td>
</tr>
<tr>
<td>MAr (38...0.07%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>OAr</td>
<td>.204</td>
</tr>
<tr>
<td>M2+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>Cd2+</td>
<td>24.07</td>
</tr>
<tr>
<td>112</td>
<td>Sn2+</td>
<td>.96</td>
</tr>
</tbody>
</table>
either polyatomic or analyte oxide ions. $^{36}$ArO$^+$ is a well documented polyatomic ion, however other elements, if they were introduced at a sufficiently high level, could form interference ions (KO$^+$ and CaO$^+$ in this case). This might prompt the analyst to look at other masses for problems, if, for example, high levels of Ca were found in the sample. Next on the list are other interference ion suggestions. As pointed out above, these ions do not necessarily occur, but are theoretically possible. Figure 43 suggests $^{112}$Cd$^{2+}$ and $^{112}$Sn$^{2+}$ might occur at mass 56. Both are extremely unlikely in the argon plasma and would only occur at very low levels. Abundances listed are those of the matrix ion involved in the interference ion and are not intended to give any indication of actual peak size. The program is not intended as the ultimate predictor of interference ions, but as an aid to the analyst, for the identification of rogue peaks or the possible effect on a spectrum from the introduction of a particular matrix.

4.7 Conclusions

Spectroscopic interferences are the limiting factors which restrict the lower limits of detection for some elements below mass 80. In some circumstances this makes elemental determinations virtually impossible. Reports from workers investigating spectroscopic interferences have cited water content of the plasma and sample matrix as the major source of interference ions (17, 80, 99, 103, 114, 116, 117, 118). Reducing the amount of solvent reaching the plasma by use of a water cooled spray chamber has gone some way to
controlling interfering ions, in particular water based polyatomic ions. Water content plays a vital role in the potential assumed by the ICP (110, 118) used in instruments with asymmetrical load coils, such as the PlasmaQuad. This partly affects the kinetic energy of the ions, which in turn affects the potential settings of the ion optics for maximum ion transmission. This is only one of several causes of instrument instability, others being mass analyser drift (resolution affecting sensitivity) and nebuliser/flow rate. Apart from interference ions arising from the sample/plasma matrix, straightforward contamination is often evident in the blank spectrum, arising from inadequate cleanliness in operating or insufficiently pure reagents. The solutions to such problems are self evident.

In terms of the interferences generated by doubly charged and oxide species, the levels of the latter are the most significant, particularly for the lighter elements that commonly occur in the sample matrix. Elements whose bond strength lies above about 500 kJ.mol\(^{-1}\) can show ratios of \(\text{MO}^+/\text{M}^+\) rising from about 0.1\% up to values of a few percent. For the most refractory species, and where these are present as the matrix, it is important to be aware of potential levels of interference and where necessary correct for them. Fortunately their levels are found to be stable and thus lend themselves to correction from standard solutions. This re-emphasises the advantage of a survey scan of an unknown sample, before deciding which elements to select in an analytical programme.
The effect of doubly charged ions on the pattern of interferences is generally less serious than that of oxides. It is most likely to be a nuisance from heavy elements as the $M^{2+}$ ion occurs at half the parent mass, but except for metals and alloys these are not usually present at high levels in the matrix. One of the most serious interferences is from $^{138}\text{Ba}^{2+}$ as Ba commonly occurs at significant levels in minerals and has the largest $M^{2+}$ response, which coincides with $^{69}\text{Ga}^{+}$.

Interferences from elements where $M^{2+}/M^+$ lies below $10^{-4}$, such as $^{133}\text{Cs}$ whose $2^+$ ion is seen between $^{66}\text{Zn}^+$ and $^{67}\text{Zn}^+$, can only arise from very high concentrations and will cause no problems at trace levels. For an element of odd mass the doubly charged ion can be resolved on both the PlasmaQuad and the research instrument without unacceptable loss of sensitivity in the rare instances where they are found to be present.
CHAPTER FIVE

ICP-MS SYSTEM OPTIMISATION
In a relatively short time (1), ICP-MS has generated considerable interest in the atomic spectroscopy community. Most work in the field, until commercial systems became available, was restricted to the design, development and refinement of ICP-MS at the pioneering laboratories, Ames (1), Sciex (31) and the University of Surrey (45). Few systematic studies of the effect of instrument parameters on factors such as analyte signal, interference ion signal and ion kinetic energies had been reported. Following the launch of the commercial systems, extensive studies of the effect of parameter variation performance were carried out for the Sciex ELAN (41, 98, 114). At this time only one similar study had been carried out on the VG PlasmaQuad and reported (96), but this work took place on an early model, not representative of the current 'state of the art' and employing non-standard 0.45mm sampling cones.

Studies of this type are important in investigating the technique and have an important role in establishing mechanisms, but reports of an exhaustive nature can lead to confusion.

Some aspects of the work reported on both commercial systems are so different from those experienced on the systems used in this project, in particular the PlasmaQuad, that a fairly thorough investigation of the behaviour of this system was carried out and recorded.
Previous studies of this type had only looked at the effects of parameter variation on analyte signal, refractory oxide and hydroxide signal and doubly charged ion signal. These are important factors to consider, however, other criteria play an important part in the performance of ICP-MS systems, namely polyatomic ions and ion kinetic energies. In chapter 4 the occurrence of interference ions and the role played by water in the plasma in the formation of these species was discussed. The following chapter discusses the effect of operating parameter variation on performance and the process of optimisation described for the preferred operating conditions selected for routine analysis. Some of the data has been reported elsewhere (117).

5.2 Experimental
All parts of this study were carried out on the PlasmaQuad, unless otherwise stated. The instrument used was a standard version at the time of manufacture, in all but two respects. The two changes made were the use of the water cooled spray chamber, described in detail in Chapter 4, and the fitting of a Negretti and Zambra APR pressure regulator on the gas supply to the nebuliser, as a precision flow controller. In current models of the PlasmaQuad, nebuliser gas control is carried out by mass flow controller and water cooled spray chambers are fitted as standard. The gas supply to the instrument was maintained at constant pressure by a precision regulator (Type R182) also from Negretti and Zambra. Most studies of this type on either the ELAN or
PlasmaQuad instruments have only used the Meinhard concentric nebuliser. This work was also carried out using a Meinhard nebuliser, however, the studies were repeated using a Jarrel-Ash cross-flow nebuliser supplied as standard with the instrument. Essentially identical results were obtained for both nebulisers, so for brevity and to allow comparison with other work, only the Meinhard results will be reported. Other types of nebuliser have been used on this instrument, such as the high solids Babington type, where sample conditions require it.

In order to study instrument performance the instrument was operated in the normal way, except that plasma parameters were varied from the default values (Table 14) by changing the central channel gas flow in steps, between about 0.5 and 1.1L.min\(^{-1}\), at three power levels (1100W, 1300W and 1500W) in turn. All other parameters (other plasma gas flows, load coil-sampling cone separation, sample uptake rate etc.) were not changed. References to gas flow in the following discussion are to central channel or injector gas flow. Multi-element standards were used at a concentration of 1\(\mu\)g.mL\(^{-1}\) for studies of \(M^+\) response against flow rate. For polyatomic, analyte oxide and doubly charged ions, solutions containing the elements shown in Table 17 were run at concentrations of 1 and 10\(\mu\)g.mL\(^{-1}\). ClO\(^+\) polyatomic ion values were obtained from a dilute HCl solution containing Cl at 100\(\mu\)g.mL\(^{-1}\). At each new flow and power setting the lens system was re-optimised and the solutions introduced in turn. Peak integrals were recorded in the scanning mode.
Table 14

Normal System Parameters for Multi-Element Operation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Power</td>
<td>1300W</td>
</tr>
<tr>
<td>Reflected Power</td>
<td>&lt;10W</td>
</tr>
<tr>
<td>Coolant Argon Flow</td>
<td>14L.min⁻¹</td>
</tr>
<tr>
<td>Auxiliary Flow</td>
<td>0</td>
</tr>
<tr>
<td>Carrier Flow</td>
<td>0.73L.min⁻¹</td>
</tr>
<tr>
<td>Spray Chamber Temperature</td>
<td>13°C</td>
</tr>
<tr>
<td>Pumped Sample Uptake Rate</td>
<td>1.1mL.min⁻¹</td>
</tr>
<tr>
<td>Extraction Orifice</td>
<td>1.0mm</td>
</tr>
<tr>
<td>Skimmer Orifice</td>
<td>0.7mm</td>
</tr>
<tr>
<td>Load Coil-Aperture Spacing</td>
<td>10mm</td>
</tr>
</tbody>
</table>
across a mass range from 25 to 260u using 2048 multichannel analyser channels, 120 scans with a dwell time of 250μs per channel, giving a total integration time for one analysis of 61s. The elements in the standards were chosen to provide a range of second ionisation energies and monoxide bond strengths. They are fully ionised in the argon plasma over the whole mass range and exhibit a range of different chemical behaviour.

Polyatomic ion yields were monitored by observing three species, ArO⁺, ArAr⁺ and ClO⁺. These ions are amongst the most troublesome and prominent and their behaviour is believed to be representative of most other species of this nature in this system. In a study of this type, adjusting more variables than necessary would only lead to confusion and for normal operation is not necessary.

The water content of the carrier gas is an important parameter because H⁺ and O⁺ together contribute a substantial fraction of the total plasma electron population (147) and it is therefore important that this is kept stable. While the use of a peristaltic pump keeps the water introduced as aerosol constant, evaporation from water surfaces in the spray chamber at temperatures above 25°C can add considerably more vapour to the carrier gas than the aerosol. However, this variable has been eliminated by the use of the WCSC.
The extraction cone to load coil spacing is normally set at 10mm on this system and not varied. This spacing is related to the plasma operating parameters as it is important that dissociation and ionisation are as complete as possible before the carrier gas flow reaches the extraction cone. As the spacing is reduced or the carrier gas flow increased, the ion response rises as more ground state ions are extracted, but this carries an increased risk of incomplete dissociation of major matrix species. In an extreme instance where an operator is seeking the maximum signal on setting up with an aqueous standard without a significant matrix, the system may be made vulnerable to the matrix of a real sample, when the initial radiation zone (IRZ) is pushed forward so far that it reaches the extraction cone allowing undissociated material to be extracted (78). Operation close to the brink of this situation is not necessary with this instrument. At the spacing used, high sensitivity is obtained at flow rates which keep the IRZ more than 5mm from the extraction cone and high matrix concentrations do not cause increased oxide levels.

5.3 Results and Discussion

5.3.1 Elemental Ion Response
In an initial study, 12 elements (Li, Mg, Al, Co, Ba, Ce, Rb, In, W, Pb, Bi and U), representing several groups of the periodic table, a range of masses and range of ionisation energies were studied. A solution containing the elements at 1μg.mL⁻¹ was repeatedly analysed, each time at a new
power/gas flow setting with the ion optics re-optimised at each setting. Response at three forward power levels (1200W, 1300W and 1400W) was studied at a gas flow range of 0.33 to 1.27L.min\(^{-1}\) in steps of about 0.12L.min\(^{-1}\). Gas flow was not measured directly; a calibration curve was drawn for gas flow against nebuliser pressure drop, which could be read directly from the instrument gauge. Separate flow measurements were made using a gas flowmeter connected to the tip of the injector tube of the (unlit) plasma torch. Figure 44 shows the calibration curve for the Meinhard nebuliser. Figures 45-50 show the effect of increasing nebuliser flow on elemental response for the three powers studied. The response plots are split into two parts, with the lighter elements (Li-In) shown in Figures 45-47 and the heavier elements (Ba-U) shown in Figures 48-50. At a given power, the responses for all elements rise to a maximum at a very similar gas flow. However, the curves for the heavier elements show narrower peaks compared with those of the lighter elements.

The light elements also show a more distinct movement towards maximum signal at higher flow for higher powers than the heavier elements. This can be seen more clearly in Figures 51-53, where the response for a single element is displayed against gas flow for the 3 powers. \(^7\)Li shows a definite shift towards higher flow rates for maximum response with increasing power. \(^115\)In shows a similar trend, but the shift to higher flow for increased power is not complete, resulting in a broader response curve. \(^238\)U
Figure 44  Meinhard Nebuliser Calibration Curve
Figures 45–47  Signal Response of Li to In against Flow for Forward Powers of 1200 to 1400 W. Responses Normalised to 100% Abundance
Figures 48–50  Signal Response as Figs. 45 to 47, for Elements Ba to U
Figures 51—53 Signal Response against Flow at 3 Powers for Li, In and U Responses Normalised to 100% Abundance
gives only the slightest indication of a shift of point of maximum response with respect to flow, for changes in power. The behaviour of an element, reaching a maximum for a flow range before decreasing, is consistent with behaviour reported for ICP-MS systems elsewhere (41, 74, 96, 101). However, in some of these reports, the maximum response for elements across the mass range were at different gas flows (41), where no one nebuliser flow is truly optimal for all elements. Studies of this nature carried out on the PlasmaQuad showed much less mass dependence for maximum signal response, with response curves very similar to those shown here (96, 101). They do, however, show a more pronounced dependence on plasma power for relative maximum response position with respect to gas flow, particularly for heavier elements. This may be a reflection of the interface configuration (0.75mm sampling cone and 1mm skimmer cone in reference 101, and 0.45 sampling cone used in reference 96) used in these projects. Zhu and Browner (101) made the observation that it would be predicted from the Saha relationship that a lower ionisation potential would give rise to a higher degree of ionisation and hence to greater sensitivity. Their data did not reflect this; in fact a change of operating conditions resulted in a change of order of elemental response. They conclude from this that sensitivity is dependent on other factors and not solely degree of ionisation. The elements chosen for their study and the ones in this study are assumed to be 100% ionised, having ionisation potentials <8eV. This makes drawing
conclusions on the role of ionisation potential in signal response less than straightforward. Table 15 lists the elements in this study with their ionisation potentials and signal rates at several gas flows for 1300W. The ionisation potentials are in the order Rb < Ba < Li < Ce < In < Al < U < Bi < Pb < Mg < Co < W, but the signal order observed at 1300W power and 0.73L min⁻¹ (maximum signal for most elements) is W > Pb > U > Bi > Co > In > Ce > Ba > Rb > Li > Al > Mg.

Table 16 shows the different orders of increasing signal response for the elements, at all flows studied at 1300W. The only flow with an order of increasing signal response for the elements, that can be explained simply, is at 0.59L min⁻¹. At this flow, the order of sensitivity ascends almost directly with increasing elemental mass. It is interesting to note that W gave the highest signal response in this study and in the work of Zhu and Browner (101), even though it has the highest ionisation potential of all the elements studied and has a mass close to the centre of the range.

The signal response behaviour for all elements as a function of central channel gas flow may be explained by referring to Figure 54. At a low gas flow the normal analytical zone (NAZ), containing the ground state ions will be drawn back from sampling cone with fewer ground state ions entering the orifice, the majority undergoing electron recombination before extraction can occur. At high gas flow the IRZ is pushed toward the extraction cone, a region of incomplete dissociation and ionisation, as described above.
### Table 15

Elemental Responses at Several Carrier Gas Flows

<table>
<thead>
<tr>
<th>Element</th>
<th>$\text{E}^1_\text{c}$ (eV)</th>
<th>Carrier Gas Flow (L.min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.32</td>
<td>0.59</td>
</tr>
<tr>
<td>$^{85}\text{Rb}$</td>
<td>4.18</td>
<td>1845</td>
</tr>
<tr>
<td>$^{133}\text{Ba}$</td>
<td>5.21</td>
<td>225</td>
</tr>
<tr>
<td>$^7\text{Li}$</td>
<td>5.39</td>
<td>303</td>
</tr>
<tr>
<td>$^{140}\text{Ce}$</td>
<td>5.57</td>
<td>558</td>
</tr>
<tr>
<td>$^{115}\text{In}$</td>
<td>5.79</td>
<td>5996</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>5.99</td>
<td>18960</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>6.20</td>
<td>37</td>
</tr>
<tr>
<td>$^{209}\text{Bi}$</td>
<td>7.29</td>
<td>243</td>
</tr>
<tr>
<td>$^{208}\text{Pb}$</td>
<td>7.42</td>
<td>851</td>
</tr>
<tr>
<td>$^{24}\text{Mg}$</td>
<td>7.65</td>
<td>32</td>
</tr>
<tr>
<td>$^{59}\text{Co}$</td>
<td>7.87</td>
<td>5335</td>
</tr>
<tr>
<td>$^{184}\text{W}$</td>
<td>7.98</td>
<td>1319</td>
</tr>
</tbody>
</table>

Forward Power 1300W
Responses in Area Counts sec$^{-1}$
Responses corrected to 100% abundance

### Table 16

Order of Increasing Sensitivity for Elements across the Mass Range at several Carrier Gas Flows. 1300W Forward Power.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (L.min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>Ce</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>W</td>
</tr>
<tr>
<td>Rb</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>In</td>
</tr>
<tr>
<td>Al</td>
</tr>
</tbody>
</table>
Figure 54  Plasma Regions with respect to the Interface
This argument is well supported by Figure 55, which shows cobalt signal response, on the research instrument, versus increasing carrier gas flow for sampling distances of 5mm, 10mm and 15mm. Maximum signal is achieved or approached at increasingly higher gas flows for greater sampling distances. The actual maximum signal response is lower at each new sampling distance because the higher gas flow required to achieve the optimum sampling point, with respect to the extraction cone, lowers the temperature of the central channel. This pattern of signal response was also reported by Zhu and Browner (101), although in their study, greater sampling distances were used. A few elements were studied over a smaller gas flow range, but a larger power range (1100W, 1300W, 1500W). Figures 56-58 show Co, Rb, Ce and Bi signal response against flow for the 3 powers. The patterns are essentially the same as those over the narrower power range, except that the Co curve is distinct from the other elements, reaching a maximum at a higher flow for all powers. This may be a result of having fewer points than in the previous curves, making it appear more separate than it is in reality. The uncertainty surrounding factors affecting elemental response is reflected in Figure 57, for the ascending order of response at 0.73L.min⁻¹ is Rb >Co >Bi >Ce. In the previous exercise at these conditions the order was Rb >Ce >Co >Bi. This implies that setting up and optimising the instrument (i.e. the ion optics) affects the elemental response. For operation of an analytical instrument these findings are important, in that it shows
Figure 55  Go Signal Response against Nebuliser Flow at three Sampling Distances
Figures 56–58  Signal Response of Co to Th against Flow for Forward Powers of 1100 to 1500 W. Responses Normalised to 100% Abundance
that for a given power, optimisation for one element in terms of obtaining maximum signal, results in optimisation for all others, although specific elements may be optimised to different levels.

5.3.2 Polyatomic Ions

In order to relate the levels of polyatomic ions experienced to real analytical problems, the practice has been adopted of quoting the size of those ion peaks in terms of equivalent concentration. Reference is usually made to a nearby monoisotopic elemental peak, in this case Co, which has been included in the test matrix solution. Co experiences very little interference, so forms a useful reference. Referencing the polyatomic ions to a nearby elemental ion provides a reasonable guide to the significance of the interference to be expected from the matrix concerned.

Polyatomic ion formation occurs in the interface region as the result of several processes which have been discussed. Their formation can be influenced by variations in plasma parameters. The water content of the plasma, for example, has been shown to affect the levels of polyatomic ions. Three species ArO⁺, ClO⁺ and Ar⁺ which are among the most prominent and troublesome observed were monitored. Their behaviour is believed to be representative of most of those observed on the PlasmaQuad. The responses of the three polyatomic ions monitored are shown for three power levels both as the ion intensity and as the ratio to the intensity.
of the Co ion from a 1μg.mL⁻¹ solution. Figures 59 and 60 show the results for ArO⁺ which apart from a high peak at 1500W, the intensity changes very little above 0.61L.min⁻¹, as the flow increases. As a result of this, the relative level of ArO⁺ compared to the Co⁺ signal is at a minimum when the response is optimised at the normal flow rate of about 0.8L.min⁻¹, where there is a sharp trough.

The ClO⁺ response shown in Figures 61 and 62 shows a similar sharp fall in ClO⁺, and as with the ArO⁺, a trough at about 0.8L.min⁻¹ when compared to the Co⁺ signal. However, as the ClO⁺ response continues to fall, there is very little increase in the ClO⁺/Co⁺ ratio, unlike the comparable ArO⁺ responses. Figures 63 and 64 show the argon dimer response. They display the now familiar hump at the lower flow rates, at which the Co⁺ signal is below optimum, but fall off sharply at higher flows, both as the ion and relative to the Co⁺ response.

Even though these ions are amongst the most troublesome in the mass spectrum, these response curves show that the operating conditions that would be chosen for maximum elemental signal give minimum levels of interferences, both as individual ions and relative to elemental ion signal. The behaviour of these interference ions can be explained by referring to Figure 65. Here the response of Ar, derived from ³⁶Ar⁺, is shown against flow for 3 powers. At a flow of 0.61L.min⁻¹ with 1500W power, the argon response is relatively high, which corresponds to the conditions under
Figure 59 Variation of ArO Response with Flow at 3 Powers

Figure 60 Ratio ArO/Co from Fig. 59
Figure 61  Variation of ClO Response with Flow at 3 Powers

Figure 62  Ratio ClO/Co From Fig. 61
Figure 63 Variation of ArAr Response with Flow for 3 Powers

Figure 64 Ratio ArAr/Co from Fig. 63

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Figure 65 Variation of Argon Response (from $^{36}\text{Ar}$) with Flow for 3 Powers
which the polyatomic ions were at their highest. Under these operating conditions, more Ar ions are generated than at the same flow but at a lower power, or at a greater flow for the same power, because the residence time of the argon gas in the plasma is much longer and greater heating of the gas occurs. For a given power, as the flow increases from 0.61L.min⁻¹, there is increased cooling along the central axis of the plasma and decreased residence time. This results in a decreasing number of argon ions being formed and thus available for polyatomic ion formation. The same effect applies for changes in power at a given flow. At 0.6L.min⁻¹, decreasing forward power results in a corresponding loss of Ar⁺ signal, due to cooling of the plasma as a result of the power reduction and reduction in the levels of Ar⁺ ions. Below 0.6L.min⁻¹ the response of argon against power is reversed. This may be a result of constriction of the central channel at higher powers, and a higher flow/shorter residence time of the gas along the central channel in the plasma. As ClO⁺ has a very similar pattern to ArO⁺, it is reasonable to assume that Cl and O undergo the same processes in the plasma, as Ar, with respect to parameter variations.

5.3.3 Analyte Oxide Species

The elements studied for refractory oxide formation are shown in Table 17, together with their bond strengths and the levels of oxides at 3 powers for a gas flow rate of 0.73L.min⁻¹, the sensitivity optimum for most elements. The
Table 17
Oxide Formation (MO/M%) at 0.73L.min⁻¹ Nebuliser Flow for Elements with a Range of Oxide Bond Strengths

<table>
<thead>
<tr>
<th>Element</th>
<th>Bond Strength (kJ.mol⁻¹)</th>
<th>1100W</th>
<th>1300W</th>
<th>1500W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>255</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cl</td>
<td>272</td>
<td>0.87</td>
<td>0.96</td>
<td>2.69</td>
</tr>
<tr>
<td>Bi</td>
<td>343</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cr</td>
<td>427</td>
<td>0.08</td>
<td>0.11</td>
<td>0.23</td>
</tr>
<tr>
<td>Tm</td>
<td>557</td>
<td>0.19</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>Ho</td>
<td>623</td>
<td>0.33</td>
<td>0.30</td>
<td>0.47</td>
</tr>
<tr>
<td>Ce</td>
<td>795</td>
<td>1.22</td>
<td>1.29</td>
<td>1.79</td>
</tr>
<tr>
<td>Th</td>
<td>854</td>
<td>2.13</td>
<td>1.87</td>
<td>2.78</td>
</tr>
</tbody>
</table>

ND, Not Detected
behaviour of the oxide response from elements of increasingly refractory nature as a function of bond strength, is shown in Figures 66-70, where each figure represents one of the flow rates studied. Apart from Cl, the values for which suggest a different origin for this ion, the values for the non-refractory elements of low bond strength such as Bi and Rb are below background for solutions of 10µg.mL⁻¹ and lower. At each flow rate the level of oxide increases as a function of bond strength as would be expected. For a given flow and bond strength, higher powers give increased levels of oxides. This can be more clearly seen in Figure 71, where the oxide ratio of the most refractory element, Th, is shown against flow for 3 powers. It has been tentatively suggested that reductions in ion energy at higher powers, resulting in less collisional ionisation may be partly responsible for this effect (117).

Increasing flow rate for any given power for a refractory element results in increasing levels of oxide ions (except for Cl) which can be more clearly seen in Figure 72, where the variation with flow rate for the three most refractory elements is shown, at the usual operating power level of 1300W. The sharp rise at the highest flow rate is evident, but at the flow rate of 0.73L.min⁻¹ at which maximum elemental signal is obtained, acceptably low oxide levels are obtained without any special precautions.

At the higher flow rates, for elements with greater bond strengths such as Ho, Ce and Th, the increased levels of
Figures 66–68 Variation of Oxide Response Ratio MO/M with Bond Strength at 3 Powers for Flow Rates of 0.46 to 0.75 l/min.

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Figures 69 and 70 as figs 66 to 68 for Flow Rates 0.56 and 1.13 l/min.
Figure 71 Variation of ThO/Th with Flow at 3 Powers

Figure 72 Variation of Mo/M for Refractory Elements with Flow Rates at Forward Power of 1300 W
oxides show the effect of reduced dwell time in the central channel. The resulting poorer dissociation of the most refractory oxides, even under the most adverse operating conditions (1.13L.min⁻¹ flow), gives rise to oxide levels of below 4%.

The behaviour of the oxide species shown here is very similar to that observed by Zhu and Browner (101) and Long and Brown (96), who reported similar levels of oxides at given parameter settings. Vaughan and Horlick (98), Horlick et al. (41) and Longerich et al. (74) reported different behaviour on the Sciex ELAN. In general, oxide levels are higher than those reported here (e.g. CeO⁺ 10%). They reported that minimum oxide levels occur away from maximum signal intensity and that MO⁺/M⁺ ratios decrease with increasing power for a given flow, the complete opposite of the behaviour reported here. If ion energy does play a role in bond dissociation, the lower ion energy produced by the ELAN may explain why the oxide levels are generally higher. However, this does not explain why the oxide levels decrease with power; according to Fulford and Douglas (94) ion energies are not dependent on forward power.

5.3.4 Doubly Charged Ions

The doubly charged ion responses for the two elements studied having the lowest second ionisation energies, Ba and Ce, are shown as a function of flow rate in Figures 73 and 74. The M²⁺ response (abundance corrected) is shown as a ratio to Co⁺ response (both M and Co at the same
Figure 73 Variation of Doubly Charged Ion Ratio $\text{Ba}^{2+}/\text{Co}^+$ with Flow Rate for 3 Powers

Figure 74 as Fig. 73 but for $\text{Ce}^{2+}/\text{Co}^+$. 

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concentration). This means that the ratio does not exactly correspond to the $M^{2+}/M^+$ often quoted. The true ratio is difficult to determine as it is not clear whether the ion transmission, and as a result the mass discrimination, of the overall system is a function of ion mass or $M/2$ ratio. Comparison of doubly charged ion results reported from different ICP-MS systems have to be studied in the light of this problem. From an analytical point of view, the interference is only relevant to the particular instrument concerned and the size of the interferant compared to the ions affected. Expressing the $M^{2+}$ response in relation to $Co^+$ response is a convenient method.

The responses shown for the two elements are very similar to responses reported elsewhere (57, 95, 99, 101, 103) for PlasmaQuad (type) instruments, with a sharp rise for Ba at the highest flow rate. In systems of this type there is a reproducible relationship between the central channel gas flow and the proportion of doubly charged ions found in the extracted gas sample for elements with second ionisation energies ($E_i''$) lower than the first, $E_i'$, of argon at 15.76eV. At any given gas flow rate and power the extent of the double ionisation depends on the energy gap between ionisation energies. As shown in Figures 73 and 74, $M^{2+}/M^+$ ratio decreases with increasing power and increases with increasing gas flow. This is opposite to the expected behaviour, i.e. with increase in aerosol gas flow the temperature ($T_{ion}$) of the plasma would fall with a
corresponding fall in electron density \((N_e)\) along with a reduction in analyte residence time. This would translate to lower efficiency for doubly charged ion formation. Higher forward power should cause \(N_e\) and \(T_{1+}\) to increase, with a corresponding increase in doubly charged species (51). Table 18 shows the effect of increasing flow on a series of elements with increasing \(E_{i}\), and the mean stopping potential of \(Co^+\). Stopping potential was measured by observing the analysing rod decelerating potential (or pole bias) required to reduce the signal rate for the ion concerned from the normal level observed to background. The mean stopping potential used is the mean of this value and the potential at full signal rate. Although this is not a true measure of extracted ion energy it gives a very good approximation (93, 99). Clearly elements with \(E_{i}\) above \(E_{i}\) of argon do not have detectable levels of doubly charged ions. It can also be seen that mean stopping potential (closely related to mean ion energy) increases with increasing gas flow. This behaviour has been reported elsewhere on this type of system (51, 93, 95, 99, 103). Stopping potential decreases with power, as can be seen in a plot of Figure 75, the mean stopping potential of \(^{115}\text{In}^+\) against gas flow at three powers.

As long as parameters such as water loading (118) and sampling cone-load coil spacing remain unchanged, optimising the systems for maximum elemental signal response (i.e. ca 0.73L.min\(^{-1}\)) sets doubly charged species levels of ca 1\% for Ce and 5\% for Ba. Thus the analyst is never unknowingly
### Table 18

Ratio $M^{2+}/Co^+(\%)$ against Nebuliser Flow and Ion Stopping Potential

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_{i}''$ (eV)</th>
<th>Carrier Gas Flow (L.min$^{-1}$)</th>
<th>Mean Stopping Potential Co (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>10.00</td>
<td>0.15 1.43 5.73 4.69 16.25</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>10.85</td>
<td>0.06 0.53 1.88 2.23 5.32</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>13.13</td>
<td>N.D. 0.03 0.22 0.27 1.58</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>15.03</td>
<td>N.D. N.D. 0.03 0.01 0.18</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>18.56</td>
<td>N.D. N.D. N.D. N.D. N.D.</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>25.08</td>
<td>N.D. N.D. N.D. N.D. N.D.</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>27.5</td>
<td>N.D. N.D. N.D. N.D. N.D.</td>
<td></td>
</tr>
</tbody>
</table>

Forward Power, 1300W

$E_{i}''$, Second Ionisation Potential

N.D., Not Detected
Figure 75 Variation of Mean Ion Stopping Potential with Flow Rate for In ions at 3 Powers

Figure 76 Dependence of Ion Stopping Potential on Flow Rate for Four Ions of Different Masses at 1300 W Power
operating under conditions that produce unacceptably high levels of doubly charged species, so long as maximum elemental response is always sought.

The behaviour seen here is completely contradictory to that reported by Horlick et al. (41, 98) who found that $M^{2+}/M^+$ decreased with gas flow and increased with power; behaviour that the Saha equation predicts. Fulford and Douglas (94), in their study of ion kinetic energies on the Sciex ELAN ICP-MS system, showed that ion energies were not dependent on plasma parameters (gas flow and power) and were generally lower than values reported here. This implies that doubly charged ion formation is dependent on significant ion energy levels or that ion energy contributes to doubly charged species formation and where ion energies are low, doubly charged ion formation is dependent on plasma parameters as predicted by the Saha equation.

5.3.5 Ion Energy

The potential assumed by the ICP central channel above ground depends on the extent of r.f. capacitative coupling from the load coil to the plasma (117). A variety of coil grounding arrangements have been used to control the plasma potential (95, 99, 107) which may lie between 0 and 20v in practical systems. The operation of the ion lens system needed to produce an ion beam along the axis of the quadrupole mass analyser is affected by the energy at which the ions enter the interface, which in turn is derived from the potential at which the ions are formed. The final
energy of ions reaching the mass analyser is of little importance (as long as the spread is small), as any excess energy can be offset by using the pole bias of the analysing rods. Obviously if there is a large spread of energies, then offsetting all ion energies equally would be impossible. The most important consequence of the extracted ion energy lies in ion lens performance and in collisional ionisation effects within the interface. It is these two parameters that have led to the considerable contrast in instrument performance for the different types of systems investigated.

So far two types of ion energy behaviour have been reported:

i) The Sciex ELAN system whose mass dependent performance is characterised by ion energies which are unaffected by changes in plasma parameters and

ii) The Ames/Surrey/PlasmaQuad (A/S/P) systems which have ion energies that are dependent on changes in plasma parameters but are much less mass dependent.

No ion energy measurements have been reported for the home made system at Indiana University, Bloomington (105, 119) but it does show interference characteristics (oxides, doubly charged) of the A/S/P systems, which suggests that ion energies will behave in a similar way to the A/S/P systems. The individual characteristics reported for each of the different systems are probably the result of ion energy obtained by the ions leaving the plasma.
With the ELAN, a range of elements across the mass range reach maximum signal under different plasma conditions (41) making optimisation of the system almost impossible for all elements at the same time, which rather detracts from the multi-element capability of ICP-MS. This effect is the result of two factors; the mass dependent ion energies and the ion-lens configuration. The ion lenses used in ICP-MS systems have zero mass dispersion for all ions of constant energy, a particularly desirable property in an elemental analysis system where the ions to be focused have a mass range of almost 250 u. The dispersion is dependent on the ion energy, a property exploited by the electrostatic energy analyser used in double focusing mass spectrometers. Quadrupole instruments use a 'Bessel box' type energy analyser, the same device incorporated in the lens system of the ELAN. For uniform transmission of ions, the energy spread across the mass range has to be as small as possible. Magnetic instruments achieve this by accelerating the ions through a high potential difference after leaving the source, so that the relative energy spread of ions from the source is small. With the centre tap load coil used in the ELAN (107), the ICP ion source potential is close to ground, probably below 1 v (100). Fulford and Douglas (94) have shown that with a very low source potential, the principle source of ion kinetic energy is the supersonic expansion during extraction. During extraction of the plasma gas, the ions, which constitute about 0.1% of the total plasma gas together with the neutral species acquire the same
supersonic velocity. As their velocity is the same, the heavier ions gain more energy than the light ones during the expansion. The ion energies have an observed range from 2 to 9eV, across the elemental mass range and are barely affected by changes in plasma parameters. The result is that ions leaving the plasma have a larger relative ion speed and enter an energy selective ion lens system which sorts the ions according to their mass (a result of mass dependent ion kinetic energies) and only allows a selected mass range to enter the quadrupole mass spectrometer.

In systems employing an asymmetrically grounded load coil, coil geometry and plasma operating parameters enable plasma potential to be set within a 2 to ±20V range. In these systems, unlike the ELAN, the value is dependent on both carrier gas flow and plasma power. However, these are very easily stabilised and would never be changed by the operator in the course of analysis. At low flows (low potentials) there is a mass dependence for ion energy, similar to the effect reported by Fulford and Douglas (94). As flow is increased so does plasma potential, which has more influence on the ion energy and only a small spread of energy across the mass range remains as shown in Figure 76. Here the variation of mean ion stopping potential on the analysing rods (closely related to mean ion energy), with carrier gas flow is shown for the PlasmaQuad, for four ions ranging from $^9$Be to $^{238}$U. Above the usual operating flow rate, the ion energies diverge again, but with the lighter ions showing the higher energies. The flow at which the ion energies...
converge is where maximum signal response is obtained for all elements across the mass range, as shown in Figures 73 and 74. Optimisation is achieved with a multi-element standard containing elements with a range of masses which shows the response across the mass range. As the same flow rate is close to optimum for all elements, there is no reason to change it and the system may be used for analysis in any part, or over the whole of the mass spectrum without resetting either the gas flow or ion lenses.

Collisional ionisation within the extracted gas may be a disadvantage of a high plasma potential if the resulting ion energy becomes high enough to generate significant numbers of doubly charged ions. This may be expected at energies above 10eV, the lowest value of $E_i^+$ (Ba) when $M^2+$ yields may greatly exceed those expected from the plasma alone (117). The presence of a small controlled plasma potential is thought to be advantageous as a means of suppressing refractory oxide species formation during the extraction process and may explain why oxide levels are consistently lower for A/S/P systems compared with the ELAN.

5.3.6 Ion Lens Optimisation

Optimisation of the ion lens system on the PlasmaQuad is carried out using a set of 12 control potentiometers, of which in practice, two are never used and 4 others rarely require adjustment. Figure 77 shows the ion extraction, analysis and detection system on this instrument and Figure 78 shows the lens system itself, except for the
extractor. The 4 potentials that rarely need adjustment are the differential aperture, which has a fixed potential. The entrance plate and entrance rod bias are usually set at ground and the analysing rods are given a small fixed positive bias. The remaining six controls deal with beam formation and focusing and are generally operated in pairs, being adjusted in order along the ion path. The lenses are normally tuned whilst monitoring Co⁺ and then retrimmed at a high mass, e.g. Bi⁺ or U⁺ followed by Co⁺ again and repeated in turn for level response across the mass range. As long as this is carried out systematically from front to back lens components, full mass range optimisation is easily achieved. A typical mass response curve is shown in Figure 79, for elements across the mass range (normalised to 100% abundance) after setting up in the normal way under the conditions given in Table 14.

If a different nebuliser is used in place of the Meinhard, such as a cross-flow or high solids type, a different gas flow rate may be required. The lens settings can be quickly re-optimised for the new flow rate by using the above procedure. Resetting a required flow is straightforward on the controller used with this instrument, although the flow has to be monitored by the pressure drop across the nebuliser using a calibration graph. Mass flow controllers have the advantage of direct readout of flow, although they are probably not necessary from a stability point of view.
Figure 77  Schematic Diagram of the Ion Extraction, Analysis and Detection System of the VG PlasmaQuad. Coll. and Ext. are collector and Extractor Electrodes. DA is the Differential Aperture and L1—L4 the Lens Cylinders. Pole Bias is applied to the Analysing Rods.

Figure 78  PlasmaQuad Ion Lens System without Extractor Element.
Figure 79  Elemental Response of PlasmaQuad for this Work. Normalised for 100% Abundance and Referred to Co=1; All Elements have E_i < 8eV and are assumed to be 100% Ionised; Gas Flow Rate 0.73 l/min.; Power 1300 W.
5.4 Conclusions

The data shown here demonstrate the range of response variation of polyatomic, oxide and doubly charged ions obtained by parameter variation and their relationship to elemental ion response. The ions shown here are commonly quoted as sources of interference and quite clearly high levels of these ion can be generated if the system is not optimised correctly. However, if the instrument is set up for maximum elemental response, near minimal levels of interference ions will be obtained.

Careful system optimisation for specific analytical problems is not necessary. Gas flow and plasma power are the parameters that have most effect on ion response. In the course of normal analysis these do not need to be varied, as the system is optimised for all elements, whether scanning over a large or small range or peak jumping across selected peaks. There is never any risk of obtaining high levels of interferences, so long as maximum signal is always sought.
6.1 Introduction

The initial part of this study was devoted to investigating some fundamental aspects of ICP-MS: system performance, spectroscopic interferences and factors affecting system optimisation. Having assessed the optimum operating conditions and potential drawbacks of ICP-MS, the final part of this study was devoted to elemental and isotope ratio determinations using conventional and 'novel' sample introduction methods.

6.2 Analysis of Solutions

The most common method of introducing liquid samples into the ICP is by pneumatic nebulisation, where the liquid is dispersed into a fine aerosol by the action of a high velocity gas stream. This ensures homogeneity of the sample which can be simply introduced into the plasma and allows straightforward calibration to be carried out, with the relevant standards. This method of sample introduction also allows use of solutions for internal standardisation and standard addition.

The equipment required for solution sample introduction into ICP-MS has been described. For the work reported in this section a Jarrel-Ash cross flow nebuliser was used in conjunction with a WCSC unless otherwise stated.
With the rapid acceptance of ICP-MS in the analytical community have come successful elemental determinations in a wide range of sample matrices, from the life and environmental sciences right through to industrial applications. For the purposes of this project metallurgical materials are discussed.

In metallurgy, the trace element composition of the material can significantly effect its properties. Many atomic analytical methods have been employed to determine trace elements. These include flame and furnace atomic absorption and optical emission using a number of emission sources (e.g. ICP, DCP, Arc and Spark, Hollow Cathode). ICP-MS would seem to be ideally suited for metals analysis, with high sensitivity and selectivity. However, interference ions from matrix materials may have to be considered as a potential problem.

6.2.1 Analysis of 'pure' Copper Reference Materials

6.2.1.1 Introduction

In order to obtain some background information on the ability of ICP-MS to determine trace elements in pure metals, certified copper materials were analysed to determine their trace element content. One of the many uses for copper is in the electronics industry, where the properties of the materials may be severely degraded by elemental contaminants at or below the μg.g⁻¹ levels.
6.2.1.2 Experimental

Three copper standard reference materials (SRM), SSC-1, SSC-2 and SSC-3, (Spectroscopic Society of Canada) were analysed for Fe, Ni, As, Ag, Sb, Te, Pb, Bi and U as 0.1% (w/v) solutions in 1% nitric acid.

Turnings of the SRM's were made using a tungsten carbide tool; outer surfaces were discarded. Solutions were prepared from the turnings as follows:

Stock sample solutions were prepared by dissolving nominal 1g amounts of copper sample in 10mL of Arista nitric acid at approximately 80°C in covered conical flasks. After cooling, the solution was transferred to a 100mL volumetric flask and made up to volume with double distilled, deionised water (DDDI). Further dilution to 0.1% (w/v) dissolved solids was carried out with DDDI water and made up to 1% nitric acid with Arista nitric acid. Blank solutions were similarly prepared. Aqueous standard solutions of the elements of interest were prepared in 1% nitric acid from Specpure grade reagents (Johnson Matthey Chemicals).

Analysis was carried out on the research instrument under normal operating conditions.

6.2.1.3 Results of Copper Analysis

The results displayed in Table 19 are the means from 3 analyses on each of 3 dilutions (to 0.1%, w/v) from the stock solution (1%, w/v), thus a total of 9 analyses on each SRM were carried out.
Table 19
Comparison of Measured and Certificate Values for Copper SRM's

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
<th>Te</th>
<th>Pb</th>
<th>Bi</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SSC-1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>36.6</td>
<td>13.4</td>
<td>2.61</td>
<td>17.0</td>
<td>2.52</td>
<td>3.32</td>
<td>50.6</td>
<td>0.88</td>
<td>0.08</td>
</tr>
<tr>
<td>σ</td>
<td>1.69</td>
<td>1.86</td>
<td>0.68</td>
<td>0.85</td>
<td>0.71</td>
<td>0.86</td>
<td>1.34</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>Cert</td>
<td>39.2</td>
<td>17.6</td>
<td>1.16</td>
<td>18.8</td>
<td>2.64</td>
<td>4.5</td>
<td>65.3</td>
<td>1.15</td>
<td>n.d.</td>
</tr>
<tr>
<td>σ</td>
<td>7.18</td>
<td>3.36</td>
<td>0.48</td>
<td>5.81</td>
<td>0.54</td>
<td>0.78</td>
<td>7.02</td>
<td>0.33</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
<th>Te</th>
<th>Pb</th>
<th>Bi</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SSC-2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>34.2</td>
<td>4.25</td>
<td>3.52</td>
<td>10.0</td>
<td>7.08</td>
<td>0.75</td>
<td>5.75</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>σ</td>
<td>1.50</td>
<td>1.19</td>
<td>0.57</td>
<td>0.55</td>
<td>0.82</td>
<td>0.56</td>
<td>0.53</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>Cert</td>
<td>31.9</td>
<td>3.17</td>
<td>1.18</td>
<td>13.9</td>
<td>5.8</td>
<td>1.24</td>
<td>6.12</td>
<td>0.097</td>
<td>n.d.</td>
</tr>
<tr>
<td>σ</td>
<td>7.05</td>
<td>1.04</td>
<td>0.61</td>
<td>3.38</td>
<td>0.66</td>
<td>0.51</td>
<td>1.2</td>
<td>0.04</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
<th>Te</th>
<th>Pb</th>
<th>Bi</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SSC-3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>41.8</td>
<td>40.2</td>
<td>7.95</td>
<td>13.4</td>
<td>0.70</td>
<td>2.19</td>
<td>3.67</td>
<td>0.28</td>
<td>0.03</td>
</tr>
<tr>
<td>σ</td>
<td>3.18</td>
<td>2.97</td>
<td>1.22</td>
<td>1.17</td>
<td>0.19</td>
<td>0.56</td>
<td>0.25</td>
<td>0.11</td>
<td>0.006</td>
</tr>
<tr>
<td>Cert</td>
<td>40.0</td>
<td>48.0</td>
<td>5.45</td>
<td>16.1</td>
<td>1.63</td>
<td>2.53</td>
<td>4.58</td>
<td>0.59</td>
<td>n.d.</td>
</tr>
<tr>
<td>σ</td>
<td>8.82</td>
<td>7.68</td>
<td>1.93</td>
<td>3.59</td>
<td>0.99</td>
<td>0.63</td>
<td>1.51</td>
<td>0.01</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

LoD  1.5  1.5  0.6  0.6  0.4  1.6  0.2  0.59  0.04

All concentrations in μg.g⁻¹ in the solid
Mean - based on 9 replicate analyses
σ  - standard deviation
Cert - Certified value for SRM
LoD  - Limit of Detection
n.d. - not determined
For most of the elements studied, the results fall within one standard deviation (1σ) of the certified value. Even arsenic and tellurium, generally regarded as difficult elements to determine, are within 2σ of the certified value. All elements are well above the limits of detection except for bismuth and uranium. U was a previously undetermined element in these samples, but in this analysis, levels of 0.03 to 0.1μg·g⁻¹ in the solid were found. Rapidly identifying the elemental contents of an unknown sample is a major asset to the analyst.

Figure 80.1 shows a portion of the spectrum of SSC-3, with As, Te and U highlighted to show their signal level above background. Xe a contaminant in the liquid argon, can be seen between the two peaks of Te. Although the levels of both are low, they are clearly visible above background and resolved from one another.

6.2.1.4 Semi-Quantitative Copper Analysis

It is often sufficient in materials analysis to determine the elemental composition to an accuracy of only about an order of magnitude. ICP-MS has the ability to perform full mass range semi-quantitative analysis to an accuracy of about 30%.

The accuracy of semi-quantitative analysis for 'pure' metals analysis was assessed by determining the trace element composition of four industrial copper foil solutions. Three analyses were carried out on each.
Figure 80.1 Spectrum of Standard Reference Copper SSC-3.
Co, Y, In, Sb, Ce, Bi and U at 100ng.mL\(^{-1}\) was used to define the response curve shown in Figure 80.2. All samples were 'calibrated' against this curve. Elemental values were corrected for isotopic abundance for elements with more than one isotope and degree of ionisation for elements that are less than 100% ionised.

Table 20 shows the effect of referring the response curve standard to the defined curve. As this standard was used to generate the curve, it should, in theory, give the best accuracy of all the samples. The degree of error ranges from 1% for Be to 45% for Co.

The results of the semi-quantitative analysis of SSC-1 are shown in Table 21. Generally the agreement with the certified values is good, in view of the calibration method, with only 2% error in the best case (Te) and about 60% error in the worse case (Ag). Table 22 shows the results for the four industrial copper samples. Only elements with concentrations, in the solid above 1µg.g\(^{-1}\) are listed.

6.2.1.5 Conclusion

It is encouraging that the results are in good agreement with the certified values, especially as the standards were not matrix matched to the samples. This greatly simplifies the task for the analyst in determining the composition of samples such as 'pure' metal alloys. There is no evidence of any interference ions derived from Cu, such as CuO or CuAr. Oxides of copper would occur at 79 and 81u, the only
Mass (u)

Figure 80.2 Response Curve of Selected Elements for Semi-Quantitative Analysis of 'Pure' Copper Materials

Table 20

Semi-Quantitative (S-Q) Analysis of 100ng.ml\(^{-1}\) Standard used to generate S-Q Response Curve

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. ng.ml(^{-1})</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>101</td>
<td>+ 1</td>
</tr>
<tr>
<td>Al</td>
<td>112</td>
<td>+12</td>
</tr>
<tr>
<td>Co</td>
<td>145</td>
<td>+45</td>
</tr>
<tr>
<td>Y</td>
<td>119</td>
<td>+19</td>
</tr>
<tr>
<td>In</td>
<td>126</td>
<td>+26</td>
</tr>
<tr>
<td>Sb</td>
<td>134</td>
<td>+34</td>
</tr>
<tr>
<td>Ce</td>
<td>109</td>
<td>+ 9</td>
</tr>
<tr>
<td>Bi</td>
<td>79</td>
<td>-21</td>
</tr>
<tr>
<td>U</td>
<td>139</td>
<td>+39</td>
</tr>
</tbody>
</table>
### Table 21
Semi-Quantitative Analysis of Reference Copper SSC-1

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. µg.g(^{-1})</th>
<th>Cert. µg.g(^{-1})</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>35</td>
<td>39.2</td>
<td>-11</td>
</tr>
<tr>
<td>Ni</td>
<td>14</td>
<td>17.6</td>
<td>-20</td>
</tr>
<tr>
<td>As</td>
<td>N.D.</td>
<td>1.16</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>7.8</td>
<td>18.8</td>
<td>-58</td>
</tr>
<tr>
<td>Sb</td>
<td>1.9</td>
<td>2.64</td>
<td>-28</td>
</tr>
<tr>
<td>Te</td>
<td>4.4</td>
<td>4.5</td>
<td>-2</td>
</tr>
<tr>
<td>Pb</td>
<td>67</td>
<td>65.3</td>
<td>+3</td>
</tr>
<tr>
<td>Bi</td>
<td>N.D.</td>
<td>1.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Cert., Certified Value for SRM  
N.D., Not Detected

### Table 22
Results of Semi-Quantitative Analysis of 4 Industrial Copper Samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Industrial Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>(-)</td>
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<tr>
<td>Na</td>
<td>370</td>
</tr>
<tr>
<td>Mg</td>
<td>4.7</td>
</tr>
<tr>
<td>Al</td>
<td>9.3</td>
</tr>
<tr>
<td>K</td>
<td>150</td>
</tr>
<tr>
<td>Ca</td>
<td>75</td>
</tr>
<tr>
<td>Ti</td>
<td>160</td>
</tr>
<tr>
<td>Cr</td>
<td>23</td>
</tr>
<tr>
<td>Fe</td>
<td>13</td>
</tr>
<tr>
<td>Ni</td>
<td>4.2</td>
</tr>
<tr>
<td>As</td>
<td>35</td>
</tr>
<tr>
<td>Se</td>
<td>1.1</td>
</tr>
<tr>
<td>Ag</td>
<td>7.7</td>
</tr>
<tr>
<td>Cd</td>
<td>24</td>
</tr>
<tr>
<td>Ba</td>
<td>4.9</td>
</tr>
<tr>
<td>La</td>
<td>4.9</td>
</tr>
<tr>
<td>Ce</td>
<td>(-)</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
</tr>
<tr>
<td>Bi</td>
<td>(-)</td>
</tr>
</tbody>
</table>

Results in µg.g\(^{-1}\)  
(-), Not Detected or below 1µg.g\(^{-1}\)

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isotopes of Br and copper argides would mainly occur at 103 and 105u. Whilst $^{105}\text{Pd}$ is one of several isotopes, $^{103}\text{Rh}$ is monoisotopic. Determination of these elements in the presence of copper interferences would be difficult, especially for Br. Fortunately, this problem does not arise as no copper interference ions are found.

6.2.2 Analysis of Alloy Materials

6.2.2.1 Introduction
Analysis of a 'pure' material such as copper is apparently quite straightforward, with no problems from interference ions or suppression or enhancement effects. It has been reported however, that the determination of trace elements in alloyed materials can be extremely difficult, due to severe interference problems arising from the major alloy components (80). A potentially important application for ICP-MS is the determination of trace elements in Ni-base alloys, where increasingly, alloy manufacturers are having to meet lower and lower control specifications. The following ICP-MS study of Ni-base alloys resulted in severe positive errors for many trace elements which can be attributed to the occurrence of matrix metal oxide and doubly charged ions.

6.2.2.2 Experimental
The study was restricted to the analysis of two Ni-base alloys, MMAT1 and MMAT2, supplied by the Ministry of Defence (MoD), for which 14 elements had been determined,
with concentrations ranging from 0.1-155\mu g.g^{-1} in the solid. The samples were diluted to 0.1% dissolved solids from the original supplied stock solution prepared at MoD using an HF/HNO₃ solvent acid. A multi-element standard containing Pb, Bi, Sn, Cd, Ag, Zn, Tl, Se, Ga, Te, In, As, Sb and Mg was prepared at 1\mu g.g^{-1}. No matrix matching was carried out. Analysis was carried out on the PlasmaQuad under normal operating conditions.

6.2.2.3 Results of Alloys Analysis

The results, of which very few agree with the accepted values, are shown in Table 23. The mass spectrum of the alloy sample MMAT1, Figures 81.1 and 81.2, shows the source of the inaccuracies. The major components of these alloys are Ti, V, Cr, Co, Ni, Nb, Mo, Hf and W. Table 24 gives a list of the possible oxide and doubly charged ions obtained from these matrix elements. Table 25 gives a list of the isotopes available for the elements of interest. Comparing Tables 24 and 25 shows that most isotopes of any trace element of interest are covered by an interfering ion. Running the interference prediction computer program, ISOMASS, indicated that more exotic species, such as MAr⁺, might be responsible for the inaccuracies of other elements. The species are generally never seen, but the levels of the interference ions of matrix material, in comparison to the trace elements may be sufficiently high to cause these errors. Table 26 shows the ISOMASS interference suggestions from the Hf in the alloy matrix. It is clear that there is
Table 23
Results from Analysis of 2 Ni-Base Alloys

<table>
<thead>
<tr>
<th>Element</th>
<th>Alloy MMAT1</th>
<th></th>
<th></th>
<th>Alloy MMAT2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Accepted</td>
<td>Found</td>
<td>Accepted</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>7000</td>
<td>3.3</td>
<td>6000</td>
<td>7.4</td>
<td></td>
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<tr>
<td>Zn</td>
<td>40</td>
<td>0.2</td>
<td>28</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>17</td>
<td>15</td>
<td>52</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>270</td>
<td>1.0</td>
<td>290</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>80</td>
<td>0.2</td>
<td>71</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1.5</td>
<td>0.1</td>
<td>2.2</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>18</td>
<td>0.1</td>
<td>11</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>1.5</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>20</td>
<td>5.4</td>
<td>66</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>51</td>
<td>0.1</td>
<td>18</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>2.5</td>
<td>0.5</td>
<td>2.3</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>24</td>
<td>N.D.</td>
<td>27</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>110</td>
<td>0.1</td>
<td>88</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

All Values in µg.g⁻¹
Accepted Values Supplied by MoD, by Optical Emission Spectrometry
Figure 81.1 Part of a spectrum (45-140u) from the analysis of Ni base alloy, MMAT1, showing major elements and their oxides. Full scale is $3.2 \times 10^5$.

Figure 81.2 Part of a spectrum (140-210u) from the analysis of Ni base alloy, MMAT1, showing major elements and their oxides. Full scale is $3.2 \times 10^3$. 
Table 24
Potential Interferences from Major Components of Ni-Base Alloys

<table>
<thead>
<tr>
<th>Major Element</th>
<th>Potential Oxides (u)</th>
<th>Potential $M^2^+$ (u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>62-66</td>
<td>23-25</td>
</tr>
<tr>
<td>V</td>
<td>66,67</td>
<td>25.5</td>
</tr>
<tr>
<td>Cr</td>
<td>66,68-70</td>
<td>(-)</td>
</tr>
<tr>
<td>Co</td>
<td>75</td>
<td>(-)</td>
</tr>
<tr>
<td>Ni</td>
<td>74,76-78,80</td>
<td>(-)</td>
</tr>
<tr>
<td>Nb</td>
<td>109</td>
<td>46.5</td>
</tr>
<tr>
<td>Mo</td>
<td>108,110-114,116</td>
<td>(-)</td>
</tr>
<tr>
<td>Hf</td>
<td>190,192-196</td>
<td>87-90</td>
</tr>
<tr>
<td>W</td>
<td>196,198-200,202</td>
<td>(-)</td>
</tr>
</tbody>
</table>

(-), $E_i^{uu}$ too high to form $M^2^+$

Table 25
Isotopes of Elements of Interest in Ni-Base Alloys

<table>
<thead>
<tr>
<th>Element of Interest</th>
<th>Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>24-26</td>
</tr>
<tr>
<td>Zn</td>
<td>64,66-68,70</td>
</tr>
<tr>
<td>Ga</td>
<td>69,71</td>
</tr>
<tr>
<td>As</td>
<td>75</td>
</tr>
<tr>
<td>Se</td>
<td>74,76-78,80,82</td>
</tr>
<tr>
<td>Ag</td>
<td>107,109</td>
</tr>
<tr>
<td>Cd</td>
<td>106,108,110-114,116</td>
</tr>
<tr>
<td>In</td>
<td>113,115</td>
</tr>
<tr>
<td>Sn</td>
<td>112,114-120,122,124</td>
</tr>
<tr>
<td>Sb</td>
<td>121,123</td>
</tr>
<tr>
<td>Te</td>
<td>120,122-126,128,130</td>
</tr>
<tr>
<td>Tl</td>
<td>203,205</td>
</tr>
<tr>
<td>Pb</td>
<td>204,206-208</td>
</tr>
<tr>
<td>Bi</td>
<td>209</td>
</tr>
</tbody>
</table>
Table 26

Interference Masses of MO+, MOH+ and M²+ From Hf

<table>
<thead>
<tr>
<th>Abund.</th>
<th>Hf⁺</th>
<th>HfO⁺</th>
<th>HfOH⁺</th>
<th>Hf²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>174</td>
<td>190</td>
<td>191</td>
<td>87</td>
</tr>
<tr>
<td>5.2</td>
<td>176</td>
<td>192</td>
<td>193</td>
<td>88</td>
</tr>
<tr>
<td>18.5</td>
<td>177</td>
<td>193</td>
<td>194</td>
<td>88.5</td>
</tr>
<tr>
<td>27.2</td>
<td>178</td>
<td>194</td>
<td>195</td>
<td>89</td>
</tr>
<tr>
<td>13.8</td>
<td>179</td>
<td>195</td>
<td>196</td>
<td>89.5</td>
</tr>
<tr>
<td>35.1</td>
<td>180</td>
<td>196</td>
<td>197</td>
<td>90</td>
</tr>
</tbody>
</table>

Interference Masses of MH+, MO₂+ and MO₂H⁺ From Hf

<table>
<thead>
<tr>
<th>Abund.</th>
<th>Hf⁺</th>
<th>HfH⁺</th>
<th>HfO₂⁺</th>
<th>HfO₂H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>174</td>
<td>175</td>
<td>206</td>
<td>207</td>
</tr>
<tr>
<td>5.2</td>
<td>176</td>
<td>177</td>
<td>208</td>
<td>209</td>
</tr>
<tr>
<td>18.5</td>
<td>177</td>
<td>178</td>
<td>209</td>
<td>210</td>
</tr>
<tr>
<td>27.2</td>
<td>178</td>
<td>179</td>
<td>210</td>
<td>211</td>
</tr>
<tr>
<td>13.8</td>
<td>179</td>
<td>180</td>
<td>211</td>
<td>212</td>
</tr>
<tr>
<td>35.1</td>
<td>180</td>
<td>181</td>
<td>212</td>
<td>213</td>
</tr>
</tbody>
</table>

Interference Masses of MAr⁺ From Hf

<table>
<thead>
<tr>
<th>Abund.</th>
<th>Hf⁺</th>
<th>Hf³⁶Ar⁺ (0.34)</th>
<th>Hf³⁸Ar⁺ (0.07)</th>
<th>Hf⁴⁰Ar⁺ (99.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>174</td>
<td>210</td>
<td>212</td>
<td>214</td>
</tr>
<tr>
<td>5.2</td>
<td>176</td>
<td>212</td>
<td>214</td>
<td>216</td>
</tr>
<tr>
<td>18.5</td>
<td>177</td>
<td>213</td>
<td>215</td>
<td>217</td>
</tr>
<tr>
<td>27.2</td>
<td>178</td>
<td>214</td>
<td>216</td>
<td>218</td>
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<tr>
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<td>179</td>
<td>215</td>
<td>217</td>
<td>219</td>
</tr>
<tr>
<td>35.1</td>
<td>180</td>
<td>216</td>
<td>218</td>
<td>220</td>
</tr>
</tbody>
</table>

Abund. - Isotopic Abundance of Elemental Species
potential for interference at several masses. If these suggestions are compared with ions actually found in the mass spectrum it can be seen that ions such as HfO₂⁺ are not detected but HfAr⁺ is present at very low levels.

6.2.2.4 Conclusion
Clearly there is not a straightforward method of determining trace elements in complex alloys of this type. McLeod (80) suggests that the use of a high resolution mass spectrometer would be an effective solution to the interference problem. Alternatively mathematical correction schemes such as those used in spark source mass spectrometry might be applicable in ICP-MS. Analysis of the solid material by laser ablation ICP-MS may prove to be an attractive method, as the analysis would be carried out with a dry plasma, so that the occurrence of oxygen related species should be significantly reduced.

6.2.3 Determination of ⁹⁹Technetium

6.2.3.1 Introduction
In the wake of the recent nuclear accident at Chernobyl in the U.S.S.R. and with increased public awareness of environmental issues, it is imperative that the nuclear industry is seen to maintain a high level of environmental monitoring. ICP-MS is well suited to the task, with features such as limits of detection in the low ng.g⁻¹ range for most elements and high sample throughput.
The wide elemental coverage of the technique allows the measurement of all the possible decay products of a nuclear event, e.g. $^{99}$Tc, $^{129}$I, $^{137}$Cs $^{239}$Pu in a single rapid analysis. This nuclear fingerprint can be used to determine the source of the radioactivity, whether it was fall-out from a bomb test or an accident at a reactor. In certain cases, for relatively stable radionuclides with long half-lives, ICP-MS can prove more sensitive than radioactivity monitoring techniques.

The application of ICP-MS to environmental monitoring for radioactive decay products is demonstrated here by the determination of $^{99}$Tc in standard solutions and in some environmental samples originating from a site associated with nuclear reprocessing.

6.2.3.2 Properties and Determination of Technetium

Technetium was first found in a sample of molybdenum which had been bombarded with deuterons and was the first element to be produced artificially. Sixteen isotopes of Tc are known, with masses ranging from 92 to 107u. Half-lives of Tc range from 5 seconds for $^{102}$Tc to $2.6 \times 10^6$ years for $^{97}$Tc. Natural technetium, $^{99}$Tc, is formed from spontaneous fission of U and has a half-life of $2.12 \times 10^5$ years, decaying to $^{99}$Ru through β emission. The chemistry of this element is similar to that of Re. It is highly resistant to corrosion and is used as a corrosion inhibitor in steel.

Appreciable quantities of Tc are present in waste products from radiochemical processing plants and from nuclear power
stations and it has been estimated that many kilograms of the element are potentially available (154).

Traditionally $^{99}$Tc is determined using a radiometric counting method. This method of analysis does have problems as $^{99}$Tc is a low energy $\beta$ emitter and requires long counting times, the order of 20 hours, to carry out an analysis. In addition, $^{129}$I which often occurs with $^{99}$Tc, causes interference problems with the counting method and has to be separated from $^{99}$Tc. This is a very time consuming process, which involves using complexing agents to separate $^{99}$Tc from $^{129}$I, which can take up to 1 day to carry out.

6.2.3.3 Standard Solutions and Limits of detection
A solution of $^{99}$Tc with a nominal concentration of 4ng.mL$^{-1}$ was obtained from the National Physical Laboratory, Teddington, Middlesex. The accuracy of the concentration of the $^{99}$Tc was in question because of the problems associated with using radiometric counting methods to determine its concentration.

A limit of detection (3σ) of 6pg.mL$^{-1}$ was obtained from 12 one minute replicate blank acquisitions over a mass range of 98 to 103u, using 512 MCA channels, a dwell time of 1000μs and 120 sweeps across the mass range.

6.2.3.4 Analysis of Environmental Samples
Determination of $^{99}$Tc was carried out on 4 solutions of grass and 1 of seaweed. The samples had originated from within the vicinity of a nuclear
reprocessing plant. All solutions for analysis were in 2MHC1, necessary to stabilise Tc in solution. No Cl based polyatomic ions occur at masses above 80u. The ICP-MS instrument was operated under normal conditions and data was acquired with the same scanning conditions as used for determination of the limits of detection. No isobaric interference from $^{99}$Ru on $^{99}$Tc was detected; if Ru was present in the samples, a peak from $^{101}$Ru (17.1% abundant) would have been observed. A typical spectrum of $^{99}$Tc is shown in Figure 83.

6.2.3.5 Results and Discussion

The results from the analysis of the five samples are shown in Table 27. The levels of three of the samples are above the limit of detection, the levels of the other two (Grasses 1&2) could not be considered significant.

ICP-MS has considerable advantages over conventional methods for the determination of radio decay products. $^{99}$Tc can clearly be determined in the pg.mL$^{-1}$ range with a very short analysis time. Each result presented in Table 27 was obtained from 5 replicate analyses. Thus the total analysis time including standard and blank analysis was about 45 minutes. This compares very favourably with the several hours of counting necessary to determine $^{99}$Tc by radiometric methods. In addition, samples can be directly analysed by ICP-MS, no separation is required to remove species such as $^{129}$I, as they do not pose any interference problems.
Figure 82  Spectrum showing the analysis of 4ng.mL$^{-1}$ of $^{99}$Tc. Peak integral is 6.5x10$^3$.

Table 27

Concentration of $^{99}$Tc in Solutions of Plant Material

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
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</thead>
<tbody>
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<td>Seaweed</td>
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<tr>
<td>Grass 1</td>
<td>0.004 ± 0.002</td>
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<tr>
<td>Grass 2</td>
<td>0.006 ± 0.002</td>
</tr>
<tr>
<td>Grass 3</td>
<td>0.021 ± 0.001</td>
</tr>
<tr>
<td>Grass 4</td>
<td>0.019 ± 0.001</td>
</tr>
</tbody>
</table>

Results in ng.ml$^{-1}$
Error is 1σ
The ease with which decay products such as $^{99}$Tc can be determined by ICP-MS means that the technique is potentially a very useful tool for the nuclear industry.

6.3 Analysis of Slurries

6.3.1 Introduction

Conventional pneumatic nebulisation of sample solutions for plasma spectrometry suffers from a number of disadvantages. The most serious of these are the time consuming and often complex dissolution procedures necessary to produce solutions from solid samples submitted for laboratory analysis. In addition, dissolution may introduce errors, from reagent contamination or volatile analyte loss. Dissolution procedures may require strict codes of safety, or increase the dissolved solids content of the sample, e.g. fusion procedures. The latter is of particular concern in ICP-MS as polyatomic ion interferences may arise from the acid matrix used for dissolution as well as cone blockage or suppression of ion response. Clearly direct analysis of solid samples has several advantages. The aspiration of aqueous suspensions of finely powdered solids, slurry nebulisation, has been shown to be a useful method for introducing solid samples into the injector gas flow of plasmas for emission spectrometry.

Slurry nebulisation has advantages over laser ablation for solid sample introduction in that it is an inexpensive technique and can be calibrated with simple aqueous
standards. Sample introduction is by pneumatic nebulisation, using a Babington type nebuliser with a peristaltic pump in place of a more conventional nebuliser (120, 121).

Apart from this modification, the only other deviation from conventional ICP instrumentation is the use of a 3.0mm injector tube in place of the standard 1.5mm tube. This ensures that the particle size cut off to the plasma is not too small. Good results have been reported for slurry nebulisation ICP-AES from a variety of matrices (122-126) and a detailed review has been given elsewhere (127). The feasibility of using slurry nebulisation for ICP-MS was first reported by Williams et al. (92) and so will not be dealt with in detail here.

Major, minor and trace elements were successfully determined in three certified reference material soils and three industrial catalysts and the values compared with those obtained by slurry and solution nebulisation ICP-AES.

The procedure for introducing slurries into an ICP for mass spectrometry is virtually identical to the one used for optical emission, except that the level of suspended solids must be kept below about 1g in 100mL, as levels exceeding this tend to lead to sampling cone blockage. This is directly analogous to introducing levels of total dissolved solids above about 1%, which would also lead to cone blockage. ICP-AES does not suffer from this problem; slurries of about 40% can be introduced.
6.3.2 Principles

The preparation of slurries has been described elsewhere (92, 127). Essentially, powders of the samples in question (approx. 1g) are shaken in plastic bottles (30mL) with zirconia beads and 2mL of a dispersing agent (tetrasodium pyrophosphate in this case) on a laboratory shaker, over a period of time, usually greater than 2 hours. This is sufficient to reduce the particle size of the material to <8μm. Obviously the hardness of the material will be an important factor in considering the length of time for sample grinding and determine the final sample particle size. This method of sample preparation does have some drawbacks. The determination of Zr and Hf is not possible, because of contamination from the zirconia beads, not only from Zr and Hf but also Pb and Th. In addition, interference from species such as ZrO and HfO make the determination of elements such as Ag difficult. Contamination also arises from the dispersing agent used. Figure 83 shows a blank spectrum (90-240u) for the dispersing agent after shaking for 18 hours with zirconia beads. The dispersing agent used in these studies gives rise to polyatomic ions of P (31P16O+ and 31P16OH+), which could interfere with Ti determination, however other isotopes are available for Ti determination. Dispersing agents that form polyatomic ions which do not interfere with isotopes of interest would be more suitable.

Reducing the particle size <8μm ensures that the particles behave in a manner analogous to aerosol droplets in the spray chamber and ICP, thus allowing calibration to be
Figure 83 Part of a spectrum from the analysis of zirconia bead grinding blank.
carried out with simple aqueous standards, with the dispersant in solution the only form of matrix matching.

This work showed very good agreement between slurry nebulisation ICP-MS, ICP-AES and the certified values for the soil samples and between the slurry techniques and solution ICP-AES. In addition, semi-quantitative determinations of the rare earth elements in one of the certified soils showed results that were all within an order of magnitude of previously reported values; some were accurate to within about 5% of previously reported values.

As slurry nebulisation is preferable where dissolution of the sample in question is difficult or complex, it would seem an ideal method of sample introduction for the determination of ceramic materials. Fusion dissolution methods are usually required as these compounds are extremely difficult to dissolve.

6.3.3 Analysis of Ceramic Materials

Four ceramic materials (supplied by MoD), TiO₂, Nb₂O₅, BN and ZrO₂, were analysed to determine their minor and trace element composition by slurry nebulisation. The PlasmaQuad was used for the analysis and was modified in the same manner as described above. In place of the PTFE Babington type nebuliser, used previously, a De Galan high solids nebuliser was used. The gas orifice diameter of this type of V-groove nebuliser is made to customers requirements. The one used here had an orifice diameter that had the same gas
flow for a given nebuliser pressure as the cross flow nebuliser supplied as standard with the instrument. All instrument parameters were as previously described (92). Samples were prepared as 1g/100mL suspensions, but were analysed as 0.1g/100mL suspensions to avoid the possibility of cone blockage.

Semi-quantitative analysis was carried out, as the samples were very poorly characterised. This type of analysis is a good method of assessing the elemental content of samples with a completely unknown composition and it offers an approximation of their concentration.

6.3.4 Results and Discussion

Table 28 shows the results of the analysis of the four ceramic materials. Only elements with a concentration of >10ng.mL\(^{-1}\) in the suspension (i.e. at 0.1g/100mL) are included, equivalent to 10μg.g\(^{-1}\) in the solid material, given that the accuracy that can be obtained by semi-quantitative analysis is between about 1% and 60%. It appears that the ceramics have relatively few elemental contaminants, although the samples were analysed with a dilution of 1000, which may be too great for elements at ultra-trace level. The raw data obtained from this analysis has to be treated with some care. Figure 84 shows the spectrum from the analysis of TiO\(_2\), where peaks from TiO\(^+\) (62-66 u) and Ti\(^{2+}\) (24 & 25 u) can clearly be seen. This makes the determination of Cu impossible and the determination of Mg and Zn would have to be carried out
Figure 84  Part of a spectrum from the analysis of TiO$_2$ by slurry nebulisation. 
Full scale is 6.4x10$^4$ c.s$^{-1}$

Table 28
Results from Semi-Quantitative Analysis of 4 Ceramic Materials by Slurry Nebulisation ICP-MS

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<th>K</th>
<th>Ca</th>
<th>Cr</th>
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<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Values in µg.g$^{-1}$  ND, Not Detected

206
Figure 85  Part of a spectrum from the analysis of \( \text{Nb}_2\text{O}_5 \) by slurry nebulisation. Full scale is \( 6.4 \times 10^4 \text{c.s}^{-1} \).

Figure 86  Spectrum of Pb and Th from the analysis of \( \text{Nb}_2\text{O}_5 \) by slurry nebulisation. Note the enriched \( ^{206}\text{Pb} \) isotope. Full scale is \( 640\text{c.s}^{-1} \).
using minor isotopes, assuming more exotic interference ions do not exist.

Figure 85 shows sections from the spectrum obtained from the analysis of Nb₂O₅ by slurry nebulisation. Peaks at masses 109 and 110, from NbO⁺ and NbOH⁺ would interfere with isotopes of Ag, Pd and Cd. Fortunately other isotopes clear of interferences are available for determination of these elements. NbO₂⁺ (125 u) is present, but causes no serious interference. However this might not be the case with some other ceramic materials. Figure 86 shows the region of the spectrum occupied by Pb and clearly shows that ²⁰⁶Pb is enriched with approximately the same abundance as ²⁰⁸Pb. ²⁰⁶Pb is a radiodecay product of Th, which can also be seen in this spectrum. This type of information may be very important to the final users of the Nb₂O₅. Few other techniques could have obtained this kind of information so rapidly and with a minimum of sample preparation.

Boron has only two isotopes (12 and 11 u) which can form a very limited number of interference ions. However the interferences that are formed in the analysis of BN, from combinations of B, H, N and O, preclude the determination of Al, K and Mg. The BN ceramic sample appears to be the most impure of all the ceramic samples, as the results show. Both first row transition elements and some rare earth elements are present. Figure 87 shows sections of the BN spectrum, illustrating the presence of elements from masses 50-70 and 120-175 u.
Figure 87 Part of a spectrum from the analysis of BN by slurry nebulisation. Full scale is $6.4 \times 10^3$. 
The analysis of the ZrO₂ sample suffers from the most serious interference problems. Zr has 5 isotopes and the occurrence of ZrH⁺ ions stretch the effective Zr spectrum from 90 to 97 u, shown in Figure 88, which makes the determination of Mo difficult and Nb impossible. Interference from ZrO⁺ and ZrOH⁺ species covers the mass range from 106 to 113 u, which obscures most of the major isotopes of Pd and Cd and both the isotopes of Ag. Dioxides of Zr also occur and can be seen from 122 to 128 u in Figure 88. These ions would make Te determination difficult and I impossible. Doubly charged ions of Zr occur at masses 45-48 u, obscuring monoisotopic ⁴³Sc and some of the isotopes of Ti (also minor Ca isotopes) as shown in Figure 89.

6.3.5 Conclusion

Although ICP-MS of these ceramics is by no means conclusive, due to the lack of certified values, they do highlight some of the advantages and disadvantages of this method of sample introduction and the difficulty of analysing ceramic materials. Clearly, useful analysis of these materials can be carried out with minimal sample preparation, but this is overshadowed by some severe spectral interferences. It would appear that complete dissociation of the ceramic molecule does not occur in the plasma, indicated by the presence of oxide and dioxide species in the spectrum. Investigations of different plasma operating conditions, along the lines of those described in chapter 5,
Figure 88 Part of a spectrum from the analysis of ZrO₂ by slurry nebulisation showing Zr⁺, ZrH⁺, ZrO⁺ and ZrO₂⁺ and Hf⁺ and HfO⁺. Full scale is 64 x 10³.

Figure 89 As Figure 88, but showing the doubly charged zirconium species.
may produce a set of plasma operating conditions that significantly reduce levels of interference ions for the determination of elemental species in ceramic samples. Analysis of some certified ceramic materials and particle size analysis of ground ceramic slurries would be the obvious next step in ascertaining the complete viability of slurry nebulisation ICP-MS for the analysis of ceramic materials.

6.4 Isotope Ratio Determinations

6.4.1 Introduction

Early work in the U.K. on the development of ICP-MS was directed towards the determination of lead isotope ratios and trace elements as an aid to uranium prospecting (129, 145). Ironically, compared to the work on trace element determinations, there are far fewer reports of isotope ratio investigations carried out on ICP-MS instruments. There have been, however, a range of isotope ratio studies carried out on fundamental aspects (7, 23, 102, 104), nutrition and life sciences (58, 65, 66, 67, 88, 110) and earth sciences (55, 61, 76, 77, 108, 129). One of the most important capabilities of ICP-MS is determining isotope ratios in solution. ICP-MS allows stable isotope labelling studies in nutrition and the life sciences to be carried out. Isotope ratio information can help geologists and geochemists to determine the source or geochemical history of their samples. Isotope dilution can be employed for elemental
analysis by ICP-MS which may give reliable and accurate results, even in complex matrices.

In the measurement of isotope ratios, thermal ionisation mass spectrometry (TIMS) is the accepted method of analysis, because it is capable of exceptional precision (0.01-0.1% RSD). Although the reported precisions of isotope ratios measured by ICP-MS are in the range 0.2-1.0%, it has an advantage in sample throughput; around 10 samples can be analysed in an hour as they are handled in solution form and at atmospheric pressure.

6.4.2 Precision and Accuracy

The precision of isotope ratio measurements is a combination of two uncertainties present in the count rate of each isotope: the first is due to the counting statistics or the total number of ions counted and the second is due to fluctuations in the rate at which ions arrive at the detector. In the first case, electron multipliers have an inherent uncertainty in pulse counting, which amounts to $1/\sqrt{N}$, assuming random counting errors, where $N$ is the total number of counts made during the measurement period. Secondly count-rate fluctuations can be caused by various factors such as nebuliser instability, the condition of the sampling interface, ion optics instability, mass calibrations, discriminator settings, electron instability and rf interference. If this second group of error sources prevail, precision cannot be improved above a certain level, unless the ICP-MS stability is improved. If the counting
statistics error is dominant, with low concentrations of analyte for instance, precision can be improved by increasing the analyte count rate, either by increasing the concentration of the analyte or increasing the integration time of the analysis. There is a lower limit of precision of about 0.2% in ICP-MS, irrespective of integration time on analyte concentration (55, 58, 64, 65, 67, 104). As long as the linear range of the multiplier is not exceeded, or correction is made for the loss of linearity, isotope ratio accuracy does not appear to change with concentration (55, 58, 64, 65, 67).

Better precision is obtained the closer the isotope ratio is to unity. Counting statistics dictate that for two isotopes of the same nominal abundance (1:1), each having an integral of $1 \times 10^6$, a precision of 0.14% should be obtained. Isotopes with a 1:10 abundance ratio, with the major isotope exhibiting an integral of $1 \times 10^6$, would have a theoretical precision of 0.33%. For the same integral, an isotope abundance ratio of 1:50 would have a calculated precision of 0.71%. If the isotope abundance ratio is too large then the linear dynamic range of the multiplier becomes important and dead time corrections are necessary. Continuous and discrete dynode multipliers have been compared in regard to the mass bias produced in uranium isotope ratios (104).

ICP operating conditions, particularly aerosol gas flow rate and forward power (65), as well as ion optics settings, sample uptake rate (55) and the presence of concomitant
elements (58, 65, 67, 104) have all been reported as having an effect on the precision and accuracy of isotope ratios. To correct for isotope ratio inaccuracies, NBS certified standards are commonly used to calibrate instruments (58, 67, 104).

6.4.3 Sample Introduction by Pneumatic Nebulisation

6.4.3.1 Determination of Platinum Isotope Ratios

To assess the accuracy and precision of isotope ratio analysis by ICP-MS using conventional pneumatic nebulisation sample introduction, Pt isotope ratios were determined on the research instrument from a 0.6μg.mL⁻¹ solution of natural Pt. Normal ICP operating conditions were employed, together with 1024 channels, a dwell time of 100us and 600 sweeps set on the MCA and a scan range of 190 to 200 u. 10 replicate analyses were carried out on the Pt solution to allow precision of the analysis to be carried out.

The instrument was operated with the mass spectrometer set up for near baseline resolution between adjacent masses. A typically resolved platinum spectrum is shown in Figure 90. In this spectrum the full width of the ¹⁹⁵Pt peak at the baseline is ≈1.0u. The valley between two adjacent peaks of equal intensity (¹⁹⁴Pt and ¹⁹⁵Pt) is 0.1% of the peak top intensity and the resolution using the 5% valley definition is 1.4M.
Figure 90 Spectrum of Natural Platinum, from a Solution of 0.6µg/ml
6.4.3.2 Platinum Isotope Ratio Results

Table 29 shows the results of the isotope ratio determinations of the Pt solution. Counting statistics show that the precisions achieved on all the ratios are about as good as can be expected for the acquired integrals. This implies that instrument instability problems are not the dominant source of error and that the precision, in this case, is a function of the counting statistics. There is some bias for all isotope ratios, in particular for those ratios involving isotopes of quite different abundances (e.g., 192/195, 0.78%:33.8%). This implies that there is a loss of detector linearity. Applying a dead time correction of 57 ns significantly improves the bias, (Table 30). Some kind of mass bias is still exhibited by 198/195 ratio, probably due to one of the factors already discussed. Although relatively good precision and accuracy is possible on ICP-MS systems, integrals of about $2 \times 10^8$ would be needed to approach the precision of TIMS, if counting statistics were the only source of error.

6.4.4 Sample Introduction by Electrothermal Vaporisation

6.4.4.1 Introduction

Isotope ratio determinations have been reported for samples introduced by several transient techniques, such as gas and liquid chromatography (87, 88), flow injection (25, 51), arc nebulisation (79), laser ablation (49) and electrothermal vaporisation (ETV) (45, 129). The precision of the isotope ratios for these methods is poorer, (1-3%), than for
Table 29

Isotope Ratios of Natural Platinum

Peak Integrals

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Mean 26034 1031349 1055081 810300 248324
Standard Deviation 509 16540 17344 12758 3742
Relative Standard Deviation (%) 1.95 1.60 1.64 1.57 1.51

Isotope Ratios

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<td>0.7686</td>
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<td>0.7684</td>
<td>0.2353</td>
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<tr>
<td></td>
<td>0.0246</td>
<td>0.9765</td>
<td>0.7682</td>
<td>0.2359</td>
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</table>

Mean 0.0247 0.9775 0.7680 0.2354
Standard Deviation 0.0001 0.0015 0.0014 0.0008
Relative Standard Deviation (%) 0.55 0.16 0.18 0.32
Counting Stats (%) 0.63 0.14 0.15 0.22
True Isotope Ratio 0.0231 0.9733 0.7495 0.2139
Error (%) 6.81 0.43 2.47 10.04

218
Table 30
As Table 29, with 57ns Dead Time Correction

<table>
<thead>
<tr>
<th>Peak Integrals</th>
<th>192</th>
<th>194</th>
<th>195</th>
<th>196</th>
<th>198</th>
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</thead>
<tbody>
<tr>
<td>Mean</td>
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<td>1100388</td>
<td>1127574</td>
<td>851654</td>
<td>251943</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>510</td>
<td>18886</td>
<td>19878</td>
<td>14116</td>
<td>3851</td>
</tr>
<tr>
<td>Relative Standard Deviation (%)</td>
<td>1.96</td>
<td>1.72</td>
<td>1.76</td>
<td>1.66</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Isotope Ratios

<table>
<thead>
<tr>
<th>192/195</th>
<th>194/195</th>
<th>196/195</th>
<th>198/195</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.0231</td>
<td>0.9759</td>
<td>0.7553</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.0001</td>
<td>0.0016</td>
<td>0.0015</td>
</tr>
<tr>
<td>Relative Standard Deviation (%)</td>
<td>0.51</td>
<td>0.17</td>
<td>0.20</td>
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<tr>
<td>Counting Stats (%)</td>
<td>0.63</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>True Isotope Ratio</td>
<td>0.0231</td>
<td>0.9733</td>
<td>0.7495</td>
</tr>
<tr>
<td>Error (%)</td>
<td>0.10</td>
<td>0.27</td>
<td>0.78</td>
</tr>
</tbody>
</table>

219
continuous nebulisation of solutions, probably because the sample is not present in the ICP for as long, an important factor in determining the precision obtainable for isotope ratio measurements with transient techniques.

6.4.4.2 Application of Sample Introduction by ETV

Although transient techniques can only offer inferior precision compared to continuous nebulisation, they do have advantages for certain specific applications. Techniques such as laser ablation and electrothermal vaporisation are dry sample introduction methods—samples are introduced into the plasma with no accompanying water, either as vapour or aerosol. This is of considerable benefit in the determination of isotope ratios for elements that normally suffer from water-based polyatomic ion interferences, such as iron. Iron has 4 isotopes, of which $^{56}$Fe is only 0.31% abundant. Of the remaining isotopes $^{54}$Fe and $^{56}$Fe suffer from interference by $^{54}$ArN and $^{56}$ArO polyatomic ions in solution nebulisation, as can be seen in Figure 91, which also has 10ng.mL$^{-1}$ Mn for comparison. This makes the precise and accurate determination of 54/56 and 57/56 iron isotope ratios very difficult. Typical data for the determination of iron isotope ratios by solution introduction are shown in Table 31. Figure 92 shows the same part of a blank spectrum as Figure 91, but with sample introduction by ETV.

The precise and accurate determination of iron isotope ratios will be important to many fields of research.
Figure 91 Spectrum of 10ng.ml⁻¹ Mn for Comparison against ArN (54u) and ArO (56u). 10 second integration time. Nebulised solution.

Figure 92 ETV Rod Blank spectrum. 5 second vaporisation with a 10 second integration.
### Table 31

<table>
<thead>
<tr>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Relative Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11653</td>
<td>781.7</td>
<td>6.709</td>
</tr>
<tr>
<td>205905</td>
<td>7224.6</td>
<td>3.509</td>
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<td>5676</td>
<td>207.7</td>
<td>3.660</td>
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<table>
<thead>
<tr>
<th>Peak Integrals</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
</tr>
<tr>
<td>11079</td>
</tr>
<tr>
<td>12395</td>
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<tr>
<td>13123</td>
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<td>12415</td>
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<td>12118</td>
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<td>11261</td>
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<td>10804</td>
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<table>
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<th>Isotope Ratios</th>
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</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>0.06046</td>
</tr>
<tr>
<td>0.06205</td>
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<tr>
<td>0.05920</td>
</tr>
<tr>
<td>0.05652</td>
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<td>0.05454</td>
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</tr>
<tr>
<td>0.05243</td>
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<tr>
<td>0.05297</td>
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</table>

<table>
<thead>
<tr>
<th>Mean</th>
<th>0.05659</th>
<th>0.02757</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Deviation</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>Relative Standard Deviation (%)</td>
<td>5.688</td>
<td>2.253</td>
</tr>
<tr>
<td>Counting Stats (%)</td>
<td>0.486</td>
<td>0.618</td>
</tr>
<tr>
<td>True Isotope Ratio</td>
<td>0.06359</td>
<td>0.02393</td>
</tr>
<tr>
<td>Error (%)</td>
<td>11.00</td>
<td>-15.22</td>
</tr>
</tbody>
</table>
including tracer studies in bio-medical, environmental and industrial subjects and trace element determinations by isotope dilution.

Sample introduction using ETV has several other advantages, applicable to many other elemental determinations, not just iron. Only small sample volumes, typically 5-15uL can be introduced; in cases where only a very small volume is available of a sample with elements at trace or ultra-trace level introduction by ETV is ideal. Samples that are in an organic matrix, where the matrix may cause interference of the elements of interest, can be more readily analysed; by using the drying and ashing steps of the ETV unit, the matrix can be 'burnt off', so that analysis is only carried out on the elemental material. The feasibility of ETV introduction for the determination of isotope ratios of natural and isotope enriched iron samples is described.

6.4.4.3 Experimental
The research instrument was used for these investigations as it offers greater flexibility for this type of development work. The nebuliser spray chamber arrangement was replaced by a tube connecting the ICP torch injector tube to the outlet of the ETV unit. Figure 93 shows a schematic of the system arrangement. The flow rates shown were found to give maximum signal. The total injector Ar flow closely coincides with the flow rate found to give maximum elemental ion response for minimal interference ion levels. Figure 94 shows the complete system and Table 32
Figure 93  Schematic Diagram of Electrothermal System

Figure 94  Research ICP-MS instrument, with Electrothermal System in foreground.
Table 32

Operating Parameters for Isotope Ratio Analysis of Iron by ETV-ICP-MS

Plasma

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Plasma Power</td>
<td>1200W</td>
</tr>
<tr>
<td>Reflected Power</td>
<td>&lt;50W</td>
</tr>
<tr>
<td>Coolant Argon Flow</td>
<td>12 L min⁻¹</td>
</tr>
<tr>
<td>Auxiliary Flow</td>
<td>1.0 L min⁻¹</td>
</tr>
<tr>
<td>Carrier Flow: Through ETV</td>
<td>0.5 L min⁻¹</td>
</tr>
<tr>
<td>Add-In</td>
<td>0.2 L min⁻¹</td>
</tr>
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</table>

Mass Spectrometer and MCA

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan Range</td>
<td>53 - 59 u</td>
</tr>
<tr>
<td>No. of Channels</td>
<td>1024</td>
</tr>
<tr>
<td>No. of Sweeps</td>
<td>100</td>
</tr>
<tr>
<td>Dwell Time</td>
<td>100 µs</td>
</tr>
</tbody>
</table>

ETV Cycle

<table>
<thead>
<tr>
<th>Step</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>25 s</td>
</tr>
<tr>
<td>Ash</td>
<td>0 s</td>
</tr>
<tr>
<td>Vaporise</td>
<td>5 s</td>
</tr>
</tbody>
</table>

MCA data acquisition begins at start of Vaporise Step
summarises all instrument conditions. The ETV unit was a graphite rod system (Baird Atomic) originally developed for atomic absorption spectrometry but modified for use with an ICP by placing the rod assembly into a specially designed bell jar (45, 129, 131). The manufacturers standard 8uL cavity cup-type graphite rod was used. The ICP-MS system (ion optics, plasma-sampling cone alignment) was optimised for a dry aerosol by first monitoring the signal for $^{12}\text{C}^+$ (which could easily be generated from a blank firing of the ETV but was also present as a CO$_2$ impurity in the argon) then fine tuning the ion optics using the signal for $^{114}\text{Cd}^+$, which was volatilised slowly off the rod. Solution aliquots (5μl) added to the rod from a pipette were dried at low power before vaporisation. For the feasibility study no ashing step was used, although if for example, an organic matrix was present, the ashing step could be used to remove the matrix. In the absence of a system for measuring rod temperature, the applied voltage settings for drying (and ashing) was determined by trial and error. The optimum vaporisation temperature was determined from repetitive iron sample vaporisation, each at a higher rod voltage setting. Figure 95 shows signal response at 56u for a series of rod voltage settings. The loss of signal at higher rod voltages (and temperature) is probably a result of excessive injector flow disruption, the result of expanding Ar in the bell jar (from heating by the rod) causing the gas flow rate through the injector and plasma to be increased at the critical time when the analyte ions are entering the plasma. As has
Figure 95 Signal Response of $^{56}$Fe against Increasing Rod Voltage

Figure 96 Single ion Monitor at 56u. The Solvent (Water) driven off is Reflected by the ArO Response during the 30s drying. Vaporisation (Vap.) takes place for 5 secs. and Integration (Integ.) is for 10 secs.
already been shown, an injector gas flow rate that is too high (or low) significantly reduces signal response. Low signal response at lower rod voltages is the result of insufficient sample vaporisation from the rod.

Initially the multichannel analyser was set up to integrate over a 30 second period (1024 channels, 100μs dwell, 300 sweeps). This setting was found to give Fe isotope ratios with poor precision and accuracy. A single ion monitor at 56u (1 sec. dwell) over the whole of the drying and vaporisation cycle, shown in Figure 96, revealed that all the sample passed through the plasma within 10 seconds of the start of vaporisation, after this period of time background signal began to appear. Reducing the MCA integration period to only 10 seconds (100 sweeps) acquired all the elemental signal response but rejected the background signal.

6.4.4.4 Results and Discussion

Table 33 shows the details of the iron solutions that were analysed, Fe of natural abundance and 54Fe enriched. The enriched samples (AERE Harwell) are typical of the type of material used in stable isotope tracer studies and are ideal for assessing the potential of ETV-ICP-MS for ion isotope ratio determinations. Table 34 shows the isotope ratio results for natural Fe. The precision of the individual isotopes is about 20%, which is probably a result of both the manual pipette loading of the carbon rod and the transient signal obtained from the ETV sample introduction.
Table 33
Abundance of Isotopes of Iron in the Standards

<table>
<thead>
<tr>
<th>Fe Isotope</th>
<th>Abundances</th>
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<tr>
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<td>Natural Fe</td>
<td>Enriched</td>
</tr>
<tr>
<td>54</td>
<td>5.80</td>
<td>95.6</td>
</tr>
<tr>
<td>56</td>
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<tr>
<td>57</td>
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<td>0.08</td>
</tr>
<tr>
<td>58</td>
<td>0.31</td>
<td>0.014</td>
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</table>
### Table 34
Natural Fe Isotope Ratios by ETV-ICP-MS

#### Peak Integrals

<table>
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<tr>
<th></th>
<th>54</th>
<th>56</th>
<th>57</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counting Stats %</td>
<td>28246</td>
<td>439324</td>
<td>11968</td>
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<tr>
<td>True Isotope Ratio Error %</td>
<td>27681</td>
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<td>11891</td>
</tr>
<tr>
<td>Mean</td>
<td>33535</td>
<td>520067</td>
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<tr>
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<td>30326</td>
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<td>8133</td>
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<td>35754</td>
<td>549414</td>
<td>15516</td>
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<tr>
<td>Standard Deviation</td>
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<td>378846</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>21551</td>
<td>349739</td>
<td>9900</td>
</tr>
<tr>
<td>Relative Standard Deviation (%)</td>
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<td>75993</td>
<td>2101</td>
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<tr>
<td>Mean</td>
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<td>417757</td>
<td>11646</td>
</tr>
<tr>
<td>Mean</td>
<td>19.56</td>
<td>18.19</td>
<td>18.04</td>
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</table>

#### Isotope Ratios

<table>
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<th>57/56</th>
</tr>
</thead>
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<td>0.0272</td>
</tr>
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</tr>
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<td>0.0276</td>
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<tr>
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</tr>
<tr>
<td>Mean</td>
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<td>0.0282</td>
</tr>
<tr>
<td>Mean</td>
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<td>0.0286</td>
</tr>
<tr>
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<td>0.0283</td>
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<td>0.0004</td>
</tr>
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<td>1.59</td>
</tr>
<tr>
<td>Mean</td>
<td>0.63</td>
<td>0.94</td>
</tr>
<tr>
<td>Mean</td>
<td>0.0632</td>
<td>0.0233</td>
</tr>
<tr>
<td>Mean</td>
<td>0.32</td>
<td>19.50</td>
</tr>
</tbody>
</table>

230
method. This implies that the current ETV-ICP-MS system would not give very accurate elemental determinations. Some form of autosample introduction method, such as those used in current electrothermal atomisation atomic absorption spectrometry would probably improve the precision on individual isotopes. The precision, whilst not as good as those obtained by solution introduction, are acceptable, with 1.5% precision for both ratios.

Although the actual integration time is only 10 seconds, the precision of the isotope ratios is between approximately 1% and 2% for both isotope ratios. These figures can be considered good, particularly when the counting statistics indicate that precisions of about 0.6% for the 54/56 ratio and about 1% for 57/56 ratio are theoretically possible. The poorer accuracy in the latter ratio is most likely a result of the much lower abundance (2.14%) of $^{57}$Fe. Dead time corrections of 50-100ns do not make any improvements in the accuracy of the ratio. Figure 97 shows an ETV-ICP-MS spectrum of natural iron and Figure 98 shows a spectrum of enriched $^{54}$Fe with the results in Table 35. Due to the very limited volume available only 5 replicates were possible. The precision is not as good as with the natural Fe but the accuracy of the 56/54 ratio is good. Unfortunately limited sample volume prevented further investigation, however it is clear from these results and those of the natural iron that ETV-ICP-MS is an acceptable method of determining iron isotope ratios, and is superior to nebulised sample introduction in both precision and accuracy. This method of
Figure 97  Spectrum of 1µg.ml\(^{-1}\) Natural Fe by ETV-ICP-MS. 10 second integration.

Figure 98  As Figure 97 for 54 Enriched Fe at 10ng.ml\(^{-1}\).
Table 35
Isotope Ratio for 54 Enriched Iron by ETV-ICP-MS

<table>
<thead>
<tr>
<th>Peak Integrals</th>
<th>Ratio</th>
<th>56/54</th>
</tr>
</thead>
<tbody>
<tr>
<td>584399</td>
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<td>570589</td>
<td>25395</td>
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<td>487367</td>
<td>22097</td>
<td>0.0453</td>
</tr>
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<td>536451</td>
<td>23144</td>
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</tr>
<tr>
<td>591922</td>
<td>28238</td>
<td>0.0477</td>
</tr>
</tbody>
</table>

Mean 554146 24839 0.0448

Standard Deviation 38432 2121 0.0017

Relative Standard Deviation (%) 6.94 8.54 3.70

Counting Stats % 0.65

True Isotope Ratio 0.0451

Error % -0.62
determining isotope ratios could be applied to other elements with interference problems such as selenium. Some initial studies have indicated that precisions of <5% are possible, although the accuracy is not good (about 15%).

6.4.5 Conclusion
ICP-MS can be applied to a number of problems involving the measurement of isotopic ratios. In order to interpret the data properly careful corrections must be made for the effects of dead time, blank, interferences and mass bias. Severe spectral problems such as those encountered in the determination of Fe isotope ratios may be overcome with alternative methods of sample introduction such as ETV. Although ETV has been already reported as a method of sample introduction for isotope ratio determinations, there are no previous accounts of it being used to solve this particular problem.

In both the investigations reported here the precision is at or close to that predicted by counting statistics. It is unlikely however that significant improvements in precision would be possible as the plasma is a 'noisy' ion source and is probably the ultimate limiting factor for isotope ratio precision.

6.5 Summary
It would appear from these experiments that ICP-MS is an extremely flexible analytical tool, although it does suffer from severe spectroscopic interferences when samples that
contain certain matrices, such as Ni-base alloys, are introduced.

Samples that are highly insoluble, such as ceramic materials, can be introduced as slurries, as long as the suspended solids concentration does not exceed 0.1g/100mL; suspensions in excess of this level can cause sampling cone blockage. Sample preparation is straightforward and calibration can be carried out with simple aqueous standards.

Isotope ratios can be determined to a maximum precision of about 0.1% with sample introduction by pneumatic nebulisation and a precision of approximately 1.5% can be obtained with sample introduction by ETV. This method of sample introduction was found to be particularly useful where polyatomic ion interferences are a problem.
CHAPTER SEVEN
CONCLUSION AND FUTURE WORK
Conclusions and Future Work

The aim of this project was to gain further insight into factors affecting ICP-MS performance and identify methods of removing or controlling these factors and finally to apply this to the analysis of some 'real' samples.

Assessment of basic analytical figures of merit shows that in principle ICP-MS is very well suited to the task of sample analysis for elemental and isotopic determinations. Factors such as very low limits of detection, long linear dynamic range and resolution in excess of unit mass make ICP-MS almost the ideal analytical tool. There are however some potentially serious drawbacks to the technique.

Interference ions are an intrinsic part of the ICP-MS spectrum, but the work reported here shows that in many cases they can be reduced to a minimum and maintained at a given level. The occurrence of polyatomic ions has been shown to be controlled by a number of factors, but most significantly carrier gas flow, water content of the plasma. Use of a WCSC, high precision gas flow regulators and choice of optimum operating conditions both ensures low levels of many of the more serious interferences and maintains them at a fixed level. Analyte oxide ions are more difficult to deal with as particular oxide ions only occur with a given matrix. Although the use of the WCSC goes some way to reducing these ions, operating at the correct carrier gas flow is the most important factor to consider, as it is this that has the most effect on levels of these ions. In the
same way, although far less serious as interferences, the formation of doubly charged ions is seriously affected by the carrier gas flow rate.

The analysis of certain samples can lead to the formation of enough interference ions to make successful elemental determinations almost impossible. This was the case in the analysis of complex Ni-base alloys and proved to be an irresolvable problem for solution analysis.

Although the occurrence of interference ions can be very inconvenient, in most cases they are readily predicted and a correction can be made. Relevant computer programs can help in resolving these problems and one has been written that goes someway to achieving this aim.

Analysis of some 'real' samples showed that the technique can deal with samples introduced as both liquids and solids and also as vapour following external sample vaporisation. The ability of the system to accept solid samples as slurries opens the way for the analysis of 'difficult' samples, such as ceramics, where sample dissolution is complex or impossible.

The successful use of electrothermal vaporisation as a method of sample introduction for the determination of iron isotope ratios shows that potentially impossible interference problems can be overcome using alternative introduction techniques. This method of sample introduction is going to be very useful in areas where sample volume is limited or where matrix modification may be required to
overcome a particular problem. Isotope ratio determinations to a precision of about 0.2% can be achieved with conventional nebulised sample introduction, which although at least an order of magnitude worse than can be achieved by thermal ionisation mass spectrometry (TIMS), is sufficient for many earth and natural science studies. ICP-MS does have a considerable speed of analysis advantage over TIMS as well as a much simpler sample introduction methodology which may be an important experimental consideration.

Two important areas that have not been studied but require significant investigation are sample introduction by laser ablation and fundamental studies into the causes of analyte signal suppression from matrix components.

Laser ablation has considerable potential as a method of solid sample introduction, allowing direct analysis of the unprepared sample and a certain degree of sample profile analysis. The main drawback to this technique is the problem of calibration. Work has begun on determining some of the factors affecting calibration and some promising results have been obtained.

Analyte signal suppression by sample matrix components is a serious shortcoming of ICP-MS and is poorly understood. Several causes of suppression have been identified (53,56) but as yet no real explanations have been put forward. A detailed investigation of the causes of suppression may lead to a satisfactory explanation of the effects and some means of preventing it.
Appendix 1
ISOMASS Listing

REM ****************** ISOMASS Header ******************
KEY OFF: FOR KO = 1 TO 10: KEY KO, "": NEXT
CLS
LOCATE 1, 1: FOR TOP = 1 TO 80: PRINT ";": NEXT
FOR INC = 2 TO 22
LOCATE INC, 1: PRINT "***": LOCATE INC, 78: PRINT "***"
NEXT
LOCATE 23, 1: FOR BOT = 1 TO 80: PRINT ";": NEXT
LOCATE 4, 29: PRINT "M I S O M A S S --""
LOCATE 7, 28: PRINT "ICP-MS Interference Data"
LOCATE 9, 39: PRINT "by"
LOCATE 11, 32: PRINT "John G. Williams"
LOCATE 13, 29: PRINT "Department of Chemistry"
LOCATE 15, 30: PRINT "University of Surrey"
LOCATE 17, 25: PRINT "Guildford Surrey GU2 5XH U.K."
LOCATE 21, 22: PRINT "Copyright (c) John G. Williams 1987"
LOCATE 23, 28: PRINT "Press Return to Continue "
180 R$ = INKEY$: IF R$ = "": THEN 180
IF R$ <> CHR$(13) THEN 180
LOCATE 23, 28: FOR BOT = 1 TO 26: PRINT ";" : NEXT
FOR CLR = 4 TO 22: LOCATE CLR, 22: PRINT SPC(40);: NEXT
REM **** set up printer defaults and dimension arrays ****
FF$ = CHR$(12)
LF$ = CHR$(10)
UL1$ = CHR$(27)
UL2$ = "-
UL3$ = CHR$(1)
UL4$ = CHR$(0)
DIM MA(400), EL$(400), AB(400), ISS(20), MN(20)
DIM IA(20), DC(20), IM(20), ESS(20), EM(20), EA(20)
LOCATE 12, 23: PRINT "Loading Data Base, please wait"
OPEN "ELEMENT.DAT" FOR INPUT AS £1
FOR I = 1 TO 285
INPUT £1, MA(I), EL$(I), AB(I)
NEXT I
CLOSE
CLS
M = I - 1
410 CLS
REM **** opening page ****
PRINT "**************************************************************************
ICP-MS INTERFERENCE DATA
**************************************************************************"
PRINT PRINT " (1) ISOTOPIC ABUNDANCES FOR A GIVEN ELEMENT (SCREEN DISPLAY)"
PRINT PRINT " (2) ISOTOPIC SPECIES FOR GIVEN MASS NUMBERS (PRINTER OR SCREEN DISPLAY)"
241
PRINT " (3) MASS NUMBERS FOR ISOTOPES, MO, MOH, M2+, MH, MO2, MO2H"
PRINT " AND MAr FOR AN ELEMENT (PRINTER DISPLAY)"
PRINT " (4) SPECIES M, MO, MOH, MH, MO2, MO2H, MAr AND M2+"
PRINT " FOR A GIVEN MASS NUMBER (PRINTER DISPLAY)"
PRINT " (5) MASS RANGE SEARCH (PRINTER DISPLAY)"
PRINT : PRINT : PRINT
PRINT " (0) END"
PRINT PRINT PRINT PRINT
PRINT " INPUT REQUIRED ROUTINE "
PRINT PRINT PRINT
"***********************************************************************
***********************************************************************"
REM **** options ****
510 CH$ = INKEY$
  IF CH$ = "1" THEN CLS : GOTO 590
  IF CH$ = "2" THEN GOTO 870
  IF CH$ = "3" THEN CLS : GOTO 1190
  IF CH$ = "4" THEN GOTO 1520
  IF CH$ = "5" THEN GOTO 3190
  IF CH$ = "0" THEN GOTO 3320
  IF CH$ <> "0" THEN GOTO 510
REM **** first option ****
590 J = 0
  INPUT "SYMBOL FOR ELEMENT OF INTEREST "; SY$
  GOSUB 3610
  FOR I = 1 TO M: IF EL$(I) = SY$ THEN GOTO 620
  NEXT I
  CLS : PRINT "THIS ELEMENT IS NOT KNOWN": GOTO 590
620 T = 0
  MX = 0
  FOR I = 1 TO M
    IF EL$(I) = SY$ THEN GOTO 670
  GOTO 710
670 J = J + 1
  IS$(J) = EL$(I): MN(J) = MA(I): IA(J) = AB(I)
  T = T + IA(J)
  IF IA(J) > MX THEN MX = IA(J)
710 NEXT I
K = J
REM ***** Printout Mass Table *****
CLS
PRINT " ISOTOPIC ABUNDANCES FOR "; SY$
PRINT : PRINT
PRINT "MASS"; TAB(14); "ISOTOPE"; TAB(30); "ABUNDANCE": PRINT
FOR J = 1 TO K
242
IF IA(J) = MX THEN IS$(J) = IS$(J) + " *"
PRINT MN(J); TAB(17); IS$(J); TAB(30); IA(J)
NEXT J
PRINT : PRINT TAB(19); "* = ISOTOPE OF GREATEST ABUNDANCE"
PRINT : PRINT "ANOTHER ELEMENT....Y/N"
830 RS = INKEYS
IF RS = "N" OR RS = "n" THEN GOTO 410
IF RS = "Y" OR RS = "y" THEN CLS : GOTO 590
GOTO 830
REM **** Mass Search ****
870 CLS
PRINT "(1) MASS SEARCH (PRINTER DISPLAY)"
PRINT : PRINT "(2) MASS NUMBER (SCREEN DISPLAY)"
PRINT : PRINT "INPUT ROUTINE REQUIRED"
REM **** Screen or Printer Display ****
890 RS = INKEYS
IF RS = "1" THEN 3330
IF RS = "2" THEN 930
GOTO 890
930 CLS : J = 0: INPUT "MASS NUMBER DESIRED "? MD
IF MD < 1 OR MD > 238 THEN 1130
GOSUB 970: IF J = 0 THEN 1130
GOTO 1060
970 K = 0: J = 0
FOR I = 1 TO M
   IF MD = MA(I) THEN 1010
GOTO 1030
1010 J = J + 1
   IS$(J) = EL$(I): IA(J) = AB(I)
1030 NEXT I
K = J
RETURN
1060 CLS
PRINT
PRINT "ISOTOPIC SPECIES FOR MASS NUMBER "; MD
PRINT : PRINT " MASS"; TAB(15); "ISOTOPE"; TAB(28);
"ABUNDANCE"
PRINT
FOR J = 1 TO K
   PRINT MD; TAB(17); IS$(J); TAB(30); IA(J)
NEXT J
GOTO 1140
1130 PRINT
PRINT "NO NATURAL ISOTOPE AT THIS MASS NUMBER"
1140 PRINT : PRINT "ANOTHER MASS NUMBER....Y/N"
1150 RS = INKEYS
   IF RS = "N" OR RS = "n" THEN 410
   IF RS = "Y" OR RS = "y" THEN 930
GOTO 1150
1190 J = 0
REM **** Interference Table for an Element ****

INPUT "SYMBOL FOR ELEMENT OF INTEREST "; SY$ 
GOSUB 3610: NA$ = SY$ 
FOR I = 1 TO M: IF EL$(I) = SYS THEN GOTO 1230 
NEXT I:CLS : PRINT "THIS ELEMENT IS NOT KNOWN": GOTO 1190

1230 K = 0 
MX = 0 
FOR I = 1 TO M 
IF SY$ = EL$(I) THEN 1280 
GOTO 1310
1280 J = J + 1 
IS$(J) = EL$(I): IM(J) = MA(I): IA(J) = AB(I)
IF IA(J) > MX THEN MX = IA(J) 
1310 NEXT I

K = J 
LPRINT UL1$; UL2$; UL3$ 
LPRINT "ISOTOPES..MO..MOH..M2+:FOR "; NA$ 
LPRINT 
G$ = CHR$(9) 
LPRINT "ISOTOPE"; G$; "MASS"; G$; "%"; G$; "MO"; G$; "MASS"; G$; "MOH"; G$; "MASS"; G$; "M2+"; G$; "MASS" 
LPRINT UL1$; UL2$; UL4$ 
FOR J = 1 TO K 
IF IA(J) = MX THEN IS$(J) = "*" + IS$(J) 
DC(J) = INT(10 * IM(J) / 2) / 10 
LPRINT IS$(J); G$; IM(J); G$; IA(J); G$; IS$(J) + "O"; G$; IM(J) + 16; G$; IS$(J) + "OH"; G$; IM(J) + 17; G$; IS$(J) + "2+"; G$; DC(J) 
NEXT J
LPRINT LF$
GOSUB 2970 '**** Check for Hydrides, Dioxides etc. **** 
GOSUB 2730 '**** Check for Argides ****

CLS : PRINT "ANOTHER ELEMENT...Y/N 

1480 R$ = INKEY$ 
IF RS = "N" OR RS = "n" THEN GOTO 410 
IF RS = "Y" OR RS = "y" THEN CLS : GOTO 1190 
GOTO 1480

REM **** Species Occuring at a given Mass Number ****

1520 CLS : J = 0 
INPUT "MASS NUMBER OF INTEREST "; MN : GOSUB 1540: GOTO 2680 
1540 GS = CHR$(9) 
LPRINT UL1$; UL2$; UL3$ 
LPRINT : LPRINT "SPECIES CORRESPONDING TO MASS NUMBER ": MN 
LPRINT 
LPRINT 
LPRINT "MASS (M)"; GS; GS; "SPECIES"; GS; GS; "ISOTOPIC ABUNDANCE (M)"
LPRINT 
LPRINT 
LPRINT

244
REM **** Looking for Elemental Isotopes ****

W = 0
FOR I = 1 TO M
IF MN = MA(I) THEN 1630
GOTO 1650
1630 LPRINT MN; G$; GS; EL$(I); GS; GS; AB(I)
W = W + 1
1650 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT TJL1$; UL2$; UL3$
LPRINT "MO";
LPRINT UL1$; UL2$; UL4$

REM **** Looking for Oxides ****

W = 0
FOR I = 1 TO M
IF (MN - 16) = MA(I) THEN 1740
GOTO 1760
1740 LPRINT MN - 16; G$; GS; EL$(I) + "O"; GS; GS; AB(I)
W = W + 1
1760 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1$; UL2$; UL3$
LPRINT "MOH";
LPRINT UL1$; UL2$; UL4$

REM **** Looking for Hydroxides ****

W = 0
FOR I = 1 TO M
IF (MN - 17) = MA(I) THEN 1850
GOTO 1870
1850 LPRINT MN - 17; G$; GS; EL$(I) + "OH"; GS; GS; AB(I)
W = W + 1
1870 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1$; UL2$; UL3$
LPRINT "MH";
LPRINT UL1$; UL2$; UL4$

REM **** Looking for Hydrides ****

W = 0
FOR I = 1 TO M
IF (MN - 1) = MA(I) THEN 1960
GOTO 1980
1960 LPRINT MN - 1; G$; GS; EL$(I) + "H"; GS; GS; AB(I)
W = W + 1
1980 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1$; UL2$; UL3$
LPRINT "MO2"
REM **** Looking for Dioxides ****

W = 0
FOR I = 1 TO M
IF (MN - 32) = MA(I) THEN 2070
GOTO 2090
2070 LPRINT MN - 32; GS; GS; EL$(I) + "O2"; GS; GS; AB(I)
W = W + 1
2090 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1S; UL2S; UL3S
LPRINT "M02H"
LPRINT UL1S; UL2S; UL4S
REM **** Looking for Peroxides ****

W = 0
FOR I = 1 TO M
IF (MN - 33) = MA(I) THEN 2180
GOTO 2200
2180 LPRINT MN - 33; GS; GS; EL$(I) + "O2H"; GS; GS; AB(I)
W = W + 1
2200 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1S; UL2S; UL3S
LPRINT "MAr (40...99.6%)
LPRINT UL1S; UL2S; UL4S
REM **** Looking for Argides ****

W = 0
FOR I = 1 TO M
IF (MN - 40) = MA(I) THEN 2290
GOTO 2310
2290 LPRINT MN - 40; GS; GS; EL$(I) + "Ar"; GS; GS; AB(I)
W = W + 1
2310 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1S; UL2S; UL3S
LPRINT "MAr (36...0.33%)
LPRINT UL1S; UL2S; UL4S
W = 0
FOR I = 1 TO M
IF (MN - 36) = MA(I) THEN 2400
GOTO 2420
2400 LPRINT MN - 36; GS; GS; EL$(I) + "Ar"; GS; GS; AB(I)
W = W + 1
2420 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1S; UL2S; UL3S
LPRINT "MAr. {  38 .  .  .  0 .  07% )  
LPRINT UL1S; UL2S; UL4S
W = 0
FOR I = 1 TO M
IF (MN - 38) = MA(I) THEN 2510
GOTO 2530
2510 LPRINT UL1S; UL2S; UL4S
GOTO 2530
2510 LPRINT MN - 38; G$; G$; EL$(I) + "Ar"; G$; G$; AB(I)
W = W + 1
2530 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT UL1$; UL2$; UL3$ 
LPRINT "M2+"
LPRINT UL1$; UL2$; UL4$ 
REM **** Looking for Doubly Charged ****

W = 0
FOR I = 1 TO M
IF (MN * 2) = MA(I) THEN 2620
GOTO 2640
2620 LPRINT MN * 2; G$; G$;  EL$(I) + "2+"; G$;  G$;  AB(I)
W = W + 1
2640 NEXT I
IF W = 0 THEN GOSUB 3600
LPRINT FF$
RETURN 
2680 CLS :  PRINT "ANOTHER MASS NUMBER...Y/N"
2690 R$ = INKEY$
IF R$ = "N" OR R$ = "n" THEN GOTO 410
IF R$ = "Y" OR R$ = "y" THEN 1520
GOTO 2690
REM **** Argides for an Element loop ****
2730 J = 0: G$ = CHR$(9)
K = 0
MX = 0
FOR I = 1 TO M
IF NA$ = EL$(I) THEN 2790 1
GOTO 2820
2790 J = J + 1
ES$(J) = EL$(I): EM(J) = MA(I): EA(J) = AB(I)
IF EA(J) > MX THEN MX = EA(J)
2820 NEXT I
K = J
LPRINT UL1$; UL2$; UL3$
LPRINT : LPRINT "ISOTOPES AND MAr FOR "; NAS 
LPRINT
LPRINT "ISOTOPE"; G$; "MASS"; G$; "%"; G$; "MAr"; G$; 
G$; "ARGON MASS (ABUNDANCE)"
LPRINT : LPRINT GS; GS; GS; GS; "36 (0.34)"; GS;
"38 (0.07)"; GS; "40 (99.6)"
LPRINT UL1$; UL2$; UL4$
FOR J = 1 TO K
IF EA(J) = MX THEN ES$(J) = "*" + ES$(J)
LPRINT ES$(J); GS; EM(J); GS; EA(J); GS; ES$(J) + "Ar";
GS; EM(J) + 36; GS; GS; EM(J) + 38; GS; GS; EM(J) + 40
NEXT J
LPRINT : LPRINT : LPRINT "* = PRINCIPAL ISOTOPE"
LPRINT FFS
RETURN

247
REM **** Hydrides, Dioxides etc. for an Element loop ****

2970 J = 0
K = 0
MX = 0
FOR I = 1 TO M
IF N$ = EL$(I) THEN 3030
GOTO 3060
3030 J = J + 1
IS$(J) = EL$(I): IM(J) = MA(I): IA(J) = AB(I)
IF IA(J) > MX THEN MX = IA(J)
3060 NEXT I
K = J
LPRINT UL1$: UL2$: UL3$
LPRINT "ISOTOPES..MH..MO2..MO2H..FOR "; N$
LPRINT
G$ = CHR$(9)
LPRINT "ISOTOPE"; G$; "MASS"; G$; "%"; G$; "MH"; G$
"MASS"; G$; "MO2"; G$; "MASS"; G$; "MO2H"; G$; "MASS"
LPRINT UL1$: UL2$: UL4$
FOR J = 1 TO K
IF IA(J) = MX THEN IS$(J) = "*" + IS$(J)
LPRINT IS$(J); G$; IM(J); G$; IA(J); G$; IS$(J) + "H";
G$; IM(J) + 1; G$; IS$(J) + "O2"; G$; IM(J) + 32; G$
IS$(J) + "02H"; G$; IM(J) + 33
NEXT J
RETURN

REM **** Mass Range Search ***

3190 CLS
INPUT "INITIAL MASS NUMBER OF INTEREST "; IM
PRINT
PRINT : INPUT "FINAL MASS NUMBER OF INTEREST "; FM
G$ = CHR$(9)
FOR K = IM TO FM
MN = K
GOSUB 1540
NEXT K
CLS : PRINT "ANOTHER CYCLE...Y/N"
3280 RS = INKEY$
IF RS = "N" OR RS = "n" THEN GOTO 410
IF RS = "Y" OR RS = "y" THEN GOTO 3190
GOTO 3280

3320 CLS : SYSTEM '**** Return to Operating System ****

REM **** Printout Mass Search ****

3330 CLS : J = 0: G$ = CHR$(9)
INPUT "INITIAL MASS NUMBER OF INTEREST "; IM
PRINT
PRINT : INPUT "FINAL MASS NUMBER OF INTEREST "; FM
IF IM > FM THEN 3330
IF IM = 0 THEN 3330
IF FM = 0 THEN 3330
IF FM > 238 THEN FM = 238
IF R$ = "Y" THEN GOTO 3450
LPRINT UL1$; UL2$; UL3$
LPRINT GS$; GS$; "MASS SEARCH": LPRINT
LPRINT "MASS": GS$; GS$; "ISOTOPE": GS$; GS$; "ABUNDANCE"
LPRINT
LPRINT UL1$; UL2$; UL4$
3450 FOR MD = IM TO FM
FOR MC = 210 TO 231
IF MD = MC THEN 3530
NEXT MC
GOSUB 970
FOR J = 1 TO K
LPRINT MD; GS$; GS$; " "; IS$(J); GS$; GS$; IA(J)
NEXT J
3530 NEXT MD
LPRINT LF$
CLS : PRINT "ANOTHER CYCLE...Y/N"
3560 R$ = INKEY$
IF R$ = "N" OR R$ = "n" THEN LPRINT FF$: GOTO 410
IF R$ = "Y" OR R$ = "y" THEN GOTO 3330
GOTO 3560
3600 LPRINT "SPECIES NOT KNOWN": RETURN
REM **** Check Element Input for Error ****
3610 IF LEN(SY$) = 1 THEN 3720
IF LEN(SY$) > 2 THEN RETURN
ALS$ = LEFT$(SY$, 1): ARS$ = RIGHTS(SY$, 1)
IF ASC(ALS$) > 64 AND ASC(ALS$) < 91 THEN 3670
IF ASC(ALS$) > 96 AND ASC(ALS$) < 123 THEN
ARS$ = CHR$(ASC(ALS$) - 32)
GOTO 3670
END IF
RETURN
3670 IF ASC(ARS$) > 96 AND ASC(ARS$) < 123 THEN 3700
IF ASC(ARS$) > 64 AND ASC(ARS$) < 91 THEN
ARS$ = CHR$(ASC(ARS$) + 32)
GOTO 3700
END IF
RETURN
3700 SYS$ = ALS$ + ARS$
3710 RETURN
3720 IF ASC(SYS$) > 64 AND ASC(SYS$) < 91 THEN 3710
IF ASC(SYS$) > 96 AND ASC(SYS$) < 123 THEN
SYS$ = CHR$(ASC(SYS$) - 32)
GOTO 3710
END IF
RETURN
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