The development and application of inductively coupled plasma mass spectrometry for geochemical analysis

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THE DEVELOPMENT AND APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR GEOCHEMICAL ANALYSIS

by Andrew Neville Eaton

**A thesis submitted for fulfilment of the
requirements for the degree of
Doctor of Philosophy**

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Dedicated to my Father,

Thomas Eaton (1917-1987)

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Abstract

The applicability of the technique of inductively coupled plasma mass spectrometry to the analysis of geological samples was investigated using a variety of sample introduction techniques including: solution nebulisation; slurry nebulisation; flow injection; electrothermal vaporisation; and laser ablation,

Solution sample introduction is limited by the amount of time required to prepare the sample, and the relative intolerance of the technique to high concentrations of sample matrix. The maximum level of dissolved solids for a refractory matrix such as a digested igneous rock was found to be 0.2% w/v. Good accuracy and precision are achievable.

Acceptable results can be obtained using slurry nebulisation. However, standardisation is a problem due to the difference in response for aqueous and slurried analytes. Calibration against aqueous standards and the use of an internal standard is therefore precluded. In addition, the preparation of stable slurries is a highly skilled and time consuming task.

Flow injection analysis offers the most benefit to the geochemical analyst. Flow injection was found to increase sample throughput and, more important, to improve matrix tolerance by a factor of 10x, thus allowing the direct determination of the platinum group elements and gold in geological samples without pretreatment. Small samples, such as fluid inclusion leachates can also be analysed without dilution and the matrix effects experienced when analysing samples containing high salt concentrations can be reduced by careful control of dispersion.

The potential for increased detection limits by electrothermal vaporisation was not proved for geological materials due to the same matrix tolerance problems which limit detection limits in solution work.

Laser ablation sampling allows direct analysis of the solid but quantitation requires matrix matched standards or independent variable internal standardisation, limiting the applicability of the technique for bulk screening. The use of laser ablation to analyse trace element concentrations in individual mineral grains has been investigated and partition coefficients for trace elements, including the rare earths in a large zoned pyroxene crystal, were determined.

Declaration

I declare that this thesis, which I submit for the degree of Doctor of Philosophy at the University of Durham, is my own work and is not substantially the same as any which has previously been submitted for a degree at this or another university.

Andrew N. Eaton

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Finally to my mother Kathleen whose patience has been almost unlimited, especially whilst writing up, and without whose support I could not have continued.

During the early stages of this work, my father died. His love and support were sorely missed but his enthusiasm for this endeavor enabled me to continue. I dedicate this work to him.

Contents

Chapter 1: Introduction, analytical needs, problems in geochemistry and aims.

Chapter 2: The history and technique of ICP-MS

Chapter 3: Solution introduction into ICP-MS

Chapter 4: Slurry nebulisation in ICP-MS

Chapter 5: Flow injection analysis ICP-MS

Chapter 6: Electrothermal Vaporisation into ICP-MS

Chapter 7: Laser ablation ICP-MS

Chapter 8: Conclusions & Future Directions

List of Figures

List of Tables

Chapter 1

Introduction, Analytical Needs, Problems in Geochemistry and Aims

1-1 Introduction

The purpose of this work has been to examine the recently developed analytical technique of inductively coupled plasma mass spectrometry (ICP-MS) in the particular context of its applicability as a tool for use in geochemistry. To this end, the needs of the geochemist have been reviewed and attention concentrated on those areas in which current methods have been found wanting and in which ICP-MS may yield significant improvements, or new capabilities to the geochemist.

1-1.1 Philosophy

As the roots of the word suggest, geochemistry is a multi- disciplinary subject taking as it does a great deal of theory and application from both geology and both pure and applied chemistry. It is perhaps surprising therefore that research in this field is most often carried out by graduates of geology or geochemistry, rather than chemistry. Although not unheard of, the incidence of geochemical research theses by chemistry graduates, such as this work, is small. It is perhaps even rarer that a professional analytical chemist such as this author, rather than a pure or theoretical chemist, should undertake such work.

The contribution made by analytical chemistry to the development of geochemistry has often been overlooked. Geochemists are not alone in underrating the discipline: analytical chemistry plays only a very minor part in most chemistry degree courses, despite being the field in which most chemists are employed. This lack of recognition is remarkable since without the raw analytical data on chemical composition, phase structure etc., there could be no proof nor evolution of geochemical theory. It is only by obtaining as detailed an understanding as possible of the composition of the relevant materials, by using a combination of representative sampling, accurate and precise analysis by an appropriate analytical method, and an understanding of the extent and limitations of the final results, that the chemist or geochemist can begin to examine the processes which governed the situation, to theorise and eventually understand the event.

There is a school of thought, again not restricted to geochemistry, which believes that with the current state of development of computer driven and controlled instrumentation and sample preparation, analytical chemistry is something which can either be learned by flicking through an operators manual, or better still, by getting the technician to do it (since he or she already knows which buttons to press.) This is, however, a very dangerous misconception and one which has led countless otherwise excellent scientists down theoretical blind alleys due to their misinterpretation of analytical data. Woodget and Cooper[1] highlight two contexts in which analytical chemistry can be viewed: the context of the acquisition of the results, and the context of the further use of the results. In the latter case, which is asserted by Woodget and Cooper (op. cit p2) to be the correct one, Analytical Chemistry is "concerned with decisions about the information needed, how it is to be obtained, and about implementing its acquisition in a context determined by the use to which the results are to be put." This means that the analysis is affected as much by the use to which the results are to be put, as the resulting theories are by the analytical results themselves. The analytical part of the work is therefore an integral part of the work, (Fig. 1-1.), and must be given due consideration if maximum benefit is to be achieved. This is not to say that the analysis is an end in itself, far from it, but the analysis must be clearly thought out and appropriate for the work for which the results are required.

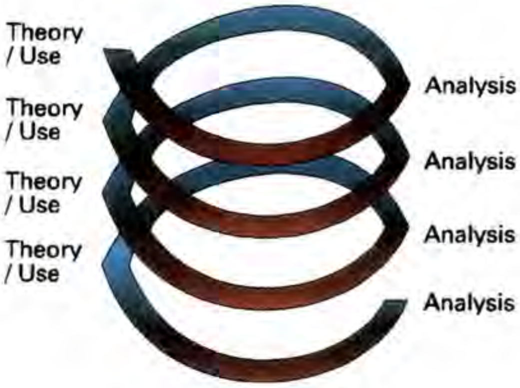

Figure 1-1: Interconnectiveness of analysis and Theory / Usage

It is likely therefore that by viewing problems from what is in essence an analyst's viewpoint, rather than that of a geochemist, a fresh perspective may be achieved. A new way of looking at a problem from a different discipline can often be the "angle" which is used to find the solution. Interfaces between disciplines are often the areas where insight and original work occur because of the new perspective brought by a student of a different discipline.

1-1.2 Analytical needs in Geochemistry

If the technique of ICP-MS is to be used in the field of geochemistry, it will do so not simply because it is a new and interesting subject, but by satisfying a need which is not met by other techniques or methods of analysis. It is therefore necessary to examine the fields of geochemistry, in order to determine what are the specific requirements in an analytical technique for elemental analysis and analytical instrumentation in order to highlight areas of capability and limitation in these fields.

For this purpose, geochemistry related elemental analysis can be divided into applied geochemistry and academic or theoretical geochemistry.

3-1.2.1 Applied Geochemistry

The most important and most widely carried out application of geochemistry lies in mineral exploitation[3]. This involves samples of material from a very large area being analysed in order to identify small areas, termed 'anomalies', where certain elements have significantly higher concentrations than the means of the sample, these often being associated with mineral deposits which have no manifestation which is visible at the surface.

The aim in this type of screening work is to survey as large an area as possible in order to eliminate areas unlikely to yield significant concentrations of useful minerals[4]. It can be seen therefore that there is a need to analyse as many samples as possible for as many elements as possible, in the minimum time, with the minimum of effort.

As time passes, the need to find new mineral sources leads to a lowering in the concentration of a mineral at which it is considered economically viable to extract. This in turn leads to the need for ever increasing resolution of survey sampling, thus an increase in the number of samples to be analysed, and greater sensitivity of the analytical techniques used in the analysis of these samples. All of this requires a continuing trend towards faster, more sensitive analytical techniques with which to analyse the samples.

Raw analytical power and speed are not, however, the only considerations. Rose *et al*[5] define a maximum of four steps which, depending upon the analytical technique used, are necessary in order to analyse geochemical samples:

- Treatment prior to transport and storage.
- Partial or complete decomposition
- Separation of analyte elements from interferences
- Analysis

When considering the applicability of an analytical technique for this type of work, consideration of the three preparative stages can have a significant effect upon the method of choice. If the amount of time and effort involved in these stages is lessened, or indeed eliminated, by using a particular technique, such as the capacity to analyse solid samples directly without dissolution, then that technique can be seen to have significant advantages to the analyst or geochemist.

All analytical techniques are subject to interferences of one form or another. These impose further limitations on the analysis which can be performed, since they restrict the ease and detection limits with which an element can be measured. Any consideration of the choice of analytical technique must take into account the nature and importance of interferences relevant to both the type of analysis and the elements to be determined. Techniques which show few interferences can often be selected above others, purely on these grounds, since the accuracy of the results is paramount to the usefulness of the work.

3-1.2.2 Academic or Theoretical Geochemistry

The academic or theoretical geochemist does not usually have at his disposal the enormous resources of the mining companies with which to undertake large scale surveys, and thus is never likely to have the same requirement in terms of sample throughput.

The nature of geochemistry, however, demands that, in order to gain an understanding of the geology of a particular area, a relatively large number of samples must be analysed. One would be very foolish to base a theory upon a single piece, or limited amount of evidence, and therefore it is necessary for the geochemist to obtain as much information as possible about a study, and this means analysing a statistically valid number of samples.

It can be seen therefore that the choice of analytical technique depends upon the same principles of high sample throughput and minimal sample preparation as are required by mineral exploration surveys.

The requirement for highly sensitive techniques will of course depend upon the nature of the problem under investigation, although it has been argued[6] that new research is often made possible by advances in other fields and thus, by inference, new geochemical research can arise from developments in the field of analytical instrumentation.

It is also felt by this author that academic or theoretical knowledge through research is not an end in itself, but a template which can be applied to real world activities such as, in this instance, mineral prospecting. The techniques and knowledge used in the research lab of today will become the day to day equipment of the applied laboratory of tomorrow. Even seemingly non relevant academic work has often been applied to the practical world, often in very unexpected ways. An illustration of this is the development of high temperature superconductors from the study of the properties of ceramics technology and the chemistry of rare earth element oxides.

One area related more to academic work than applied geochemistry lies in the analysis of localised areas of a sample, often termed feature analysis[7].

In nature, most geological materials are largely heterogeneous. Whilst the applied geochemist may only be interested in the averaged bulk composition of the material, the academic geochemist can learn a tremendous amount from the composition of localised areas, such as individual mineral grains or layers of sediments. This ability has for many years been possible using techniques such as electron and X-ray microprobes, , however, these techniques are limited in terms of their detection capability, and thus restrict this type of analysis to the major abundance elements. Of tremendous benefit to the subject would be the ability to determine the minor and trace elements.

The primary needs in geochemical elemental analysis can therefore be summarised as:

High sample throughput: To allow the geochemist to analyse as many samples as possible.

Reduced sample preparation: To further speed sample throughput, and to minimise possibilities for contamination to occur.

High sensitivity (low minimum determinable concentration): To allow the determination of all trace elements, including those with a low natural crustal abundance. For the purposes of this work, trace levels will be defined as parts per billion (10^{-9}) and below.

Feature Analysis: The ability to determine concentrations of individual areas of a sample

With the general future needs of the geochemist now defined, it is possible to examine the strengths and weakness' of existing elemental analysis techniques, and to compare these to ICP-MS, in order to identify those applications where significant advantage may be obtained from the use of ICP-MS.

1-2 Review of capabilities of Elemental analysis techniques

The geochemist has an enormous, often confusing, range of instruments and techniques at his or her disposal for the chemical analysis of geological materials. The very fact that there are so many indicates that no one technique is ideal for all applications, and that there are significant differences between them in terms of performance and applicability for a given type of analysis.

It is not the purpose of this work to provide a detailed analysis of these techniques, (readers seeking this information should refer to the references section), but merely to highlight the areas where the techniques are strong or weak in comparison to ICP-MS.

The techniques examined are by no means exhaustive, but in the main cover those commonly used by geochemists or geochemical analysts. A brief overview of each technique is given, followed by a more detailed comparison of the relative performance of each technique for those performance characteristics which are felt to be relevant to the geochemist.

1-2.1 X-Ray Fluorescence (XRF)

Essentially a method for solids analysis, XRF has for many years been the standard technique in geochemistry for the determination of major and minor element concentrations with detection limits of the order of 10 parts per million (ppm: 10^{-6}). XRF is capable of determining over 70 elements in matrices such as silicate rocks.

Instrumentation is now highly automated and very stable, allowing fairly infrequent calibration and unattended automation. Sample throughput is approximately 30 samples/hour, and this can be achieved 24 hours a day. The technique is very precise at high concentrations. The surface finish of the sample is important in XRF and thus sample preparation time is lengthy and involves the production of flat briquettes from powders or glass fusion disks.

1-2.2 Electron and X-Ray Microprobe

This technique is a development of the electron microscope whereby, in addition to imaging very small areas of sample, the analyst can also determine elemental concentrations in the same area, to levels of a few hundred ppm. Sample throughput is relatively slow typically 1-2 determinations / hour for 5 elements, (although for this type of feature analysis, throughput is not of primary significance), and samples must be coated with a conducting layer of graphite.

Elemental range is theoretically similar to XRF, but in practice is limited by the analyte concentrations to the major elements.

1-2.3 Spark Source Mass Spectrometry (SSMS)

SSMS is not new, the spark source for mass spectrometry being introduced in 1934[8], although the first commercial instrument from Vick was not available until 1958. Spectra are produced on a photographic plate thus, although sophisticated photometers are now available, data processing still takes an unacceptably long time.

SSMS produces multiply charged species and thus spectra can be very complicated, further increasing data processing time. Although sensitivity is good, typically 1-100 ppm, the range of elements which can be determined is dependent upon the nature of the sample; 70 elements being determinable in simple, monoelemental matrices, but only 40 elements in complex matrices such as silicate rocks[9].

1-2.4 Neutron Activation Analysis (NAA)

NAA is the most commonly used technique for establishing elemental concentrations of both geological, and biological, reference materials[10]. It is a somewhat specialised technique in which the sample is exposed to a strong beam of high energy neutrons for a period of time and the emission of characteristic radiation measured using scintillation counting.

Sub ppb detection limits can be achieved for solids or liquids, even in very small samples, although some separation is often required with very heterogeneous materials[11]. Where the emissions from the analyte elements are very similar, such as the lanthanide and actinide series[12], 60 elements can be determined by NAA.

The need for a source of high energy neutrons, effectively requires access to either a nuclear reactor, or cyclotron, or Van de Graff or linear accelerator[13]. This has restricted the availability of this technique. Similarly sample throughput is low due to the amount of time for which the samples must be irradiated, and the length of counting time required for some elements at low concentrations.

1-2.5 Atomic Absorption Spectrometry (AAS)

This is the commonest technique for trace element analysis[14] and can be found in even very small laboratories. It is primarily a solution analysis technique, thus digestion of the geochemical material is required. It is also a single element analysis technique, which severely restricts sample throughput to 20 elements/ hour. Typically 40 elements may be determined by AAS.

There is a variation on this basic instrument, developed over 30 years ago by L'vov[15], which involves replacing the burner and flame with a graphite tube which is resistively heated in a controlled manner. This has the effect of considerably lowering the achievable detection limits by a significant amount making the technique of graphite furnace atomic absorption spectrometry (GFAAS) one of the few techniques able to reach sub parts per billion levels. An analytical cycle with GFAAS, however, takes approximately 8 minutes, and this for the determination of a single element.

Both flame and furnace AAS suffer from a variety of interferences caused by the relatively low atomisation temperature. For GFAAS, this means that the time consuming procedure of standard additions is almost always required.

1-2.6 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Another primarily solution analysis technique, ICP-AES, can have either a scanning monochromator, or a series of detectors at fixed wavelengths to allow simultaneous determination of up to (typically) 20 of the 60 elements which can be determined simultanously by the technique. Such simultaneous instruments have the advantage of being fast, throughput typically being 60 samples per hour for the determination of 20 elements, but are restricting because there is no possibility to use a different line for different samples. Scanning systems have this flexibility but throughput is severely reduced. Detection limits of the order of ppm - 10ppb are achievable in solutions.

1-2.7 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS, although relatively new, (~10 years old), has been adopted by a large number of geochemical laboratories. It is primarily a solution technique capable of determining over 75 elements with manufacturer claimed [16]detection limits in solution, for most of these elements, of <1 part per trillion, (ppt: 10^{-12}).

Sample throughput is slower than that of simultaneous ICP-AES, typically 20 samples per hour for all determinable elements. In addition, because of the nature of the extraction of ions from the plasma into the mass spectrometer, the level of total dissolved solids has to be restricted to typically 0.2% w/v in order to prevent blocking of the sampling interface.

1-3 Performance comparison of instrumental techniques for geochemical applications.

There are a number of critical performance factors which need to be considered:

1-3.1 Detection limits

Whereas instrument manufacturers like to speak generally of detection limits as though they were constant for a particular instrument, they do in fact vary considerably with the nature of the analyte elements and the nature of the sample being analysed. As a starting point, Fig. 2 shows a comparison of detection limit ? ranges (shown as fractions) for the various techniques[17].

This graph shows clearly that XRF, FAAS and ICP-AES are inappropriate for trace and ultratrace level analyses. Of the remaining techniques which could theoretically be used for trace level analysis, ICP-MS is claimed to have the best ultimate detection limits for some elements.

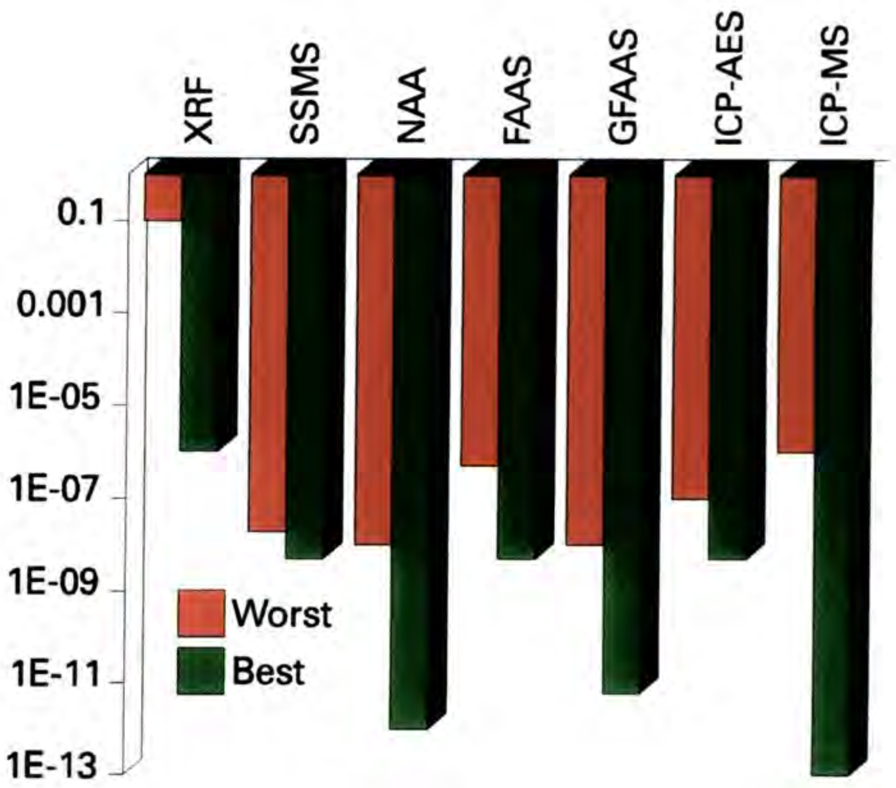

Figure 1-2: Comparison of detection limits acievable for the various techniques

1-3.2 Sample Throughput

Because of the differences between the techniques in the number of determinable elements per analysis, sample throughput must be thought of not just in terms of samples in a given time period, but also in terms of the number of elements determinable in that period. However, since not all geochemical analyses require determination of all elements, Fig. 3 shows sample throughput for analyses of 1, 10, 50 and 75 elements per sample.

The data used to produce Fig. 3 is of necessity very generalised. Sample throughput calculations are further complicated by differences in analysis time due to differing concentrations. For example, XRF instruments can be programmed to measure an element in a sample until a pre-set number of counts have been detected, so that analysis time will vary considerably with concentration of analyte elements, and will of course vary from sample to sample.

It can be seen that ICP-MS is relatively slow compared to the other techniques, only GFAAS and NAA have a lower rate of sample throughput, even when all elements need to be determined in a sample. It should be noted , however, that none of the faster techniques are capable of determining trace elements and thus, for work in this concentration range, ICP-MS offers a significant advantage. GFAAS and NAA are rejected for geochemical work because of their low sample throughput.

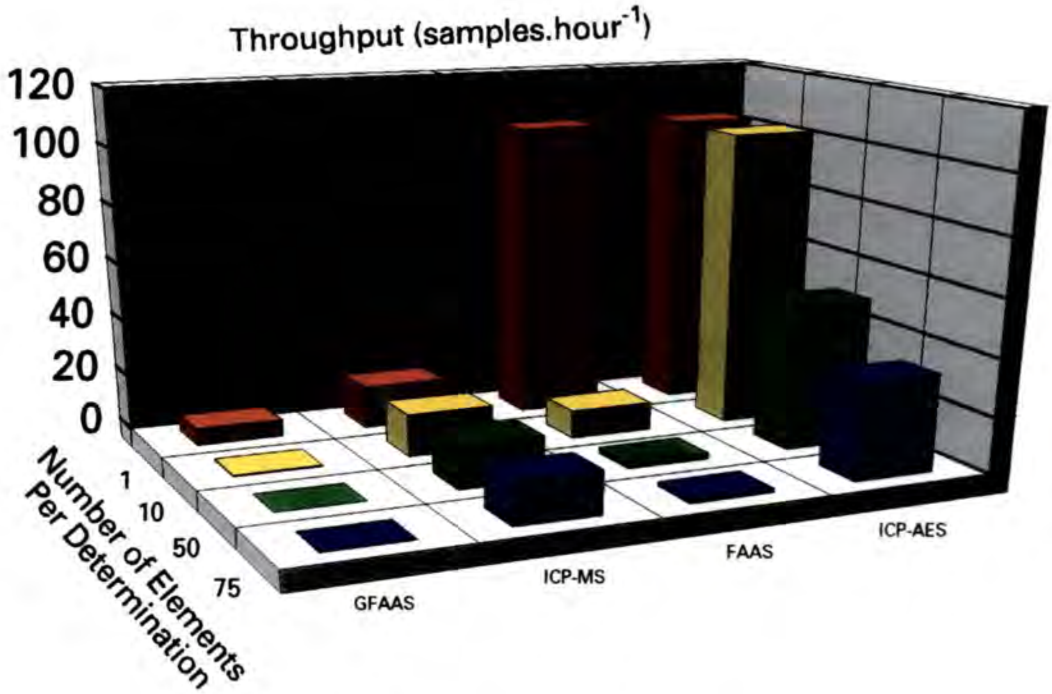

Figure 1-3: Comparison of sample throughput at various numbers of elements determined per sample

1-3.3 Range of Elements

In samples as heterogeneous as geological materials, it is often important to be able to determine as many elements as possible. This is especially true of prospecting surveys where the appearance of an unexpected element can indicate an ore body which, although not the main aim of the survey, can still prove to be commercially profitable. Table 1 shows a comparison of the range of elements for the different techniques. Just as there is variation in the detection limits achievable by each technique, there are considerable differences in the number of elements which can be determined by a technique.

Technique	Range of Elements	
XRF	60	
SSMS	70 (Simple matrix) 40 (Complex Matrix)	
NAA	60	
FAAS	30	limited by the ability to manufacture suitable hollow cathode lamps, e.g. lanthanides, and to the wavelengths accessible to air path monochromators . Primarily suited to the analysis of alkali, alkaline earth and main group transition elements. Very poor sensitivity is achieved for refractory elements.
GFAAS	28	Subject to the same limitations as FAAS, but also restricted to elements which vaporise completely from graphite surfaces at temperatures below 3000ºC.
ICP-AES	20-40 (Sim) 40-50 (Seq)	
ICP-MS	75	

Table 1-1: Comparison of elemental ranges for a variety of techniques

1-4 Aims of this work

From the examination of the needs of geochemists, and the capabilities of the techniques available, the following were identified as being important needs in geochemical analysis:

1. To determine the optimum methods, sample preparation and sample introduction systems for a variety of geochemical analytical problems to give

- High sample throughput
- Reduced sample preparation
- High sensitivity (low minimum determinable concentration)

2. To develop the technique of ICP-MS to meet the requirement for future needs in geochemistry, in particular the ability to determine minor and trace concentrations of individual areas of a sample.

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Chapter 2
The History and Technique of ICP-MS

2-1 Introduction

Despite claims to the contrary by instrument manufacturers, in order to understand the capabilities and limitations of an analytical technique, it is essential to understand how it works. Indeed, only from the possession of such knowledge can sample preparation, instrument conditions and sample introduction be optimised and the results interpreted both intelligently and correctly.

In describing the technique of ICP-MS in the following section, the purpose is not to demonstrate a working knowledge of the instrumentation, but to highlight the important considerations, from the analytical chemist's perspective, which arise from aspects of the instrument design.

Although all of the discussion and work performed relates to the VG PlasmaQuad ICP-MS instrument, which is manufactured by Fisons Instruments/VG Elemental, there are broad similarities between instrumentation from all manufacturers.

2-2 Historical development of ICP-MS

The development of the technique which was to become ICP-MS can be traced, very accurately. Excellent reviews of this history have been published, by

Gray,[1, 2] Houk and Thompson[3], Hall[4], Gray and Date[5], Jarvis, Gray and Houk[6]. The man generally credited with being the inventor of the technique of ICP-MS is Alan L. Gray who in 1970 was working for Applied Research Laboratories, the instrument manufacturer who was responsible for the introduction of the first commercial ICP-AES instrument. According to Date and Gray[7], the need was expressed for new developments in the field of multielement analysis, even though at the time, ICP-AES had not yet reached the marketplace. It was apparent that ICP-AES was going to be prone to severe matrix problems, particularly in the field of geochemistry. The close packed and overlapping emission lines in the spectra from matrix elements such as calcium, aluminium and iron left very few options for the determination of trace elements. In addition, the area of greatest need by mineral prospectors, that of determining the rare heavy elements, showed particularly complex spectra and the poorest detection limits in emission spectrometry.

The then established and emerging techniques, largely the techniques discussed in Chapter 1, were surveyed, but it was concluded that only atomic mass spectrometry had the necessary requirements in terms of elemental coverage, element specificity and relative uniform sensitivity across the Periodic Table to form the basis of the successor to ICP-AES.

Spark source mass spectrometry, at the time the main tool for multielement mass spectrometry, could not however provide either the required sample throughput, the simplicity, or the fast answers which were envisaged requirements. New developments, both in terms of sample introduction and ionisation, and ion collection and output were therefore required.

Largely due to their almost unique capabilities in the field of organic analysis, the development of mass spectrometers, their detection and data systems were the subject of enormous research and development. Gray concentrated on the ion source, the area in which the needs of organic and inorganic analysis differed fundamentally, and which although most challenging, showed most potential for development and was most likely to achieve the desired analytical performance.

Mass spectrometry requires that a sample be admitted into the ion source as a vapour. Whereas this is not a significant problem with organic compounds, the inorganic compounds, particularly geochemical samples, are often refractory and difficult to volatilize. This causes one of the problems experienced with SSMS; the production of incompletely dissociated intermediate molecular fragments, resulting in very complex spectra. The complete initial volatilisation and dissociation of the sample is therefore crucial, after which ionisation would be relatively straightforward.

According to Gray, at a seminar in Manchester in 1970, ion extraction from flames and plasmas at up to atmospheric pressure was discussed. He realised, however, that a chemical flame of up to 3000K was not hot enough because the atmospheric pressure arcs and therefore plasmas which were currently being used in emission were likely to be much more suitable. Furthermore, as temperatures of 5000K were achieved, energy transfer from the plasma was efficient and uniform, and sample introduction from solution became simple and fast. The same connection was also made, although at a much later date, by Alkemade[8], but the identification of a potential new ion source was just the beginning.

Mass spectrometers require a low pressure, both to ensure a long mean free path for the ions and, in quadrupole mass analysers, to prevent arcing between the analyser rods. To transfer ions from an atmospheric plasma to the vacuum environment of the mass analyser (typically 10^{-6}mbar), was a formidable problem.

Previous work on the mass spectrometric analysis of flames had been published by Sugden[9], and suggested a possible approach for a feasibility study performed by Gray and Moruzzi using a small DC plasma. Using an extension of Hayhurst's[5] technique, ions were extracted from the DC plasma using a sampling cone with a 70μm aperture. Behind the cone a 1700L/s diffusion pump gave a pressure of $<10^{-3}$mbar which resulted in a mean free path of >10cm, allowing ions to be focused, through a differential aperture of 2mm diameter, into a further stage which contained a quadrupole mass analyser[10]. This, the first plasma source mass spectrometer system immediately showed the potential for high sensitivity, giving essentially zero background signal between the mass peaks, and signals of between 104 and 105 counts per second for fully ionised monoisotopic elements such as cobalt at a solution concentration of 1μg.ml^{-1} (ppm), using a simple batch type ultrasonic nebulizer[11]. Although acceptable spectra of simple solutions were identified as well as isotope ratio precisions of <0.5%[12], the response was found to be dependent on the total elemental concentrations of the sample solution. Furthermore, matrix effects were too severe to allow real samples to be analysed, and the degree of ionisation for those elements with first order ionisation energies around 9eV, such as As, Se, Cd and Hg, was low, resulting in poor sensitivity for these elements.

Two limitations of the system were identified as the cause of these problems: First, the effective plasma temperature was still too low to ionise some elements adequately; and, secondly, only a small proportion of the introduced solution actually reached the central high temperature core of the plasma[13]. The answer to both of these problems, to replace the DC plasma with the hotter (and concentric) ICP, was seen, not by Gray, but Houk who had by this time set up a parallel programme at Iowa State University, USA. The two groups pooled their work and in 1980 a joint paper[14] was published detailing the extraction of the first analyte ions from an ICP.

At this stage, work was being carried out using small cone apertures which were too small to extract gas from the bulk plasma at the higher temperatures of the ICP, and were thus covered by a boundary layer of cooler gas about 0.5mm thick[15,16]. Attempts to use larger apertures were hampered by melting of the lip of the cone, caused by the high thermal flux, and by the inability of the vacuum system to pump the increased gas load. The melting problem was resolved by increasing the cooling to the sampling cone, and by adopting molecular beam techniques[17,18] which had been successfully used by Douglas and French[19] for the extraction of ions from a microwave induced plasma (MIP). An additional pumping stage was also introduced, driven by a simple rotary pump, behind which a second cone was located in front of the diffusion pumped chamber, and behind the differential aperture; the analyser chamber which was also diffusion pumped.

In 1982, the first bulk sampling of ions from an ICP, using cones of 0.4mm aperture, was performed by Date and Gray[20] and represents the last piece of fundamental research into the basic technique. Development has continued in many areas, and the technique is now used in over 1000 laboratories world-wide, with enormous improvements in sensitivity, performance, sample handling and tolerance having been made; but the quadrupole based instruments are fundamentally little different from 1982.

2-3 The Technique of ICP-MS

Fig. 2-1 shows a generalised scheme of the ICP-MS system which can be subdivided logically into a number of sections.

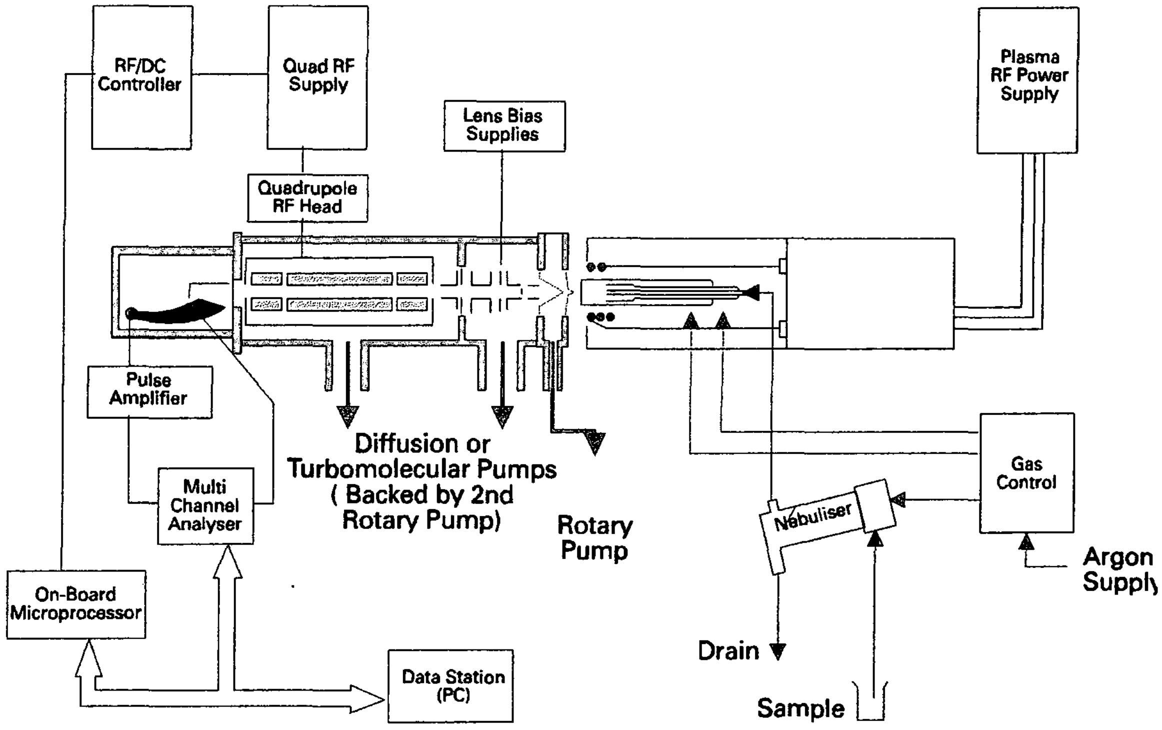

Figure 2-1: Generalised scheme of an ICP-MS instrument

2-3.1 Sample Introduction

To introduce a sample into the ion source, it must be presented in the form of an aerosol, either dry or wet; that is a suspension of small sample particles in a stream of argon gas. (For some applications it is possible to introduce a gaseous sample, but this is outside the scope or requirements of this work.)

In the standard configuration of an ICP-MS, sample introduction takes the form of nebulisation of liquid samples. The details of this and other forms of sample introduction will be discussed in subsequent chapters.

The only components common to all methods of sample introduction relate to the control of a stream of argon gas called the "nebuliser gas", which is used to transport the sample to the plasma ion source. It is important to control precisely the rate of flow of the nebuliser gas, because this is proportional to the amount of sample reaching the source. On the instrument used in this work, and on the many commercial instruments which have become available subsequently, the nebuliser gas is controlled by means of a mass flow controller. Nebuliser gas flow rate was found to vary between, 0.2-1.8l.min^{-1} depending upon the sample introduction device used.

2-3.2 Ion source

The inductively coupled plasma is an electrodeless discharge in a gas at atmospheric pressure. A radio frequency (RF) generator provides the energy which couples by means of a water cooled coil consisting of 2-3 turns of copper. This coil operates as the primary of an RF transformer, the secondary being the discharge itself. Argon is used as the primary plasma gas, despite much work having been done on the use of alternative gases as additions to argon (Choot and Horlick[21], Evans and Ebdon[22,23].) The forward RF power used in most ICP-MS work is approximately 1.3kW, operating with <10W reflected power.

The plasma is generated inside the open end of a quartz construction known as a "torch". The plasma RF generator and torch assemblies are the same as those used in ICP emission systems, and are based on a design known as the "Scott Fassel" torch[24]. A schematic diagram of a plasma torch is shown in Fig. 2-2. The design consists of an outer tube (18mm internal diameter x 100mm long), within which are two concentric tubes of 13mm and 1.5mm i.d. which end 10mm from the torch 'mouth', the latter being termed the "injector" tube. Argon gas is supplied to the two annular regions produced by the tubes from short tangential connecting tubes thus creating vorticular flow. The sample is introduced through the injector central tube.

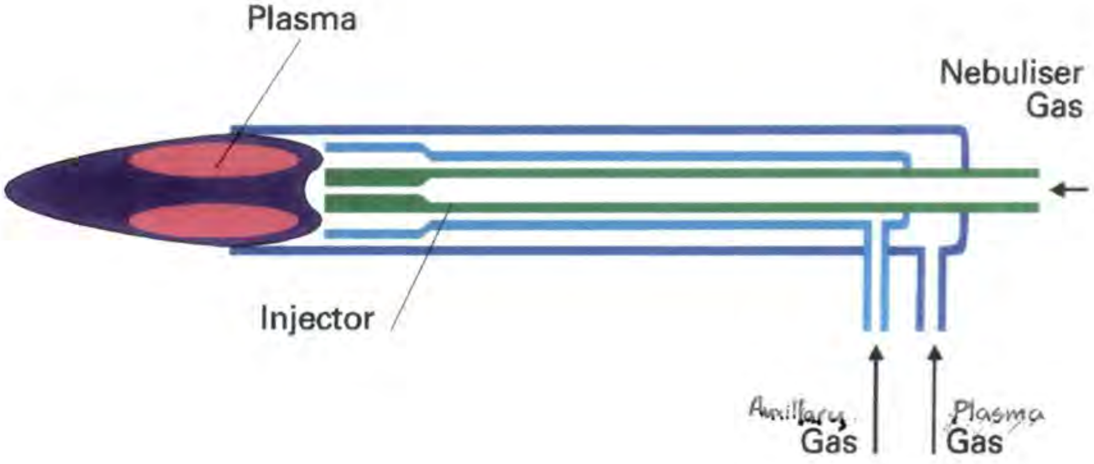

Figure 2-2: Schematic of a Scott Fassel plasma torch

There are three gas flows introduced into the plasma. The outer flow is termed the "plasma gas", or sometimes the "coolant gas", and is the highest flow rate being typically between 10-15l.min^{-1}. This gas flow forms the bulk of the plasma. The next, termed the "auxiliary gas" typically uses 0.5l.min^{-1} and is designed to move the position of the base of the plasma, largely to prevent melting of the injector tube by the plasma. As already discussed, this flow rate depends upon the nature of the sample introduction.

Under these conditions a plasma of 5000K is generated[25]. The effect of the nebuliser gas is to punch a 'hole' in the plasma producing a torroidal plasma in which the sample passes through the central channel. During it's passage through this central channel, the sample is first dehydrated (if in a solution), then atomised and finally ionised in exactly the same manner as in emission spectrometry. No definitive mechanism is acknowledged, although several have been postulated including the Penning ionisation mechanism[26,27], the charge transfer mechanism[28,29] and the recombining plasma model[30]. Using the Saha equation[31], Gray calculated that ionisation was more than 90% complete for most elements and was still at a significant level for the remaining analytically important elements[32]. For this reason he predicted that the ICP would provide an excellent ion source.

2-3.3 Sampling interface

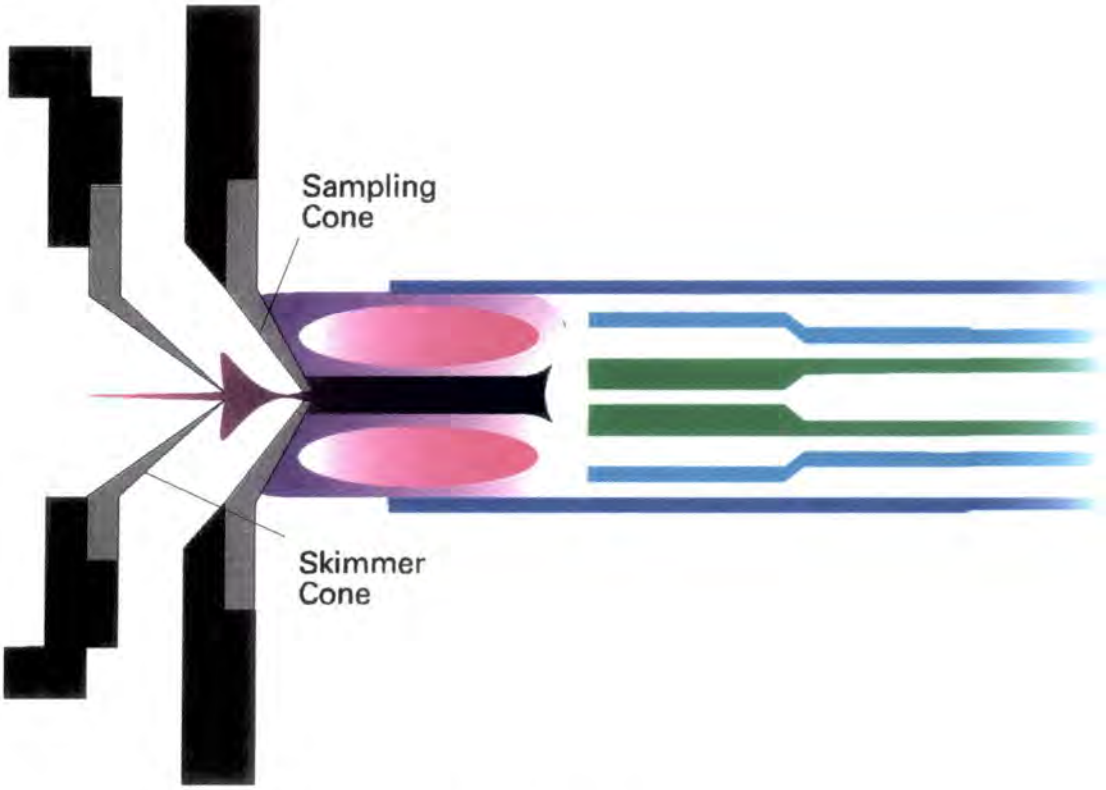

Figure 2-3: Schematic diagram of the ICP-MS sampling interface

The schematic diagram of the ion sampling interface is shown in Fig. 2-3. Extraction of ions from an ICP at atmospheric pressure involves sampling the plasma with a water cooled metal cone; (usually nickel with a 1mm orifice), termed the sampling cone. This sampling cone is positioned so that the bulk of material which passes through the orifice originates from the central channel which in turn contains the ionised sample.

Behind the sampler is a second cone, the skimmer cone, also made of nickel, and with an orifice of between 0.7 and 1.0mm. The area between the two cones, termed the interface region, is evacuated to a pressure of ~1mb by a single rotary pump. A supersonic jet forms as the ions expand into the vacuum[33], the central section of which passes through the skimmer orifice and into an intermediate pressure region of approximately 10^{-4}mb which contains the ion lenses.

An understanding of the behaviour of the interface region is particularly important to the user because it is responsible for some of the sampling limitations of the technique. Many workers in the early development of the technique, including Date and Gray[34,35] and Hutton and Eaton[36,37], have shown that, when aspirating samples with a high level of dissolved solids, material from the sample tends to deposit on the sample cone. This deposit has the effect of blocking the sample orifice thus severely reducing sensitivity. Gray and Williams[38] have demonstrated that the effects of this deposit were related to the strength of the oxide bonds of the elements, the more refractory elements showing the most pronounced effects. This observation has important implications for geological applications where the sample matrix may contain high levels of refractory elements such as silicon, aluminium, iron, barium, calcium and cerium. These influences will be discussed in chapter 3.

2-3.4 Ion Optics

The ion optics are a series of concentric rings to which user adjustable potentials are applied in order to focus the ion beam into the quadrupole mass analyser. Between the lenses there is a differential aperture which separates the interface pressure region from the analyser region which is maintained at a pressure of approximately 10^{-6}mb.

2-3.5 Mass Analyser

The mass analyser used in this work, and in the majority of instruments world-wide, is a quadrupole which gives unit mass resolution. Unfortunately this low resolution instrumentation is not sufficient to resolve interfering polyatomic species which forms an important limitation to the analyst.

In the last few years ICP-MS instruments based on magnetic sector analysers have been developed[39]. As might be expected, these are large, very expensive and require specialist operators, but have the benefit that they are able to resolve some analyte from previously overlapping polyatomic species. Such instruments have found applicability in a number of specialist areas, due largely to their detection limits being typically 3 orders of magnitude better than the quadrupole.

2-3.6 Detector

The detector on an ICP-MS is usually an electron multiplier, although newer instruments using the Faraday detectors have recently appeared on the market. On the instrument used in this research, a channeltron type detector[40] was used. This could be operated in two modes: pulse counting and analogue. This was found necessary because users were finding that the lowering of detection limits meant that the detector was saturating at concentrations above 50-100ppb, the need for which arising from the manufacturers striving towards lower detection limits.

The standard counting mode, which was preferred in the early development of the technique, is excellent for the detection of low levels, but the linear dynamic range of such detectors typically has a ceiling of 10^6cps. At the start of this work, a signal of 10^6cps per ppm for an easily ionised, monoisotopic element was considered acceptable, i.e. the multiplier would begin to saturate at signals for concentrations above 1ppm. By the end of this work, due to improvements in the design of the instrument, countrates of 10^6 cps per 10 ppb had been achieved so that the pulse counting ceiling had been reduced to 1ppb. Whilst the detection limit reduction was necessary, with the exception of high purity acids, there are almost no samples in which elemental concentrations are almost all below a ppb. Another consideration was that at high ion flux rates, the electron multiplier suffers from a short term loss of gain, and an overall shortening of life span. Since these detectors are expensive (~£500), this needs to be avoided.

To counter this, the voltage applied to the detector was reduced typically by 2kV and instead of counting the individual pulses coming from the detector, these are measured in terms of changes in the voltage produced.

By combining the two types of detection, a linear dynamic range of at least 10^8 (nearly 10^9) orders of magnitude is achieved. With software control, and pre-calibration of the two detection systems, the instrument appears to have an uninterrupted dynamic range of 10^8 orders of magnitude.

2-3.7 Data Handling

The way in which the data output of the detector is handled is of crucial importance for certain of the advanced sample introduction techniques, such as electrothermal vaporisation. The VG PlasmaQuad, as used in this work, uses a multi channel analyser (MCA), as a fast data store. The mass range for which data is being acquired is split into a number of steps, such that there are at least 10 data points per atomic mass unit (amu). To average out signal variation, a number of sweeps of the mass range are acquired. These are summed in the MCA and are only downloaded to the data system when acquisition is complete. Since data downloading is the rate determining step, this means that very fast scans of the mass range are possible, allowing short transient signals, such as those produced by electrothermal vaporisation or single shot laser ablation, to be measured.

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Chapter 3

Solution Introduction into ICP-MS

3-1 Introduction

Despite the fact that most geological samples are solids, by far the most common and most important method of sample introduction into ICP-MS is via solution nebulisation; this despite the need to perform often difficult, time consuming and potentially contaminating digestion and dissolution procedures.

As outlined in chapter 2, ICP-MS was originally developed as a technique dedicated to the analysis of solutions, even though subsequent solid sampling introduction methods have been devised. This exactly parallels the development of ICP-AES approximately 10 years earlier and offers the possibility of applying sampling techniques originally developed for ICP-AES to ICP-MS. However, even now, the majority of ICP-MS instruments are still used primarily for solution work[1]. Part of the reason for this is no doubt due both to established tradition and to the greater amount of literature for solution nebulisation that has resulted from this. But it is also significant that also as a matter of tradition and convenience, instrument manufacturers provide solution nebulisation as standard and perform all initial optimisation and troubleshooting in solution mode.

Solution introduction offers a number of advantages over solid sampling. Firstly, most laboratories have always had to perform digestions and therefore have established routines and methods for achieving this. Secondly, unlike solid sampling, it is relatively easy to prepare standard solutions against which to calibrate the samples.

When working with analyte concentrations above trace level, there is a lot of expertise and literature concerning sample and standard preparation. Whilst this can be drawn upon, it must not be assumed to be directly applicable to trace and ultratrace analytes. Even simple factors such as acid purity have been found to have a profound effect on the quality of results[2]. Similarly, there would appear to be, and indeed are, strong similarities between sample and standard preparation for ICP-MS and ICP-AES, but again, experience gained with one does not necessarily relate directly to the other.

The purpose of this chapter is therefore to examine the basics of solution nebulisation from the geochemists point of view, with a view to achieving the objectives outlined in chapter 1.

3-2 Technology of solution nebulisation

Solution nebulisation operates by converting the liquid sample into an aerosol with argon gas, the flow of which carries the sample into the central channel of the plasma. The nebuliser is the most critical part of the system.

Although there are nebulisers which vaporise the sample by means of an ultrasonic transducer[3], the pneumatic nebuliser is by far the most common[4] and operates on the principle of the disruption of a stream of liquid by a flow of argon gas (the "Nebuliser" gas flow), the latter being precisely controlled by means of a mass flow controller. The flow of liquid is produced either by the causing a Bernouili effect[5], as with the "Meinhard" concentric nebuliser[6], or by means of a peristaltic pump. Pumping of the sample solution is used where the nebuliser does not uptake naturally, as with the "Babbington" type 'V-groove' nebuliser[7], or where more control of sample uptake is required. For optimum transport efficiency, the size of droplets reaching the plasma should be <10µm[8]. Pneumatic nebulisers produce a wide variety of droplet sizes thus the larger droplets need to be removed, and this is commonly achieved by means of a "Scott" type spray chamber[9].

Often referred to as a double pass spray chamber, the design forces the aerosol flow to make a 180° turn. The smaller drops pass into the plasma whilst the larger drops impact on the end wall of the chamber and are pumped away to waste. A variety of different spray chamber designs have been developed for ICP-AES, but none have shown any significant advantages over the Scott design.

The spray chamber is usually constructed from glass, although quartz, PTFE and Ryton have also been reported in the literature for specific applications, an example being Allenby's use of a PTFE spray chamber for the analysis of solutions containing a high level of fluoride[10] which would attack glass or quartz, and Paulson's use of a quartz spray chamber for the analysis of concentrated acids[11].

Another important consideration in spray chamber design lies in the use of a water cooled chamber. Hutton and Eaton[12] predicted that a temperature controlled spray chamber would reduce the time required for thermal equilibration of the system to reach steady state and thus give a more stable signal. In addition, refrigerating the spray chamber, typically to 10°C for aqueous solutions, gave a two fold benefit. First, the amount of water vapour reaching the plasma was reduced, giving a reduction in the level of interfering oxide polyatomics (such as the overlap of $^{40}Ar^{16}O^+$ on ^{56}Fe); and secondly, by stabilising the water loading there was an overall improvement in the stability of the system.

3-3 Optimisation

Early work was directed towards the optimisation of ICP-MS systems for solution nebulisation, initially by Gray[13,14], and Date and Gray[15], followed by Horlick *et al*[16]. Much has been published subsequently on the optimisation of ICP-MS systems for solution analysis. For practical information, the instrument manufacturers operating manuals are informative and Jarvis, Gray and Houk[17] provide an excellent discussion on the background and theory of ICP-MS optimisation.

Preliminary work by this author found no deviation from published instrument conditions and optimisation methods recommended , except for certain specialist applications such as the work by Jarvis *et al*[18] on the determination of europium in barite where the presence of a large BaO^+ species completely swamped the much smaller europium isotopes.

3-4 Solution Considerations

The author's previous experience with sample preparation for optical techniques such as ICP-AES, AAS and GFAAS were used as a starting point to this part of the work. In addition to a detailed examination of geological sample preparation and digestion, it was found necessary to examine some basic considerations and limitations to the solution technique in ICP-MS.

3-4.1 Reagent Purity

In addition to the reagents needed to digest the samples, it is also necessary to acidify standard solutions in order to stabilise the metals in solution.

When dealing with detection limits in the sub ppb range, it was found that normal "analytical grade" reagents, such as the BDH "Aristar" range used in most analytical laboratories, were simply not clean enough. Trace element contamination which would be below the detection level of most techniques was found to cause significant problems in low level ICP-MS work. All of the common mineral acids which are used to stabilise the metals in samples and standards as well as normal laboratory grade deionised water were found to be contaminated in this way. Although blank subtraction was tried, the precision of such results were unacceptably compromised.

It was therefore found necessary to use freshly deionised water with a purity of 18MΩ. If left even for a few hours, trace impurities such as sodium and zinc became detectable, presumably leached from the container. Even PTFE and perfluoro acetate (PFA) containers were found to leach out metals unless they had been previously soaked in at least a 10% solution of nitric acid.

The trace element contamination differed according to the type of acid. Since the acids are commercially purified by distillation, those elements which formed volatile species with the acid anion, e.g. CeF_2, $GaCl_2$, tended to be present in the final product. For example hydrofluoric acid, necessary for the acid digestion of silicates, was found to be severely contaminated with lanthanides and silicon, presumably present as SiF_4.

The choice of mineral acids for use with ICP-MS is discussed below, but in general, it was found that, for all acids, only by redistilling the analytical grade reagents in a sub-boiling still as described by Paulsen[19] could the acids be used with any degree of confidence. Later on in the work an alternative was found in the "semiconductor grade" reagents. The nature of semiconductor manufacture is such that even trace impurities can affect the doping of semiconductor wafers[20]. As a result the demand arose for a range of acids and bases certified to have trace element impurities below the detection limits of even ICP-MS. Of the range of those analysed by the author, the best by far were produced by Tama Chemicals, Osaka, Japan and were therefore used for the bulk of this work.

3-4.2 Choice of Mineral Acids

An acid medium is necessary to keep most metals in solution, both prior to and during analysis. Of the common mineral acids available, selection of the most appropriate was based on considerations of the chemistry of the analyte elements, the number of interfering polyatomic species created, and the amount of signal suppression produced.

	Nitric	Hydrochloric	Sulphuric	Phosphoric
Indium signal (cps/ppm)	4,853,003	4,457,429	2943855	878362
% Suppression WRT In	0	8	39	82

Table 3-1: Suppression produced by various acids

10% v/v solutions of nitric, hydrochloric, sulphuric and phosphoric acid were prepared and spiked with 50ppb of indium and analysed using a 60 second full mass scan. A sample of deionised water was also run. A new sampler and skimmer cone were used for each acid in order to examine deposition on, or erosion of, the interface. The integrated counts per second obtained for the indium was converted to the equivalent countrate for a 1 part per million solution. Nitric acid gave the strongest signal and therefore suppression levels were calculated relative to this baseline (Table 3-1). Hydrochloric acid gave some suppression, equivalent to less than 10%. Examination of the cone revealed no detrimental effects. Sulphuric acid produced a significant signal suppression, almost 40%. Examination of the sampler cone revealed no deposit, but significant erosion of the cone material.

Phosphoric acid caused serious problems. A signal suppression of over 80% was observed. Furthermore, after running the phosphoric solution the signal did not return to its original value. Even after aspirating a wash solution, when the nitric acid solution was re-run, the signal remained at around 18% of the original value. Upon removing the sampling and skimmer cones, it was found that both cones were coated with a sticky substance, presumably a phosphate or polyphosphate, necessitating the cleaning of the cone. Once this deposit had been removed, significant erosion of the sampling cone was observed. It is concluded that phosphoric acid is wholly unsuited to liquid analysis by ICP-MS.

Interfering species observed in the spectra of the acids have been reported by many authors, among the first being Horlick et al[21] who reported the presence of a large number of interferences in ICP-MS, largely oxide and other recombinant species. The number of such species reported was considerably higher than were reported by Gray's group[22], it is believed by this author that this was due to differences in the design of the instruments used by the two groups. The Elan, the instrument used by Horlick and manufactured by the Sciex Corporation, used a patented centre tapped load coil. In order to prevent discharging between the coil and the sampling cone, as had been reported by Gray[23], the plasma was sited further away from the sampling cone than in Gray's design, thus ions were sampled from a cooler part of the plasma, allowing greater time for recombination and oxide formation. Although, no doubt for commercial reasons, no direct comparison has ever been published, when the design of the Elan instrument was changed to allow sampling from a distance similar to that used in Gray's original design, the spectra from such instruments showed much less of the oxide species described by Horlick.

Jarvis *et al*[24] provide a very good review of the interferences produced by the common mineral acids. In general, all acids produce molecular interferences, such as for example the presence of $O^{35}Cl^+$, $O^{37}Cl^+$, $Ar^{35}Cl^+$ and $Ar^{37}Cl^+$ in hydrochloric acid spectra which interfere on ^{51}V, ^{53}Cr, ^{75}As and ^{77}Se respectively.

Nitric acid produces fewer interferences than the other acids, only the "classic" ICP-MS interferences of ArN^+ on ^{54}Fe, ArO^+ on ^{56}Fe, $ArOH^+$ on ^{57}Fe and Ar_2^+ on ^{80}Se. These are the same species that are present in a deionised water only spectrum, in which case the nitrogen species presumably arise from entrainment of atmospheric nitrogen into the plasma, or contamination of nitrogen in the gas supply.

Solution chemistry permitting, nitric acid is therefore the preferred acid for stabilising ICP-MS solutions by virtue of it's minimal signal suppression and limited number of interferences which it produces.

3-4.3 Detection Limits

Peak jump dwell per isotope	50,000μS
No. of points per peak	3
DAC step	3
No. of peak jump sweeps	20
No. of isotopes	15

Table 3-2: Detection limit experiment acquisition conditions

The achievable detection limits in solution were determined for a range of elements which generally have a low natural abundance in most rocks[25]. A nitric acid blank was analysed 10 times in peak jumping acquisition mode using the conditions listed in table 3-2. A 10ppb solution of the elements Ru, Rh, Pd, Ag, Cd, In, Sn, Ta, W, Re, Os, Ir, Pt, Au, Hg, and Tl was also analysed under the same conditions and the detection limits for each element calculated using the equation:

$$\text{L.O.D.} = \frac{3 \cdot \sigma_{BLK} \cdot C_{STD}}{X_{STD}}$$

where: **L.O.D.** = limit of detection

σ_{BLK}= standard deviation (n-1) of the 10 blank determinations

C_{STD}= concentration (ppb) of the standard

X_{STD}= signal produced by the standard

This equation is used throughout this work to determine detection limits. The results are shown in table 3-3.

Element	Isotope	Abundance	σ_{BLK}	X_{STD}	LOD (ppb)
Ru	100	12.7	3.88	15,076	0.08
Rh	105	100	4.89	60,702	0.02
Pd	105	22.6	10.93	21,589	0.15
Ag	107	5.35	1,272	65,390	5.84
Cd	111	12.86	8.54	12,504	0.21
In	115	95.84	12.3	138,745	0.03
Sn	118	24.01	13.55	33,531	0.12
Ta	181	99.99	7.71	254,754	0.01
W	182	26.31	2.87	54,464	0.02
Re	185	37.07	4.98	85,258	0.02
Os	189	16.1	4.63	45,481	0.03
Ir	193	61.5	3.17	123,609	0.01
Pt	195	33.7	4.24	39,470	0.03
Au	197	100	68.77	70,167	0.29
Hg	202	29.8	36.33	21,313	0.51
Tl	205	70.5	4.67	162,946	0.01

Table 3-3: Detection limits obtained for solution nebulisation

For the elements selected, detection limits were typically <0.2ppb. The exception to this is silver, caused by an unnaturally high standard deviation of the blank levels. This is likely to have been caused by the use of a chloride matrix, necessary in order to stabilise elements such as rhenium and gold. Some precipitation of silver onto the glassware, as the chloride, is likely to have occurred. This would then be slowly eluted by the 1% nitric acid blank solution used.

3-4.4 Instrument Cleaning

The detection limit experiment highlighted another area in which great care was necessary. Although the manufacturers claim an uninterrupted dynamic range of 10^8 orders of magnitude, in practice it is not possible to determine low levels of an element after a high concentration of that element has been aspirated due to carry over. By cleaning different parts of the sampling system and interface after aspirating a 500ppb solution in 1% v/v HNO_3 of a range of elements, it was found that different elements were retained in different parts of the system, and that the chemistry of the elements and their matrices affected the extent of this retention.

The main area in which elements were found to linger was, not surprisingly, the spray chamber. Washout times, the time taken for an element to return to the background level, for most elements was found to be under 3 minutes. However, one exception to this was mercury which, due to its volatility, never returned to its original 'clean' background level until after the spray chamber had been removed and cleaned. Other elements such as copper, molybdenum, tungsten, silver and gold could be removed, without cleaning the spray chamber, by aspirating a solution of 5% v/v ammonia.

Boron and, to a certain extent, the alkali metals showed a tendency to deposit on the tip of the injector of the plasma torch. This has important implications for the popular use of lithium metaborate fusions, although the low level determination of these elements lay outside the scope of this work.

Osmium was found to be retained on the Teflon sample uptake tubing and the PFA surfaces of the De Galan[26] 'V-groove' type nebuliser.

Although the level (500ppb) was too low to cause deposition on the sampling orifice, the alkali metals, and most particularly sodium, were found to deposit on the back of both the sampler and skimmer cones.

All of the glassware was cleaned by steeping it for several hours in a commercial alkaline detergent such as Decon 90, after which the items were rinsed with deionised water and stored in a solution of 10% v/v nitric acid until required. It was found necessary to keep two sets of glassware so that one could be soaking whilst the other was in use.

Initially sampler and skimmer cones were cleaned by dropping 50µl of concentrated nitric acid into the back of the cone then quickly rinsing it away with deionised water. This procedure, however, was found to reduce the working life of the cones by prematurely enlarging the sampling orifice until vacuum could no longer be maintained. A more suitable alternative involved cleaning the cones with a cloth and an alumina paste such as "Polaris". Excess paste was removed by agitating the cones in an ultrasonic bath; first with deionised water and then with Aristar grade acetone. This procedure left a high aluminium signal but, since this element is present at high levels in geological samples, this was not significant.

3-4.5 Matrix Tolerance

The nature of the ion extraction process from the ICP means that there is a limit to the level of dissolved solids which can be nebulised without blocking the sampling orifice. This is a primary factor in limiting the detection limits which can be achieved with the technique, especially for geological samples, since theoretically, by aspirating a 10x more concentrated solution of sample, a 10x improvement in the detection limit could be achieved. In order to attain the best possible limits of detection it is necessary to determine the optimum matrix level at which as high a matrix concentration as possible is aspirated without causing significant blockage of the cone.

As noted earlier, Gray and Williams[27]proved that such deposition on the sampling cone is directly related to the strength of the matrix element - oxide bond, the more refractory elements tending to form and deposit faster. Since the matrix elements in most geological samples are highly refractory, this was an important consideration for this work.

The manufacturers of the instrument recommend a blanket concentration of 0.5% w/v for refractory matrices. An experiment was devised to determine the matrix tolerance of the instrument for geological materials. This involved the measurement of the percentage recoveries of a number of elements in a standard reference material when introduced at a range of matrix concentrations.

3-4.5.1 Sample Dissolution

~1g amounts of the USGS granite standard G1 were weighed into PFA digestion bombs and 10ml hydrofluoric acid, 2ml nitric acid and 0.5ml perchloric acid added. The bombs were sealed and placed in a 750W microwave oven at full power for 1½ minutes. The samples were then cooled and the heating cycle repeated a further two times. After cooling, the bombs were opened and the solutions evaporated to fumes of perchloric on a hotplate. This was to vaporise the hydrofluoric acid which would otherwise attack both the spray chamber and the plasma torch. A further 5ml of nitric acid and 1ml of perchloric acid were added and evaporated to dryness. 5ml of deionised water and 2ml of nitric acid were added and warmed until all of the solid had dissolved. After cooling the solutions were diluted to give a final concentration of 0.2%, 0.5%, 1% and 1.5% w/v of the original rock. An acid blank was also prepared using the same procedure, but without the sample. These solutions were spiked with indium such that the final concentration was 50ppb. The reported value[28] for indium in G1 is 25.2ng.g^{-1} thus the amount of indium in the solution is insignificant relative to the concentration introduced as the internal standard: the solutions actually contained 50 (blank), 50.05, 50.13, 50.26 and 50.38 ppb of indium respectively.

3-4.5.2 Methodology

Acquisition was performed in peak jumping mode for the elements Co, In, La - Lu and Pb, with a dwell time per point of 512μS, 5 points per peak and 60 sweeps. Calibration was performed relative to the blank and an aqueous 50ppb standard solution of the elements stabilised with 1% nitric acid.

3-4.5.3 Results

The reported values, values obtained and percentage recoveries are shown in Table 3-4.

It can be seen that good agreement with reference values is obtained at 0.2% and 0.5%. At 1% and above, however, there is a tendency for the obtained results to be higher than the reference values. Fig. 3-1 shows the obtained values plotted against the reference values. It can be seen that at the 0.2% and 0.5% matrix levels, the slopes are close to 1 and excellent coefficients of correlation are obtained,

Table 3-4). At the 1.0% and 1.5% levels of matrix, the slope has fallen to approximately 0.8 and the correlation coefficients are slightly worsened.

Element	Reported Value (μg.g^{-1})	0.2% w/v G1		0.5% w/v G1		1% w/v G1		1.5% w/v G1	
		Obtained (μg.g^{-1})	*% Recovery*	Obtained (μg.g^{-1})	*% Recovery*	Obtained (μg.g^{-1})	*% Recovery*	Obtained (μg.g^{-1})	*% Recovery*
Co	2.4	2.3	*96*	2.4	99	2.1	88	2	82
La	101	97	*96*	96	95	76	69	72	71
Ce	170	173	*102*	163	96	140	82	141	83
Pr	19	17	*89*	16	86	17	90	18	95
Nd	56	54	*97*	52	93	56	101	60	108
Sm	8.3	8.3	*100*	8.2	99	8.7	105	9.4	113
Eu	1.3	1.4	*109*	1.4	107	1.5	118	1.7	128
Gd	5	5	*107*	6	115	6	118	6	126
Tb	0.54	0.63	*117*	0.61	113	0.65	120	0.71	131
Dy	2.4	2.9	*119*	2.8	115	2.9	122	3.3	136
Ho	0.35	0.48	*137*	0.48	137	0.5	143	0.57	163
Er	1.15	1.25	*109*	1.26	110	1.33	115	1.5	130
Tm	0.15	0.17	*113*	0.17	113	0.18	120	0.2	133
Yb	1.06	1.05	*99*	1	94	1.05	99	1.19	112
Lu	0.19	0.16	*84*	0.15	79	0.16	84	0.18	95
Pb	48	49	*102*	47	97	45	93	51	106
Slope		1.0026		0.9997		0.8200		0.8170	
r^2		0.9990		0.9549		0.9925		0.9816	

Table 3-4: Results obtained for G1 at various matrix levels

These findings are consistent with either matrix suppression, space charge effects or cone deposition. The fact that there was no significant mass discrimination in the results suggests that the effect is not being produced by space charge effects, since these would affect the lower mass results more than the elements of a higher mass.

Although from these results alone there is no way to distinguish between matrix suppression and cone blockage, this was determined simply by examining the sample cone after each level of matrix had been run. This revealed that a slight deposition was formed at the 1.0% level, and to a much greater extent at the

1.5% level, despite their showing similar slopes. No deposition was observed for either the 0.2% or 0.5% levels. This suggests that cone deposition becomes significant at and above the 1% matrix level and therefore, under normal solution aspiration conditions, matrix levels should be kept below this value.

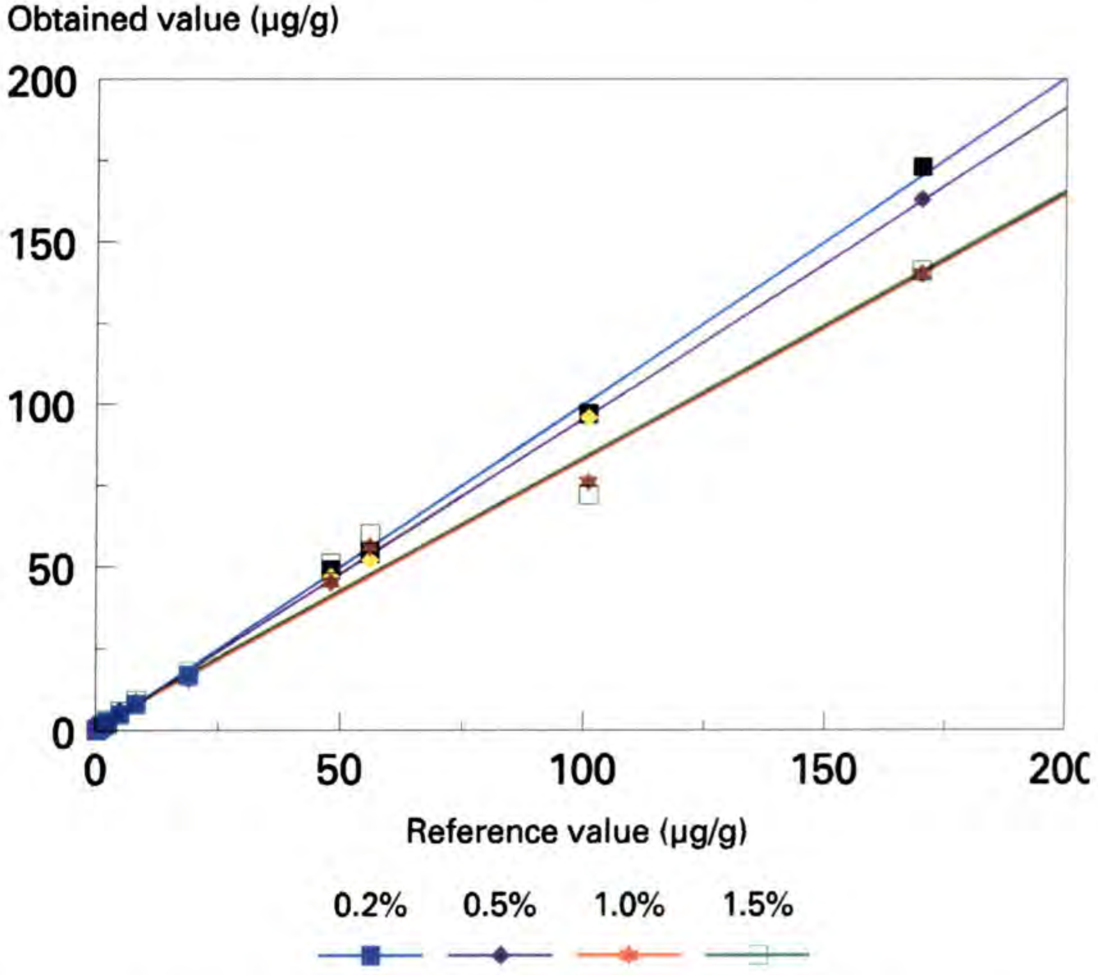

Figure 3-1:Comparison of results obtained with reference values for various matrix levels of the standard granite G1

3-5 Dissolution Procedures

The need to convert solid samples into solutions predates the development of instrumental techniques. There is consequently a great deal of published material relating to the digestion of geological samples. Maxwell[29], Jeffery and Hutchison[30] and Bock[31] have all published reviews of the subject.

There are two approaches reported for the digestion of samples for quantitative analysis; (a) methods based on the fusion of a sample; and (b) methods based on the acid digestion of the sample.

3-5.1 Fusion Techniques

These are based on the addition of a flux with which, at high temperature, the sample fuses to form glass beads which may either be analysed directly by techniques such as XRF or can be dissolved in relatively mild acid conditions to produce a solution. The major "advantage" of the fusion technique is the retention of silica in the final solution allowing its quantitative determination.

The range of fluxes and reagents used for the fusion of geological samples is extensive. Bock provides a very comprehensive review[32]. Classical fluxes such as sodium carbonate, which were used in the 1920's and 1930's by Washington[33], and sodium hydroxide, used in the 1950's by Riley[34] have largely been superceded in more recent times by borate fluxes, in particular lithium metaborate[35,36]. Although the fusion technique has been widely used for ICP-AES analysis, for example Walsh[37], Walsh and Howie[38], Brenner *et al*[39] and Burman *et al*[40], it has found little general applicability in ICP-MS.

Although, according to Cremer and Schlocker[41], a lithium metaborate flux attacks all of the major rock forming silicates and most of the accessory minerals, fusion techniques are not used in ICP-MS primarily because they add to the matrix of the solution. Since the major reason for using ICP-MS rather than ICP-AES for an analysis is to achieve lower detection limits, there is little point in using a digestion method which actually reduces the amount of sample in the aspirated solution. Consequently minimal attention was given to fusion analysis in this work.

One fusion method which has found specialist applicability for the analysis of platinum group metals is the nickel sulphide fire assay technique described by Robert *et al*[42] and Haines and Robert[43] In this procedure the sample is fused at 1150°C with sodium carbonate, basic nickel carbonate and flowers of sulphur. Under these conditions, a 'button of nickel sulphide is formed at the bottom of the crucible. Siderophilic elements are preferentially partitioned into the button, effectively preconcentrating them. The button is then dissolved to produce a solution for analysis.

Date *et al*[44], in 1987, were the first group to report the use of the fire assay technique for the determination of platinum group metals, used a variation of Robert's method to remove the nickel prior to ICP-MS analysis. The button was ground up and immersed in concentrated hydrochloric acid. The nickel sulphide dissolved leaving a precipitate of the platinum group sulphides which was filtered off. The filtrand was dissolved by means of concentrated hydrochloric acid and hydrogen peroxide, which was then evaporated to constant boiling and diluted to give a relatively matrix free solution. Reasonable agreement with reference values were reported for the standard SARM-7, albeit with some loss of palladium, platinum and gold, the latter being expected since Robert *et al*[45] had reported that gold was collected with less efficiency than other platinum group elements. Results for the standard PTC-1 showed serious losses of all platinum group elements and gold, and the authors recommended that further development of the method was essential. Detection limits in the original rock of 0.1 ng.g^{-1} were reported as being achievable by the method.

Jackson *et al*[46] reported that losses of gold and, to a lesser extent, the platinum group elements were due to dissolution of the some of the sulphides during the initial hydrochloric acid digestion. Jackson's group co-precipitated the redissolved platinum group metals with tellurium in order to achieve better recoveries, although consistently low recoveries were still reported.

Silver and osmium were not reported by either group since the former was precipitated by the chloride matrix, and the latter lost as volatile OsO_4 during the evaporation stages.

It can be seen therefore that the method has severe limitations due to the incomplete recovery of analyte elements.

3-5.2 Acid Digestion

Hydrofluoric acid is the only acid which will readily dissolve silicates, forming SiF_6^- ions in acid solution. The use of hydrofluoric acid in combination with perchloric, nitric and sulphuric acids is a well established procedure for the dissolution of silicate samples, although Thompson and Walsh[47] suggest that, despite its hazardous nature[48], perchloric acid is preferable to sulphuric as perchlorates are more readily soluble than sulphates.

There are two types of acid digestion. The first, open digestion, involves heating the samples on a hotplate, in platinum or Teflon crucibles, for several hours[49]. The second, microwave digestion, involves heating the sample by microwave radiation in a pressurised bomb[50], the latter taking only a few minutes to complete digestion.

While microwave digestion has the advantage of speed, all of the silicon in the sample, and more important, all of the hydrofluoric acid is retained in the solution. Hydrofluoric acid can be complexed with boric acid to form the fluoroborate ion, FB_6^-, but this adds considerably to the amount of dissolved solids in the solution and therefore is undesirable. Microwave digestion is therefore usually followed by evaporation of the hydrofluoric acid and silicon tetrafluoride.

3-5.3 Comparison of Fusion and Acid Digestion Methods for the Analysis of a Range of International Geochemical Standards

Although fusion techniques appear to be fundamentally unsuited to ICP-MS analysis, the availability of lithium metaborate disks for three of the South African "NIM" series of international standards gave the opportunity to perform a direct comparison of the two digestion methods.

3-5.4 Fusion Method

The fusions were performed at the British Geological Survey by Dr Alan Date, using the following method.

50mg of powdered rock was mixed with 125mg of anhydrous lithium metaborate and was placed in a 10ml graphite crucible. The crucibles were heated in a muffle furnace at 1000°C for 20 minutes. On removing the crucible, the melt was immediately poured down through a pair of rollers rotating in the opposite directions to press the fusion mixture into a thin slice. This method was developed for the preparation of disks for XRF analysis.

		NIM-G Granite			NIM-N Norite			NIM-P Pyroxenite		
		Ref	*Acid*	*Fusion*	*Ref*	*Acid*	*Fusion*	*Ref*	*Acid*	*Fusion*
Y	89	143	111	121	7	6.5	6.4	5	4.78	4.26
Zr	90	300	227	273	23	22.0	21.5	30	21.9	25.7
Nb	93	53	57.3	48.6	2	1.97	1.75	NV	3.65	7.43
La	139	109	104	110	3	2.78	2.78	2	1.86	1.65
Ce	140	195	205	202	6	5.7	5.6	NV	3.45	3.67
Pr	141	NV	20.1	22.0	0.68	0.59	0.58	NV	0.39	0.51
Nd	145	72	67.9	74.7	3	3.1	2.96	NV	1.65	1.46
Sm	147	15.8	14.7	15.3	0.8	0.74	0.83	NV	0.30	0.26
Eu	151	0.35	0.3	0.39	0.63	0.57	0.51	0.2	0.17	0.10
Gd	157	14	14.9	14.5	NV	0.87	0.79	NV	0.41	0.32
Tb	159	3	2.60	2.81	NV	0.11	0.10	NV	0.04	<0.04
Dy	163	17	16.6	17.2	NV	0.89	1.07	NV	0.48	0.46
Ho	165	NV	3.70	4.41	NV	0.26	0.24	NV	0.12	0.15
Er	167	NV	12.3	13.5	NV	0.71	0.63	NV	0.38	0.39
Tm	169	2	1.66	2.06	NV	0.06	0.09	NV	0.06	0.05
Yb	173	14.2	13.6	15.3	0.7	0.66	0.66	0.6	0.58	0.45
Lu	175	2	1.76	1.87	0.2	0.2	0.13	NV	0.19	0.27
Hf	178	12	11.6	12.2	NV	0.25	0.34	NV	0.15	0.87
Ta	181	4.5	4.52	4.7	NV	0.42	0.31	NV	0.24	0.28
Pb	208	40	35.5	25.3	7	6.3	3.67	6	5.6	3.6
Th	232	51	48.1	49.4	0.6	0.45	0.38	1	0.79	0.87
U	238	15	15	16.1	0.6	0.45	0.57	0.4	0.19	0.24

Table 3-5: Comparison of Fusion and acid digestion methods (NV=no reference value). ppm.

The disks were washed in 5% nitric acid, to remove surface contamination, then dried and weighed. The disk was then placed in a Teflon beaker with 15ml of 5% nitric acid and dissolved using a magnetic stirrer. Some particulate graphite was observed and so the sample was filtered through a Whatman 541 filter into a 25ml volumetric flask and diluted to volume. This "stock" solution contained 0.7%w/v dissolved solids, too high to be aspirated into the ICP-MS, and was therefore diluted 3 fold and a 50ppb indium internal standard added.

3-5.5 Acid Digestion Method

0.2g amounts of the powdered rock were weighed into PFA digestion bombs and 10ml hydrofluoric acid, 2ml nitric acid and 0.5ml perchloric acid added. The bombs were sealed and placed in a 750W microwave oven at full power for 1½ minutes. The samples were then cooled and the heating cycle repeated a further two times. After cooling, the bombs were opened and the solutions evaporated to fumes of perchloric on a hotplate. A further 5ml nitric acid and 1ml perchloric acid were added and evaporated to dryness. 5ml of deionised water and 2ml of nitric acid were added and warmed until all of the solid had dissolved. The solutions were transferred to volumetric flasks and diluted to 100ml, with the addition of a 50ppb indium internal standard.

3-5.6 Instrument Conditions

Acquisitions were performed in peak jumping mode, since this gives greatest sensitivity when a limited number of elements are to be determined, for the elements Y, Zr, Nb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb ,Th and U. 20 sweeps and 5 points per peak were used with a dwell time per point of 512μS, giving a total acquisition time per sample of 117 seconds.

Reagent blanks and acid digestion blanks were prepared and calibration performed relative to 20ppb and 50ppb aqueous standards containing all of the analyte elements. All of the blanks and calibration standards contained 50ppb of the internal standard indium.

3-5.7 Results

The results, table 3-5 show no systematic bias in favour of either technique, with the exception of lead which was consistently low for the fusion determination. This may be due to the formation of a volatile lead hydride during the fusion stage. Problems were encountered during the running of the fused samples due to blockage of the sampling cone, as indicated by a gradual lowering of the signal for the internal standard with time. Despite this, acceptable results were obtained, suggesting that the internal standardisation process was compensating for this effect. The fact that a single internal standard was able to correct elements of as diverse mass as yttrium and uranium suggests that there is no mass bias effect in the signal reduction, effectively ruling out suppression induced by a space charge effect.

3-6 Analysis of a Range of International Geochemical Standards by an Acid Digestion Sample Preparation.

A range of international geochemical standards, which were well characterised for a wide range of elements, were analysed after being digested by acid decomposition. Sample preparation and acid digestion conditions used were the same as for the previous experiment. In addition to the elements originally determined, the platinum group and gold were added to the element menu. These elements are of very low abundance in the analyte samples and their determination is difficult by other techniques.

The results are shown in table 3-6. Whilst good agreement was achieved between obtained and reference values for elements of high concentrations, the platinum group and gold were below the detection limit.

		G1 Granite		G2 Granite		AGV-1 Andesite		GSP-1 Granodiorite		PCC-1 Peridotite	
		Ref	*Acid*	*Ref*	*Acid*	*Ref*	*Acid*	*Ref*		*Ref*	*Acid*
Y	89	13	14.4	11	12.3	20	22.1	26	25.5	0.1	0.3
Zr	90	201	187	309	276	227	233	530	501	10	10.8
Nb	93	22.6	25.9	12	13	15	15.2	27.9	28.2	1	1.2
Ru	101	NV	<0.040	NV	<0.040	NV	<0.040	NV	<0.040	0.01	<0.040
Rh	103	NV	<0.010	NV	<0.010	NV	<0.010	NV	<0.010	0.0014	<0.010
Pd	105	0.0019	<0.075	0.00025	<0.075	0.0022	<0.075	0.0012	<0.075	0.0054	<0.08
Ag	107	0.044	<0.08	0.04	<0.08	0.078	<0.08	0.086	<0.08	0.008	<0.08
Cd	110	0.059	0.07	0.016	<0.03	0.069	0.07	0.058	0.06	0.019	<0.03
Sn	118	3.2	2.9	1.8	1.7	4.2	4.15	6.6	6.7	1.6	1.3
La	139	105	105	89	88.6	38	40.5	184	201	0.052	0.05
Ce	140	173	169	160	158	67	69.5	399	408	0.1	0.13
Pr	141	17	17.5	18	17.5	7.6	6.7	52	55.5	0.013	<0.040
Nd	145	57	56.1	55	55.0	33	27	196	197	0.042	0.05
Sm	147	8.3	7.7	7.2	7.3	5.9	6.5	26.3	26.7	0.0066	<0.040
Eu	151	1.22	1.3	1.4	1.4	1.64	1.69	2.33	2.36	0.0018	<0.040
Gd	157	4.8	4.6	4.3	4.1	5	4.9	12.1	12.2	0.014	<0.040
Tb	159	0.58	0.53	0.48	0.5	0.7	0.62	1.34	1.36	0.0015	<0.040
Dy	163	2.4	2.3	2.4	2.4	3.6	4.07	5.5	5.72	0.01	<0.040
Ho	165	0.39	0.42	0.4	0.41	0.67	0.82	1.01	0.99	0.0025	<0.010
Er	167	1.3	1.1	0.92	1.03	1.7	1.7	2.7	2.64	0.012	<0.040
Tm	169	0.15	0.16	0.18	0.18	0.34	0.33	0.38	0.42	0.0027	<0.040
Yb	173	1	0.78	0.8	0.9	1.72	1.83	1.7	1.65	0.024	<0.040
Lu	175	0.156	0.16	0.11	0.19	0.27	0.2	0.214	0.24	0.0057	<0.010
Hf	178	5.4	4.1	7.9	6.9	5.1	5.8	15.5	16.1	0.04	<0.040
Ta	181	1.5	1.8	0.88	1.1	0.9	0.87	0.97	0.96	0.02	<0.040
W	182	0.43	0.51	0.0002	<0.040	0.55	0.39	0.3	0.36	0.00002	<0.040
Re	185	0.0006	<0.01	NV	<0.01	0.0004	<0.01	NV	<0.01	0.000058	<0.01
Ir	193	0.002	<0.005	0.00004	<0.005	0.0002	<0.005	0.0003	<0.005	0.0048	<0.005
Pt	195	0.008	<0.015	0.0059	<0.015	0.0011	<0.015	NV	<0.015	0.008	<0.015
Au	197	0.0032	<0.15	0.00103	<0.15	0.0006	<0.15	0.0001	<0.15	0.00079	<0.15
Hg	202	0.085	<0.255	0.051	<0.255	0.02	<0.255	0.022	<0.255	0.006	<0.255
Tl	205	1.23	1.18	0.91	0.78	0.34	0.3	1.43	1.32	0.002	<0.040
Pb	208	46	47	30	33	36	56.6	55	53.2	10	9.8
Th	232	51	51	24.7	26	6.5	105	106	106	0.013	<0.040
U	238	3.4	3.8	2.07	2.0	1.92	2.3	2.54	2.53	0.0045	<0.040

Table 3-6. Results obained for acid digested SRM's. NV=no reference value, (ppm).

3-7 Conclusions

The solution nebulisation technique has been proved to be effective for a range of geochemical analysis. Of the two types of digestion method available, fusing the sample produces too high a level of dissolved solids when trying to determine elements at low concentration and is therefore restricted to specialist applications such as, for example, fire assay enrichment of the platinum group elements, although even this is subject to unacceptably large losses and uncertainties.

Acid digestion is more applicable to ICP-MS, since it does not add significantly to the level of dissolved solids in the sample. In fact, due to loss of silicon as volatile SiF_4, it actually reduces the amount of dissolved material in the final solution. The level of dissolved solids which can be aspirated is ultimately the limiting factor in solution nebulisation. If by some means the tolerance to dissolved solids could be improved by a factor of at least 10, then the direct determination of such elements as the platinum group metals and gold could be brought within the range of present instruments.

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Chapter 4

Slurry Nebulisation in ICP-MS

4-1 Problems with solution nebulisation

As discussed in the previous chapter, the traditional means of sample introduction for trace metal analysis is by the nebulisation of solutions. For most applications, and within the limitations already discussed, this has proved to be perfectly adequate, since it allows rapid direct analysis with fast washout times and the use of automatic samplers to relieve the analyst of the time consuming burden of actually performing the analysis. For samples which exist naturally as solutions, it is obvious that direct nebulisation is the simplest method, and is almost exclusively the preferred technique. One instance of this is where solvent evaporation is necessary to concentrate the analyte(s), for example in neutron activation analysis[1].

Most geological samples, however, occur naturally in the solid state and dissolution must be performed in order to obtain the solution required by the nebulisation technique. Depending upon the properties of the samples this can be a very difficult and laborious task and is subject to many limitations and inaccuracies, varying from a relatively small systematic error to a total inability to dissolve the sample without contamination or loss of analyte elements. A full description of the various techniques available by which to achieve dissolution would constitute a thesis in itself, but a brief description was given in chapter 3. Even so it is worthwhile to review some of the reasons why dissolution may be undesirable, and the reasons why alternatives are on occasions sought.

The problems which are most likely to be encountered in the digestion process are:

4-1.1 Incomplete Digestion

When digesting homogeneous material this is not a major problem because the amount dissolved can be calculated from the weight of the residue. It is, however, of particular importance when attempting to digest heterogeneous samples, such as geological materials, where the undissolved material may represent an entire phase or mineral in the sample, e.g. chromite in silicate melts. This situation leads to a systematic bias which can be difficult, if not impossible, to compensate for, and an alternative sample preparation method must be sought.

4-1.2 Contamination

Even the most careful chemist is likely to introduce some contamination during a digestion. The significance of contamination will depend upon both the nature and concentration of the analyte. An element such as sodium is so prevalent that contamination is almost certain, whereas indium has an extremely low natural abundance and is therefore a most unlikely contaminant. Furthermore, when determining sodium the significance of the contamination will be different depending upon whether the sample was sea water, where the contamination would constitute a very small part of the sodium signal, or a deionised water sample, where the sodium signal may be more or less entirely produced by the contamination.

4-1.3 Masking

In the course of a digestion, it is often necessary to introduce elements into a sample which it would have been desirable to measure. An example of this is the loss of information on Li and B concentrations when using a lithium metaborate fusion process. In addition to those elements in the flux matrix, it is likely that, even when using the purest of fluxes, significant levels of elements having similar chemical properties to those of the flux, such as sodium and potassium in lithium fluxes, will be present. The significance of such secondary contamination will again depend upon the concentration of the analytes. If the analyte concentration is high, a correction for such contamination may be made, for example by a blank subtraction. However, if low concentrations are being determined both the accuracy and the precision of the analysis will be severely compromised.

4-1.4 Loss of Analyte

This can occur by a variety of processes. Almost all digestions involve some form of heating and the loss of volatile elements, such as arsenic and osmium is most often encountered during the heating stage. The likelihood of losing volatiles will of course depend upon the form in which the species exist. Osmium dioxide (OsO_2) has a melting point of >300°C whilst in the oxidised state, (OsO_4) it vaporises at 130°C [2]. Another way in which analytes may be lost is due to insolubility in either the final, or an intermediate, solvent. Most metals are stable in dilute nitric acid although both tungsten and molybdenum are oxidised to the tungstate and molybdate anions, which are insoluble in acid and thus in time precipitate from the solution. At high concentrations the precipitate is instantly noticeable but when measuring trace and ultratrace amounts, such precipitation will not be evident.

It can be seen therefore that there may be many reasons why the analyst may not wish, or may be unable to convert a solid sample into a solution suitable for nebulisation. Whilst solid sample introduction techniques are the obvious answer, they almost always involve additional expensive equipment. One possible alternative is to introduce the sample into the ICP-MS using conventional nebulisation techniques, but in the form of a suspension or slurry of fine particles rather than as a solution.

Although the term "Slurry Nebulisation" is perhaps misleading - for most people it conjures up images of toothpaste - in practice such suspensions are often very dilute or colloidal. Slurry nebulisation , however, has become the accepted term for all such suspensions, no matter how dilute, and for this reason the term will be used in this work to refer to introduction of any particulate matter suspended in a liquid or gel.

4-2 The History of Slurry Nebulisation

When this research began, no previous work had been published on the use of slurry nebulisation with ICP-MS although there were a number of publications describing slurry nebulisation for optical spectrometry.

Gilbert[3] in 1962 proposed the idea of introducing suspensions for flame emission studies. Using a soil suspension in 1:1 glycerol:isopropanol, he reported qualitative analysis from flame emission spectra in oxygen hydrogen and oxygen acetylene flames, and although not providing any analytical justification he concluded that quantitative work could be carried out.

Levedev[4] was the first worker to observe the relationship between particle size and sensitivity in slurry nebulisation. In his 1969 paper he described the analysis of alkali metals in minerals by flame emission using prepared suspensions in water, and contrasted the results with those obtained for solutions of comparable concentration. He reported that the signal intensity, and therefore sensitivity, of the solutions was consistently higher than that obtained for the suspensions, and that this difference seemed to be related to the type of mineral used. He also observed that when the particle size of the suspension was reduced below a certain value, the same sensitivity could be obtained as for the solutions.

Slurry nebulisation was applied to atomic absorption spectrometry by Harrison and Juliano[5] in 1971. They aspirated oxides and sulphides of tin and ore samples and found that the form of the suspended material was significant (stannous oxide giving only about 10% of the sensitivity of stannic oxide) although they concluded that this was due to the higher dissociation energy of the stannous oxide.

In an excellent paper by Willis[6] the results of a detailed examination of particle size requirements were presented. Willis defined the "Relative Atomisation Efficiency" (RAE) of a slurry system as being the ratio of free analyte atoms in the flame to the concentration in the same part of the flame when the same amount of analyte is sprayed in a solution. This observation finds a strong parallel with the concept of dispersion, or more correctly 1/D, used in flow injection. The RAE therefore forms a useful comparison of the efficiency of various slurry nebulisation systems, with a maximum RAE of 1 being equivalence between the solution and slurry systems.

Using a schist and sulphide ore, Willis demonstrated that the RAE was <0.1 for particle sizes >38μm, below which the RAE increased almost 5 fold, suggesting a threshold particle size above which nebulisation became inefficient. Willis also determined the RAE obtained for various types of grinding mill and concluded that only by micronizing samples could the mean particle size be reduced below the >40µm threshold. The concentration of the suspension was found to have no appreciable effect on the RAE, although this does not mean that it should be ignored when applied to ICP-MS.

Whilst all of the early work was carried out with relatively homogeneous materials, which readily formed suspensions in water, in order for such a technique to be applied to 'real world' applications it was necessary to prepare suspensions of real samples, such as geological materials. Daniels and Alberty[7] noted that coating particles with a high molecular weight lyophillic species, such as gelatin, stabilised suspensions in water. Ramirez-Munoz et al[8] studied the effect of gelatin, starch and Triton-X-100 (an alkyl phenoxy polyethoxy ethanol compound) on the stabilisation of particles. Fuller[9] reported the use of 5ml in 100 solution of 0.1% w/v sodium hexametaphosphate for stabilisation of a 1% w/v TiO_2 suspension.

A year later, Fuller[10] described the use of "Viscalex HV30", an acrylic copolymer containing carboxyl groups which acts as a thixotropic thickening agent. Supplied as an acidic low viscosity emulsion, when diluted and neutralised to a pH in the range 6-10, it forms a highly viscous gel which is stabilised to a suspension for several days. The atomic absorption analysis of chromium in a 0.1g/100ml rock solution was reported for various concentrations of Viscalex. Below 2% Viscalex, the suspension decays over 3 days; at 2% and above, however, the absorbance recorded is constant, although the precision of these measurements was not noted.

In 1981, Fuller, Hutton and Preston[11] discussed the application of slurry nebulisation and the effect of particle size for sample introduction into flame and electrothermal atomisation (ETA) AAS and ICP-AES. Samples were ground in a

McCrone mill, as described by Willis, and used Fullers' Viscalex stabilisation method. For flame AAS systems results similar to Willis' were obtained. For ETV, although there was some variation in RAE with particle size, RAE values of 0.5 and above were obtained, even at particle sizes in the range 90-106μm. In ETV AAS, the sample was simply pipetted and not nebulised, therefore confirming the idea that the limiting factor in slurry introduction is the nebulisation stage.

When introducing slurries into ICP-AES, it was found that a particle size of <6μm was necessary in order to achieve significant (~0.5) values of REA. This is surprising because the hotter thermal environment of the ICP was expected to give rise to improved signal responses. The authors believed that the limitation lay in the unavailability of ICP concentric and cross flow nebulisers at the time to cope with the slurry, even when pulsed nebulisation (a modified version of flow injection) was used. Sparkes and Ebdon[12], Halicz and Brenner[13] and Ebdon and Wilkinson[14] have also studied slurry nebulisation into ICP-AES, drawing similar conclusions concerning particle size.

This requirement for small particle size gave rise to a series of experiments by Ebdon and Collier[15,16] who used kaolin to monitor fractionation of the sample in the slurry nebulisation system. They concluded that the spray chamber design, a Scott type double pass system , was significant in causing fractionation of the sample, due to the inability of large particles to remain in the aerosol after the direction change in the spray chamber. Another factor which reduced the acceptable mean particle size for ICP compared with Flame AAS was found to be the narrow injector tube used in the classic Fassel plasma torch. By using a torch with a 2mm and 5mm injector (c.f. 1mm on the standard), transport efficiency could be improved for ICP-AES.

4-3 Application to ICP-MS

The similarity between the two techniques meant that in almost all respects, the methods developed for ICP-AES could be directly applied to ICP-MS.

Given the choice between adopting one of the various phosphate based stabilising agents and the Viscalex method, it was decided to adopt the latter. This was because previous work by this and other authors (chapter 3) had indicated that phosphates and phosphoric acid cause severe depression of the analyte signal, as well as a rapid blockage of the sampling interface. Subsequently it was shown by Jarvis and Williams[17] that this was not necessarily true for the concentrations of organic phosphates used.

At the time, the majority of slurry nebulisation work had been carried out on relatively homogeneous materials. Although the possibility of sampling errors was felt to be low, due to the high degree of mixing achieved in the milling stage, it was necessary to consider the possibility of fractionation of minerals in the suspension.

4-4 Experimental

4-4.1 Reagent Purity

All reagents except the Viscalex solution were of semiconductor grade purity. An acidified 2% v/v solution of Viscalex was spiked with 50ppb indium and analysed to assess it's purity. Semiquantitative analysis, calibrated relative to the internal standard showed significant levels (>10ppb) of alkali metals but no other significant contaminant elements were detected. This simple experiment also demonstrated that no matrix effects were produced by the Viscalex. This confirms the author's experience when analysing acetic acid which was found to enhance the signal in some instances.

	CERT.	Run 1	Run 2	Run 3	Run 4	Run 5	Mean	SD	95% Confidence Interval
Be	2.4	3	2.4	2.3	2	1.5	2.2	0.6	0.9
Co	5	6.9	10.9	7.3	4.4	5.5	7.0	2.5	4
Rb	170	56	53	59	56	85	62	13	22
Sn	1.4	2.1	4.9	3.9	2.3	1.6	3.0	1.4	2
Ba	1900	729	804	656	225	93	501	320	538
La	92	132	289	213	186	167	197	59	99
Pb	30	25.7	23.4	9.3	3.8	4.2	13	11	18
U	2.1	2.2	1.5	1.2	0.8	1.3	1.4	0.5	0.9

Table 4-1: Semi quantitative results for selected elements in G2, calibrated against the aqueous indium internal standard, (μg.g^{-1}).

	CERT.	Run 1	Run 2	Run 3	Run 4	Run 5	Mean	SD	95% Confidence Interval
La*	92	92	92	92	92	92	92.0	0.0	0.0
Be	2.4	2.82	1.95	3.11	2.4	2.51	2.6	0.4	0.7
Co	5	4.9	4.9	6.7	5.4	5.8	5.5	0.8	1.3
Rb	170	138	135	179	217	181	170	34	57
Sn	1.4	0.9	1.4	0.67	1.72	1.6	1.3	0.5	0.8
Ba	1900	1873	2132	2095	2048	1977	2025	103	173
Pb	30	42.3	33.2	50.3	28	29	37	10	16
U	2.1	2.4	1.82	1.54	1.72	1.56	1.8	0.4	0.6

Table 4-2: Semi quantitative results for selected elements in G2, calibrated against the La standard value, (μg.g^{-1}).

4-4.2 Grinding

Samples of international geochemical standards were wet-milled for 30 minutes in a McCrone micronising mill with semiconductor grade acetone. Although no particle size measurements were used, this method was found by Fuller *et al* to result in a mean particle size below 6μm[18].

4-4.3 Preparation of Slurries

A major concern in adapting the method to ICP-MS was the likelihood of deposition of sample matrix onto the sample interface. Fuller's method used 1g of the milled sample, but for this work, the amount was reduced to 0.2g.

0.2g of milled sample was weighed into a beaker and 1.5ml of Viscalex HV30 added. The emulsion was diluted to approximately 5 ml with deionised water and stirred vigorously. Whilst still stirring, the solution was neutralised by the dropwise addition of 0.880 ammonia, until the solution thickened to a gel. The suspension was transferred to a 10ml volumetric flask, spiked with 50 ppb of indium and diluted to volume. Blanks containing just the reagents and the internal standard were also prepared.

4-4.4 Instrument Conditions

A mass range of 5-255amu was used skipping mass regions 12-31.5, 38-44.5, 45.5-49.5, 53.75-58.25 and 79.5-80.5 amu. Instrument conditions were: dwell time of 512µs; 2048 channels; and 50 sweeps This corresponds to an approximate scanning time per acquisition of 60 seconds.

A standard plasma torch and deGalan "V-groove" type nebuliser was used, with the solution being pumped at 0.8ml/min.

4-5 Results

Initial experiments were simple semi quantitative analyses of the standards and blanks, calibrated relative to the aqueous internal standard. The initial results bore no resemblance to certified values, being consistently low. Furthermore, precision over five determinations, as measured by the percentage relative standard deviation, was also poor. The problem was traced to the method of preparing the suspensions. The stirring of the suspension during preparation had been carried out by means of a Teflon coated magnetic stirrer. Upon close examination of this, mineral particles, presumably magnetite and other ferromagnetic minerals, were sticking to it and therefore absent from the suspension being aspirated. All of the solutions were prepared again using a mechanical stirrer, constructed from PTFE rather than metal to avoid contamination.

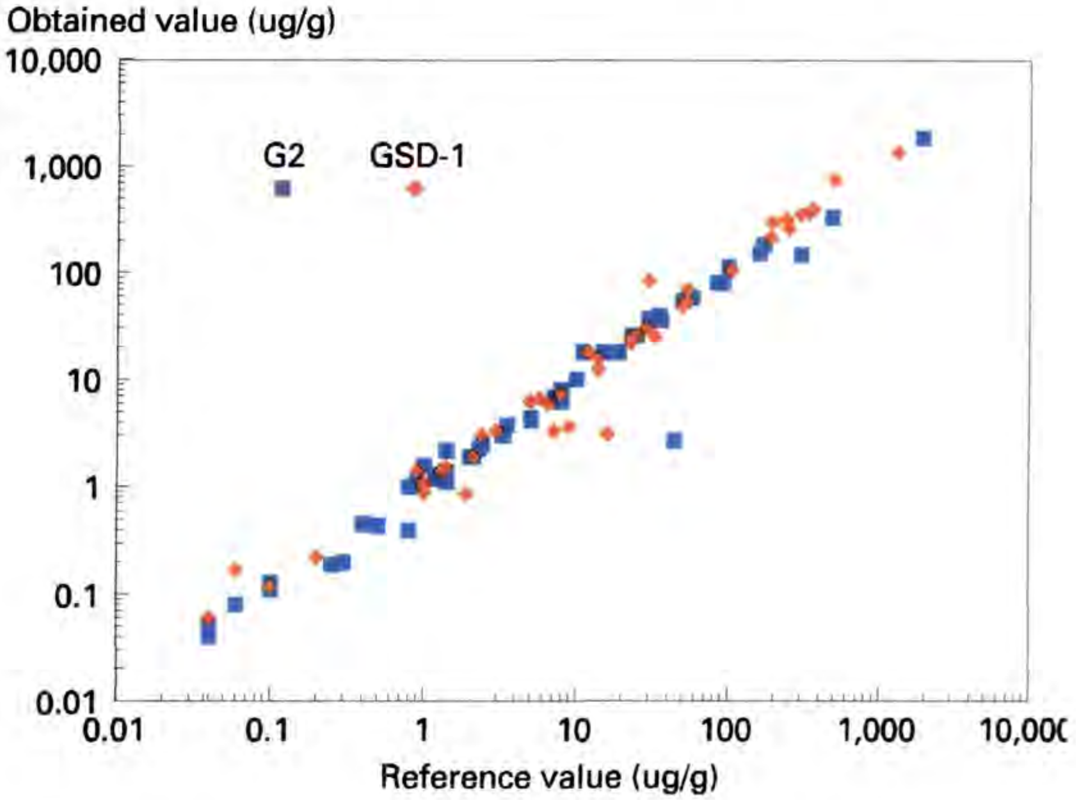

Figure 4-1: Comparison of results obtained by slurry nebulisation with reference values for various matrix levels of the reference standards G1 and GSP-1

The new semiquantitative results (table 4-1) again showed poor agreement with certified values as well as poor precision. One possible reason for this was that because indium, the element added to the suspension to form an internal standard, was present in solution rather than as a suspension, its nebulisation efficiency may have been significantly higher than that of the G2 sample. This is consistent with the observation that the mean results for most elements were lower than certified values.

The data was therefore reprocessed using lanthanum as the internal standard, taking the certified value as reference. The results, given in table 4-2, show greatly improved agreement with certified values and better, although still not good, precision. The experiment was repeated several times, always with similar results. Regrinding the samples for a longer period was also found to have little effect, suggesting that the problem was not directly related to particle size.

This disparity between aqueous standards and the suspension had serious implications for the viability of the technique for geochemical work. An internal standard is essential for ICP-MS work in order to achieve both good accuracy and good precision. However, if it was not possible to add an internal standard, then the chances of obtaining good quantitative data were limited. Furthermore, quantitative calibration against aqueous standards would also not be possible.

It was decided to carry out a quantitative analysis, calibrating against reference standards and again using the reference standard's lanthanum content as the variable internal standard. This meant that no blank subtraction could be performed, since there was now no way to spike the slurry with an internal standard. It was necessary to apply a correction for the differing amounts of lanthanum in each sample because in quantitative analysis, the PlasmaQuad software assumes that the internal standard has the same concentration in each sample.

In contradiction with Fuller's findings[19], the stability of the suspensions was found to be limited. Acceptable results could not be obtained with suspensions prepared more than an hour earlier.

Indeed great care was necessary in the preparation of the suspensions. For example the over addition of ammonia resulted in too viscous a sample which although very stable, proved to be difficult for the peristaltic pump to handle and caused the tubing connectors to burst. After a large number of failed attempts, reproducible quantitative results were obtained. The preparation of the slurries was not a task which could be readily automated and in practice was found to be as time consuming as sample digestion, and required as great if not greater skill levels from the worker.

Precision was found to vary with concentration, but in general relative standard deviations were below 10% for elements present at 1ppm or higher. The results of the quantitative analysis for a wide range of elements in the USGS standards G2 and GSD-1 are shown in table 4-3. Figure 4-1 shows the obtained values plotted against reference values. the slopes obtained for G2 and GSD-1 were 0.964 and 1.098 respectively, indicating that good agreement with certified values were obtained. The correlation coefficients for G2 and GSD-1 were 0.9888 and 0.9785 repectively.

4-6 Conclusions

Although it was found to be possible to obtain good results for geochemical standards using slurry nebulisation, there are a number of practical difficulties.

4-6.1 Standardisation

The inability to use aqueous standards poses a limitation to the technique, although this can be overcome by using suspensions of reference materials.

4-6.2 Internal Standardisation

More importantly, the inability to add an internal standard poses significant limitations to the applicability of the technique. Without the ability to use internal standardisation, the analyst is limited to running reference materials with at least one, and preferably more than one, known elemental concentration. There will be instances where the concentrations of some elements in a sample, usually major and minor elements, will be known from XRF and other techniques which can be "plugged in" to obtain an internal standard.

One other possibility is to prepare a synthetic silicate powder standard of the required particle size which has been spiked with a known concentration of an element such as indium with a low natural abundance. The use of such a standard would preclude the determination of silica in the samples, but would allow the use of a sample independent internal standard. Great care would be necessary in the mixing of sample and spiked standard to ensure homogeneity.

4-6.3 Sample Preparation

This is a highly skilled task and in this author's opinion is not for the faint-hearted. It is not easy to see how this procedure could be automated and therefore is likely to remain time consuming and labour intensive - a factor which will make it's routine adoption unlikely.

Since this work was carried out and subsequently published[20], although other workers have entered the field, there remains little (at the time of writing) which has been published on slurry nebulisation for ICP-MS. Jarvis[21] provides a review of slurry nebulisation for geological materials using ICP-AES and ICP-MS. Jarvis and Williams[22] have published results for the analysis of geological materials by slurry nebulisation ICP-MS using an alternative grinding method and tetrasodium pyrophosphate stabilisation using calibration against aqueous standards.

Given the potential advantages in terms of sample throughput which it was originally thought could have been achieved by slurry nebulisation, the fact that there have been so few papers on the subject tends to support the conclusions drawn from this work, that the practical difficulties outweigh the potential benefits.

	G2		GSD-1	
	Certified	Slurry	Certified	Slurry
Li	35	40	30	83
Be	2.4	2.5	1	0.88
B	2	1.9	...	2.16
S	100	115	300	350
Cl	50	55	340	370
Sc	3.3	3	6.6	5.9
V	36	36	54	69
Cr	8	6.3	12	18
Co	5	4.2	7.9	7.2
Ni	3.5	3.8	9	3.6
Cu	10	10	33	25
Zn	84	81	105	104
Ga	23	26	23	24
Ge	1	1.6	0.9	1.4
As	0.25	0.19		
Se	<0.7	6	...	...
Br	0.3	0.2	...	0.3
Rb	170	185	250	260
Sr	480	336	240	320
Y	11	18	29	30
Zr	300	150	500	740
Nb	15	18	23	22
Mo	0.8	0.4	...	1.16
Cd	0.04	0.04	0.06	0.17
Sn	1.4	2.2	5	6.2
Sb	0.06	0.08	7.1	3.3
Cs	1.4	1.4	1	1
Ba	1,900	1,880	1,300	1,350
La	92	80	195	297
Ce	160	154	360	390
Pr	19	18	50	48
Nd	58	58	190	213
Sm	7.2	7	25	26
Eu	1.4	1.1	2.4	3
Gd	5	4.4	14	15.4
Tb	0.5	0.44	1.4	1.5
Dy	2.3	2.3	5.7	6.6
Ho	0.4	0.46	...	...
Er	1.3	1.3	3	3.3
Tm	...	0.33	...	...
Yb	0.9	1.1	1.9	0.85
Lu	0.1	0.11	0.2	0.22
Hf	8	8.1	14	12.2
Ta	0.8	1	1	1.1
W	0.1	0.13	0.1	0.12
Au	0	0.02	0	0
Hg	44	2.7	16	3.1
Tl	1.2	1.2	1.3	1.4
Pb	30	37	54	55
Bi	0.04	0.05	0.04	0.06
Th	25	26	105	105
U	2.1	1.9	2.1	1.9

Table 4-3: Quantitative results obtained for G2 and GSD-1 by slurry nebulisation (ppm), using the respective Cs values as an internal standard.

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Chapter 5

Flow Injection Analysis ICP-MS

5-1. Introduction

Flow injection (FI) was described by its originators, Ruzicka and Hansen[1] as being (op. cit. p.1)

> *"based on the injection of a liquid sample into a moving non-segmented continuous stream of a suitable liquid. The injected sample forms a zone, which is then transported towards a detector which continuously records the absorbance, electrode potential, or other physical parameter as it continuously changes as a result of the passage of the sample material through the flow cell".*

The rapid sample throughput and small sample size used in flow injection has led to a rapid growth in application of the technique. As a sample introduction technique, it has been successfully coupled with many spectrometric techniques. Ruzicka and Hansen[2] provide a detailed review. Jacintho *et al*[3] were among the first workers to describe the application of flow injection for sample introduction into inductively coupled plasma atomic emission spectrometry (ICP-AES).

5-2. Principles

A schematic diagram of the flow injection system used in this work is shown in Fig. 5-1. Initially, the valve is in the 'load' position (Fig. 5-1a). In this state, the carrier solution is being continuously pumped through to the nebulizer. At the same time, the sampling probe is placed in the sample, which is pumped through to fill the loop with excess sample being passed to waste. Once the loop is filled the valve is switched to the 'inject' position (Fig. 5-1b) which causes the loop to be inserted into the carrier flow. Thus a fixed volume of sample, the volume of the loop, is reproducibly introduced into the carrier stream and pumped through to the nebulizer.

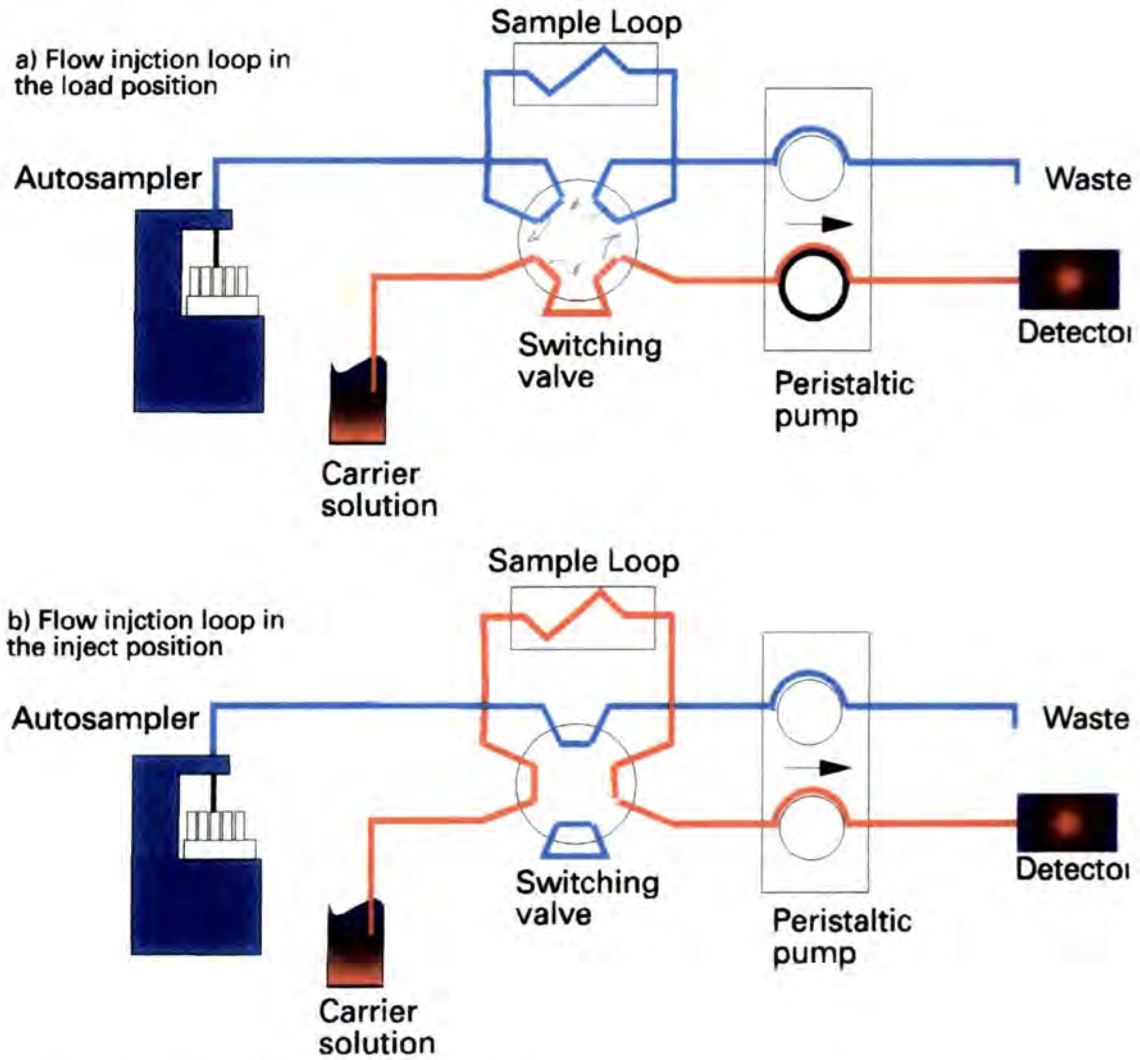


Figure 5-1: Schematic of the flow injection system

5-3. Requirements

The utility of flow injection ICP-AES is limited by the relatively slow data acquisition of scanning instruments and most work has been restricted to fixed channel, simultaneous instruments (Greenfield [4,5], McLeod [6,7], Lawrence *et al*[8], LaFreniere *et al*[9] and Hartenstein *et al*[10], Sjodin and Sundqvist[11], Israel and Barnes[12], Hirata *et al*[13], Liversage and Van Loon[14]). The use of FI with scanning detection systems is described by Valcarcel and Luque de Castro[15], and Janata and Ruzicka[16] who recognise the scanning speed of the detection system to be much higher than the flow of sample through the system.

The rapid data acquisition rates of inductively coupled plasma mass spectrometers (the entire mass range may be scanned in under 100ms[17]) make ICP-MS highly suitable to coupling with FI sample introduction. For multi-element analysis (Christian and Ruzicka [18], McLeod [19] and Hiefje *et al* [20]), however, a great deal of work on the optimisation of the combination system is necessary in order to obtain valid and meaningful results.

5-4. Aims

On the basis of earlier work and the literature, the combination of flow injection sampling with ICP-MS was considered to have the potential to overcome some of the problems which have been identified in chapter 1 as the scope of this work, namely the optimisation and operation of the flow injection ICP-MS system to achieve the lowering of detection limits, increased sample throughput, the minimisation of suppression and matrix effects and the ability to analyse traces in small volume samples such as fluid inclusions (Date[21]) increases the potential application range of ICP-MS.

5-5. ICP-MS

Plasma	Forward Power	1.35 kW
	Reflected Power	<10 W
	Nebuliser gas flow	0.75 $l.min^{-1}$
	Auxiliary gas flow	1 $l.min^{-1}$
	Plasma gas flow	13 $l.min^{-1}$
	Sample uptake rate	Various
	Sampling depth above the load coil	10 mm
Mass spectrometer	Vacuum stage 1	2.3 mbar
	Vacuum stage 2	$<10^{-4}$ mbar
	Vacuum stage 3	5.0×10^{-6} mbar
	Detector mode	pulse counting
Acquisition parameters	Number of multi channel analyser channels used	
	Dwell time per channel	Various
	number of mass range sweeps	

Table 5-1: Instrument operating conditions used

Analysis was performed using the standard VG PlasmaQuad ICP-MS instrument described in chapter 1. Instrument operating conditions are given in table 5-1. Using conventional nebulization, instrument sensitivity was ca. 2000 counts per second per ppb at mass 115 with a background level of 10 counts per second at mass 220.

5-5.1 Peristaltic Pump

The sample was pumped using an Ismatek peristaltic pump with a variety of diameters of Viton® pump tubing. The pumping rate for various tubing diameters was calibrated by weighing the volume of de-ionised water delivered in a given time for a variety of pump speeds and diameters.

5-5.2 Flow Injection Valve

The flow injection was performed using a FIAtron FIAvalve 2000, microprocessor controlled 8 port switching valve, controlled from the PlasmaQuad computer via an RS 232 interface. Switching was carried out in both serial mode whereby the valve received instructions from the PlasmaQuad computer, and in manual mode whereby switching was performed manually, using the control panel on the valve. The valve was fitted with various sized sampling loops in the range 50-1000µl.

5-5.3 Operating Variables and Performance Indicators

In conducting this series of experiments it was necessary to identify the performance indicator parameters to be monitored and the operating variables which affected them. On the basis of the aims outlined the performance monitors used were: signal duration, which ultimately affects sample throughput, sensitivity or the signal / noise ratio; and mass response which will affect sensitivity for different elements. Operating parameters were found to be the dispersion of the flow injection system and the mode and speed of data acquisition of the ICP-MS.

These variables and indicators are examined in detail in the next section. However, a simple initial experiment was found by the author to put the various considerations into perspective. A solution containing a 200µl of 50ppb indium was injected into the 'un-optimised' system as shown in Fig. 5-1, and the signal obtained with time, at mass 115, was collected, Fig. 5-2. The result is typical of the time profiles obtained by other workers using different detection systems[22,23,24,25] and is characteristic of transient analyte signals in general and of flow injection in particular.

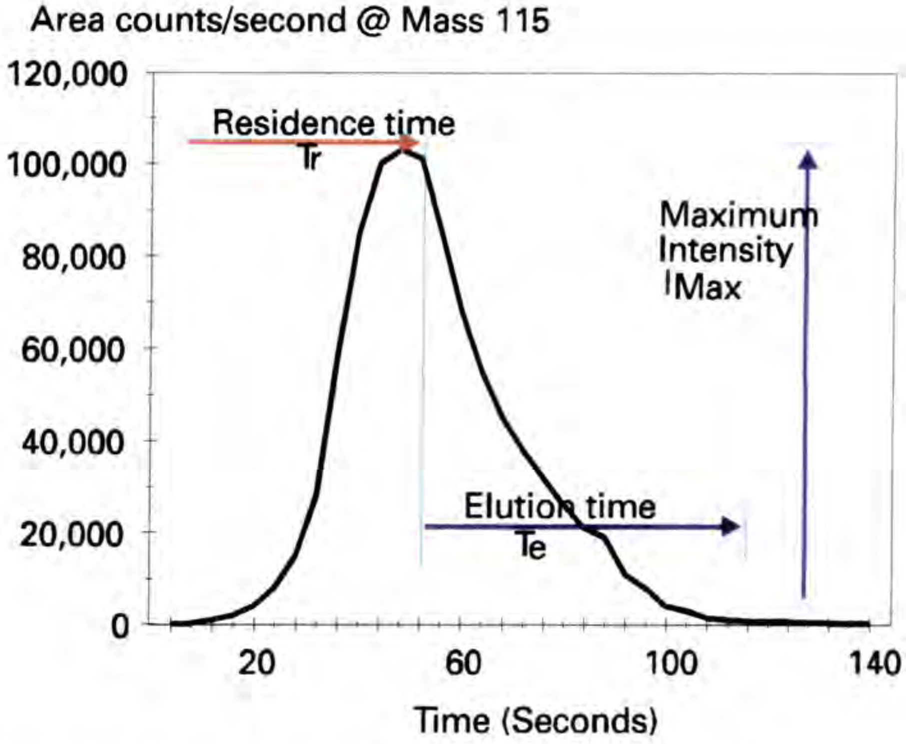


Figure 5-2. Time profile of signal at mass 115, produced by injection of 200µl of a 50ppb Indium standard solution

Since the outset of this work, with the exception of the work by Valcarcel and Luque de Castro[26], all work has been towards the coupling of FI to single property detectors or simultaneous systems such as simultaneous ICP-AES. Therefore most work has been carried out using peak height measurements (I_{max}). ICP-MS, however, is a sequential technique, albeit a rapid one, and it still requires a finite time to acquire multi-element data. Thus, in order to make use of this benefit, it is necessary to use peak area, rather than peak height measurements. This involves detailed examination of the two primary data acquisition methods, scanning and peak-jumping, and redefinition of some of the terms cited in the literature.

The residence time, T_r, is defined by Ruzicka and Hansen[27] as the time between injection of the sample and the peak maximum (I_{max}). In flow injection ICP-MS it was also found to be important to observe T_e, the time between I_{max}

and the point at which the signal returns to background level. It can be seen that in this non-optimised system the signal lasts approximately 100s from injection until returning to baseline (T_r+T_e).

It can also be seen that if only one isotope were being measured, with the ICP-MS set to monitor that isotope continuously, the peak height (I_{Max}) measurement would be adequate in theory. However, with the stated aim of performing multi-element analysis, it is necessary to scan rapidly and continuously throughout the whole duration of the signal, from a few seconds after injection until after the time at which the signal has returned to background (T_r+T_e).

The VG PlasmaQuad is capable of scanning the whole mass range (1-250 amu) in as little as 100ms[28] so that, in theory, repeated scans may be performed throughout the duration of the signal and integrated to give an elemental mass spectrum of the sample.

5-6. Optimisation

5-6.1 Reproducibility of 'Peak-Height' and 'Peak Area' Measurements

Although it has been stated that the intention is to use peak area, rather than peak height measurements, it would not be sensible to do so without first examining the reproducibility of both the peak area and the peak height measurements. To do this, an experiment was set up to inject a standard solution repeatedly and measure the relative standard deviation of the peak height and peak areas.

A series of 18 injections of a 100ng.ml^{-1} yttrium standard solution was made. Yttrium was chosen because it is monoisotopic, its degree of ionisation in an argon plasma is greater than 99%[29], thus giving the maximum possible signal, and is at the approximate middle of the mass range allowing for extrapolation to either higher or lower masses. The ICP-MS was set to monitor mass 89 (the mass of yttrium) continuously, the resultant data file being a time profile similar to a chart recorder printout. The profile obtained is shown in Fig. 5-3. Peak heights and peak areas were calculated and are given in table 5-2. Peak areas, expressed as area counts per second, have been plotted above the profiles and are also shown in Fig. 5-3.

Peak area measurements were found to be considerably more reproducible than the corresponding peak heights. This experiment was repeated a further 5 times and similar results were obtained each time. It is concluded that, in terms of reproducibility, peak area measurements are not only an acceptable alternative to peak height, but are actually significantly more reproducible.

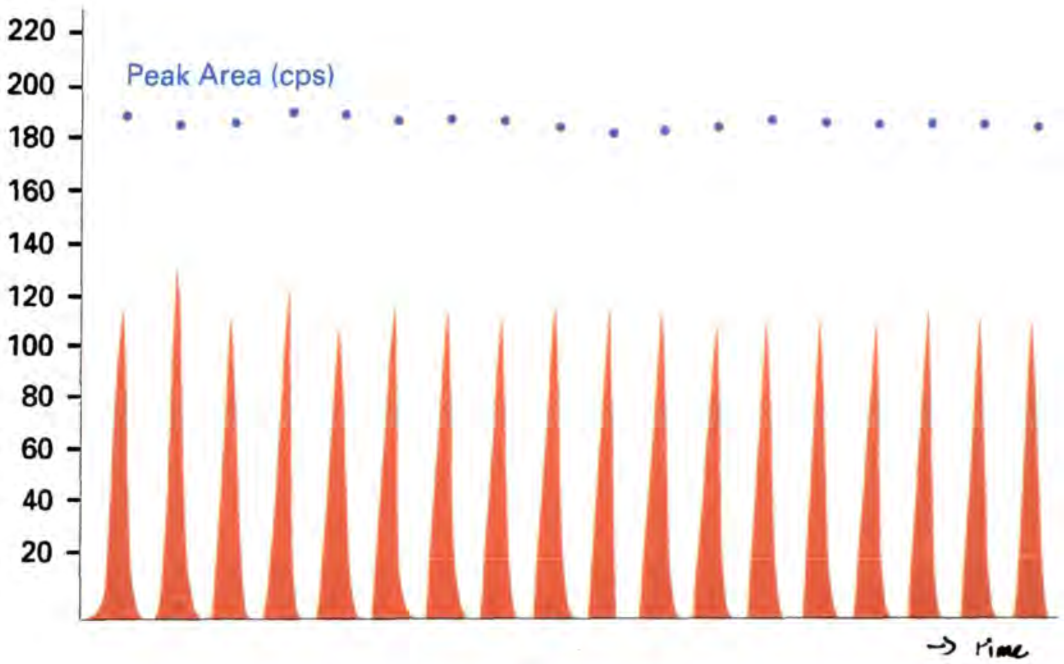


Figure 5-3. Reproducibility of peak height and peak area measurements

5-6.2 Sample Volume

The amount of sample introduced, during flow injection, is fixed by the volume of the sample loop. Where the injection volume is not fixed by constraints, such as the nature and size of the sample available, it would seem desirable to use a large sample volume in order to maximise sensitivity. However, the nature of the flow injection condition was found to invalidate such assumptions .

Peak number	Peak Height (cps)	Peak Area (Area cps)
1	114,094	9,432
2	130,722	9,275
3	111,980	9,349
4	122,544	9,565
5	108,793	9,532
6	117,771	9,423
7	115,935	9,506
8	118,574	9,361
9	119,337	9,271
10	117,470	9,338
11	111,020	9,448
12	113,694	9,588
13	115,251	9,546
14	114,718	9,539
15	120,111	9,566
16	115,987	9,570
17	117,097	9,540
18	114,229	9,229

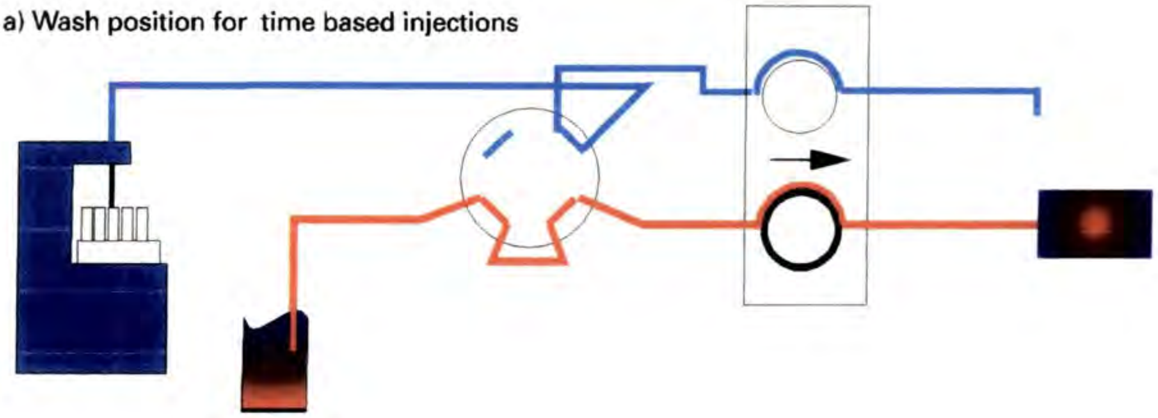
Mean	116,770	9,462
St. Dev.$_n$	4,818	105
%RSD$_n$	4.1	1.1

Table 5-2: Reproducibilities of peak height and peak area measurements for repeat injections.

For an established method, the volume of sample can be set by preparing a loop of known volume, probably best determined by cutting a length of tubing of known bore, and calibrated by measuring the difference in weight between the empty tube, and the weight of the tube filled with de-ionised water. For this experiment, where several loops of accurately known volume were required, it was decided to re-configure the computer controlled loop to act as a switching valve (Fig. 5-4) so that when pumping the solution at a known rate a timed injection would be equivalent to the injection of a fixed volume. This was only possible because the loop used had a very fast switching time, typically 60ms[30], and the timings could be precisely controlled by the computer.

100ng.ml^{-1} yttrium was again used, for the reasons detailed above, and the ICP-MS again set to monitor mass 89 continuously. Using a previously calibrated solution pumping rate of 0.876 ml/min, injections of the yttrium solution of 7,14,21,28 and 35 seconds duration were made, these times being equivalent, at this pumping rate and with a total valve dead volume of 3µl, to injections of 106µl, 208µl, 311µl, 414µl and 516µl respectively. The resulting profiles are shown in Fig. 5-5 as they were measured on the instrument, and with the peaks overlaid. It can be seen from the overlaid profiles that the rising edge of these profiles are the same, differences in volume producing differences in height up to a certain point then subsequently by a broadening of the peak. Peak heights and peak areas determined from these were calculated (table 5-3) and were used to plot graphs of injected volume vs. response obtained for both peak height and peak area (Fig. 5-6).

a) Wash position for time based injections



b) Inject position for time based injections

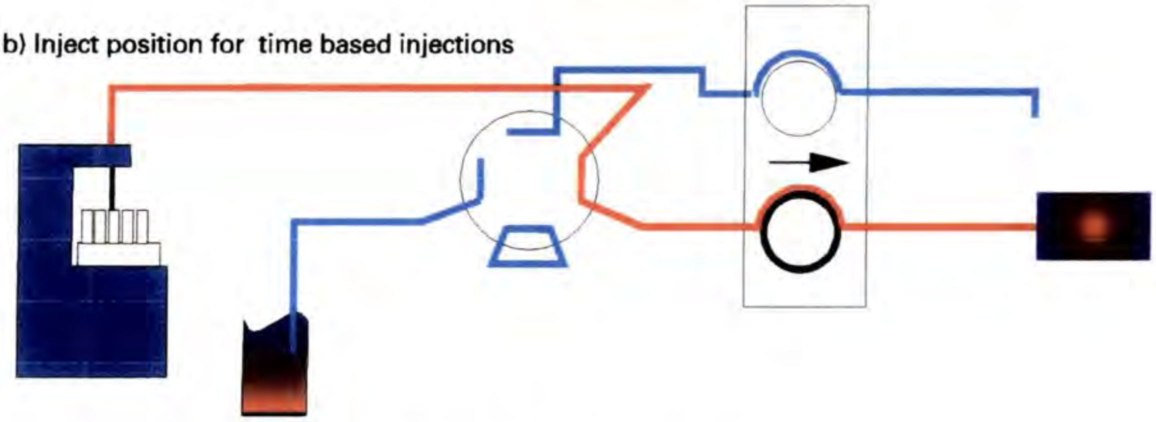


Figure 5-4: Schematic of the time based flow injection system

Injected Volume (µl)	Peak Height (cps)	Peak area (cps)
106	323,232	2,950,195
208	436,364	5,912,609
311	529,293	9,285,411
414	537,374	12,189,368
516	549,495	14,360,837
Gradient	5,535	288,070
Y axis intercept	309,090	288,070
r^2	0.83004	0.99642

Table 5-3: Correlation between volume of sample and peak height and peak area.

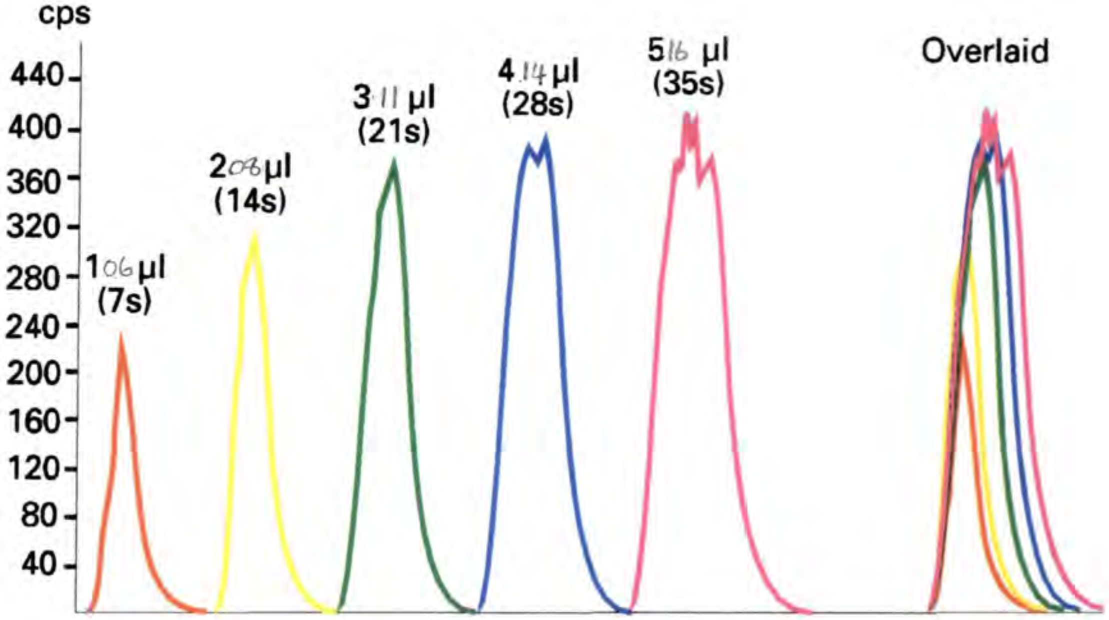


Figure 5-5: Profiles produced from different injection volumes and overlaid

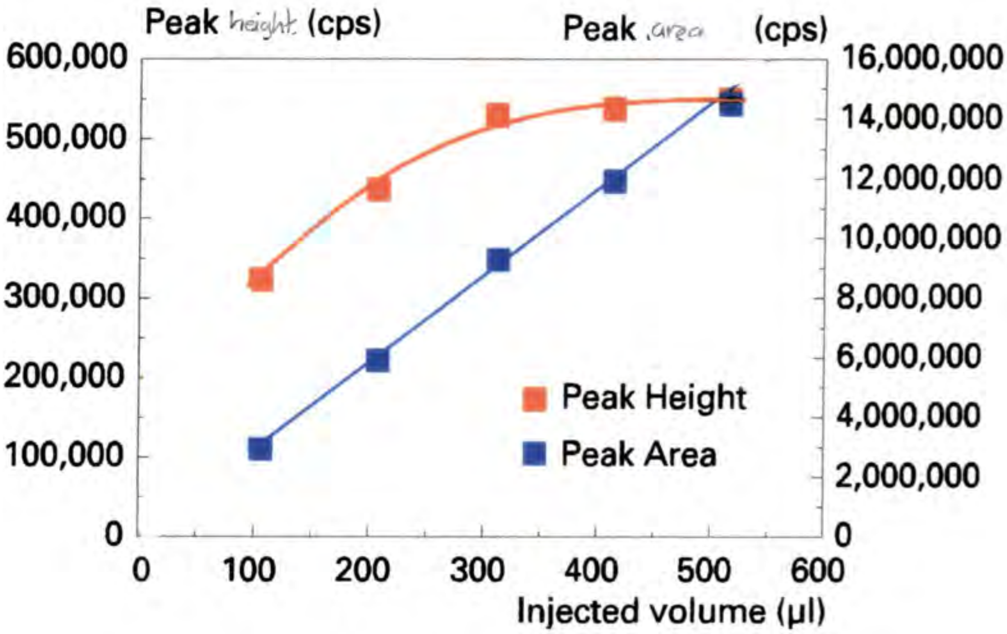


Figure 5-6: Graph of sample volume vs response for ^{89}Y from peak height and peak area measurement

An examination of the overlaid profiles (Fig. 5-5) and the plot of volume vs. peak height and peak area shows that, at 300µl and above, the height of the peak is not linearly related to the volume but reaches a plateau with the peak broadening. This peak height therefore represents the maximum intensity which would be reached if continuous injection were being used, termed "steady state" by Ruzicka and Hansen[31], at which point the criteria for the flow injection system are no longer satisfied. In their work based on peak height measurements, Ruzicka and Hansen were careful to avoid this departure from true flow injection[32] and, although the peak area measurement was found to be linear over the volume range, such a departure from the flow injection condition results in a lack of control over the dispersion of the system. For work where dispersion is not significant, or limited sample size work, an injection volume of 200µl was adopted as offering the best compromise between maximising sensitivity and losing control of the dispersion of the system.

5-6.3 Mode of Data Acquisition

As outlined in chapter 1, there are three types of data acquisition available in commercial ICP-MS instruments: single ion monitoring; scanning; and peak-jumping.

Single ion monitoring is useful when investigating the processes involved in flow injection systems, but the information provided is limited and does not meet the stated objective of developing a multi-element analysis system. The choice of scanning versus peak-jumping has been examined in the discussion of the instrumentation in chapter 2, and for solution analysis in chapter 3, but the nature of flow injection, in particular the transient nature of the signals produced by flow injection, poses different requirements for what are very similar problems.

Whereas in continuous solution analysis the options essentially centre on the choice between either the amount of additional information (peak shape, isotopic patterns and extra elements) obtainable by scanning, or the improved detection limits (but limited information) obtainable by peak-jumping.

There are four primary considerations which are specific to transient signals:

- The mass range to be investigated must be repeatedly scanned or peak-jumped, in order to compensate for the continually changing signal[33].
- This repeated passage through the mass range must be done as quickly as possible so that the signal does not change significantly during a particular pass[34].
- Since the signal is only present in the system for a fixed length of time, all acquisition must be completed during this time.

The mechanics of the two types of acquisition, while largely outside the scope of this work, must be considered in terms of the way in which the acquisition is handled.

5-6.3.1 Data Recording Overhead

Quadrupole mass spectrometers are intrinsically fast instruments[35], but they do require a finite amount of time, termed the quadrupole settle time and typically 90µs on the PlasmaQuad system[36], when making a significant change in mass. In scanning mode, because the masses are sequentially scanned at a constant rate and no incontiguous mass jumps are made, the acquisition proceeds smoothly without pauses for the quadrupole to settle, except at the start of each sweep of the mass range, and every region of skipped masses. Thus settling time is minimised.

This contrasts strongly with the peak jumping acquisition where, as the name suggests, the difference in mass from one point to the next may be a single amu or a hundred masses. In this situation a period of quadrupole settling is necessary before each move to the next mass. If repeated sweeps of the mass range are required, as has been found for flow injection, it would seem likely that the proportion of time during an acquisition, when actual data acquisition was occurring, would be less than for scanning.

Whilst this is not important in most analyses involving continuous nebulization (because the acquisition duration may simply be increased to compensate) in an analysis of fixed duration this cannot be achieved and data recording overheads must be minimised. One way would be to increase the dwell time per sampling point and reduce the number of sweeps. However, this may allow the change in signal intensity with time to distort the mass response obtained (see section 5-5.3.4 on multiple sweep rate).

In order to determine which of the two acquisition systems was the more appropriate, acquisition parameters were defined for both scanning and peak-jumping, where the parameters had been adjusted in order to give actual acquisitions of 102 seconds duration (table 5-4). In order to minimise the expected data recording overheads in peak-jumping, only one sampling point per mass, corresponding to the centre of the peak, was used. The actual data acquisition time was calculated. For scanning this is simply the product of the number of sweeps, the number of MCA channels used and the dwell time per channel. For peak-jumping the theoretical duration is the product of the number of masses selected, the number of sampling points per mass, and the dwell time per sampling point.

The difference between the duration of the acquisition and the amount of actual acquisition time is the data recording overhead.

	Scanning	Peak-jumping
Mass Range (amu)	5-240	N/A
Number of Masses Sampled	181	181
Number of Sweeps	320	38
Dwell time (μσ)	160	5,120
Number of Channels	2,048	N/A
Number of sampling points per mass	8.7	1
Skipped Mass Regions (amu)	11.5-22.5 27.5-43.5 209.5-233.5 235.5-237.5	N/A
Integration Time per Mass (S)	0.446	0.194
Theoretical Duration (S)	82	35
Actual Duration (S)	102	102
Data Recording Overhead (S) *Actual-Theoretical*	20	67
Data Recording Overhead per acquisition (%)	20	66

Table 5-4: Acquisition parameters used in comparing scanning and peak-jumping acquisition for FI-ICP-MS

The conditions used are shown in table 5-4. It can be seen that a scanning acquisition was found to have a 20% data recording overhead, compared to 67% obtained with peak jumping. This confirms the idea that for fixed duration acquisitions scanning acquisition is likely to give greater sensitivity than peak jumping, simply by spending a longer time acquiring data. This result cannot, however, be taken in isolation: consideration must also be given to peak shape and sampling efficiency.

5-6.3.2 Peak Shape and Sampling Efficiency

In scanning mode the ICP-MS, like all quadrupole instruments set to nominal mass resolution, produces a peak which is approximately Gaussian in shape. In peak jumping mode one or more points at the centre of the peak, where intensity is at a maximum, are sampled. This gives rise to the question as to whether, given that time is limited, it is inefficient to sample the whole peak.

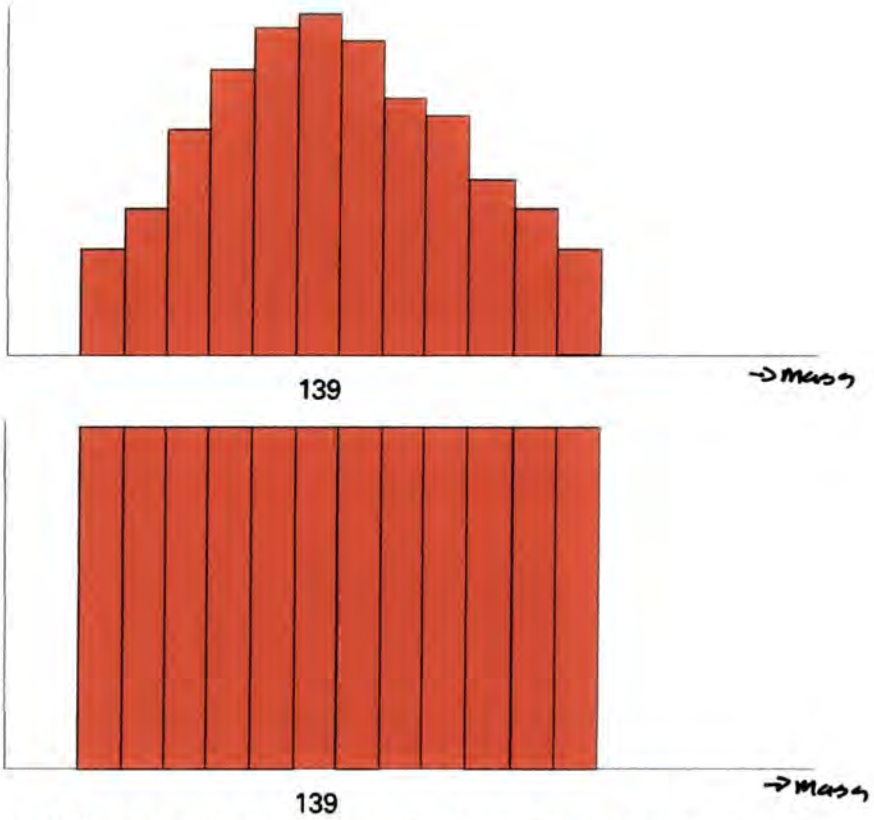


Figure 5-7. Effect of peak shape on sensitivity for Scanning (top) and Peak Jumping (bottom)

In order to examine this question a lanthanum peak, as shown in Fig. 5-7, was examined. Thirteen points across the peak had been sampled and their intensities combined to give an integral for the Gaussian peak. This was ratioed to 13x the intensity of the central sampling point, which approximates to the integral which would have been obtained by spending that amount of time on the central point. It was found that the scanning integral was only 61% of the peak jumping signal. This was repeated for a selection of other masses taken at random from previously acquired scans, Scanning was found to give between 59 and 62% of the equivalent peak-jumping signal.

By combining the relative factors obtained for the two acquisition modes for data recording overheads and peak shape intensities, it was calculated that scanning resulted in approximately 1.4 times that of peak-jumping. Thus scanning was used as the preferred mode of acquisition for flow injection.

5-6.3.3 Multiple Sweep Rate

Valcarcel and Luque de Castro[37] have explained the requirement for repeated "ultrafast" scanning. Fast scanning is necessary to prevent the signal from changing significantly during the course of a scan: if a single scan of the mass range took the same time as it takes the sample to pass through the instrument the result would be relatively high sensitivity for mid-mass elements and virtually no sensitivity for either low or high-mass elements. Fig. 5-8 shows the profile from Fig. 5-2 with a representation of a 12 sweep acquisition overlaid onto it. It can be seen that, with the larger number of narrower bands (i.e. shorter scans), the acquisition more accurately maps the profile of the sample and therefore both gains greater sensitivity and also minimises changes in response during each sweep.

The typical scanning rate for a 2 minute full mass range scan - 1 minute being the typical duration of a flow injection signal - is 100 sweeps of the mass range which for 2048 MCA channels and a 640µS dwell time per channel equates to a scanning speed of 177 amu/s.

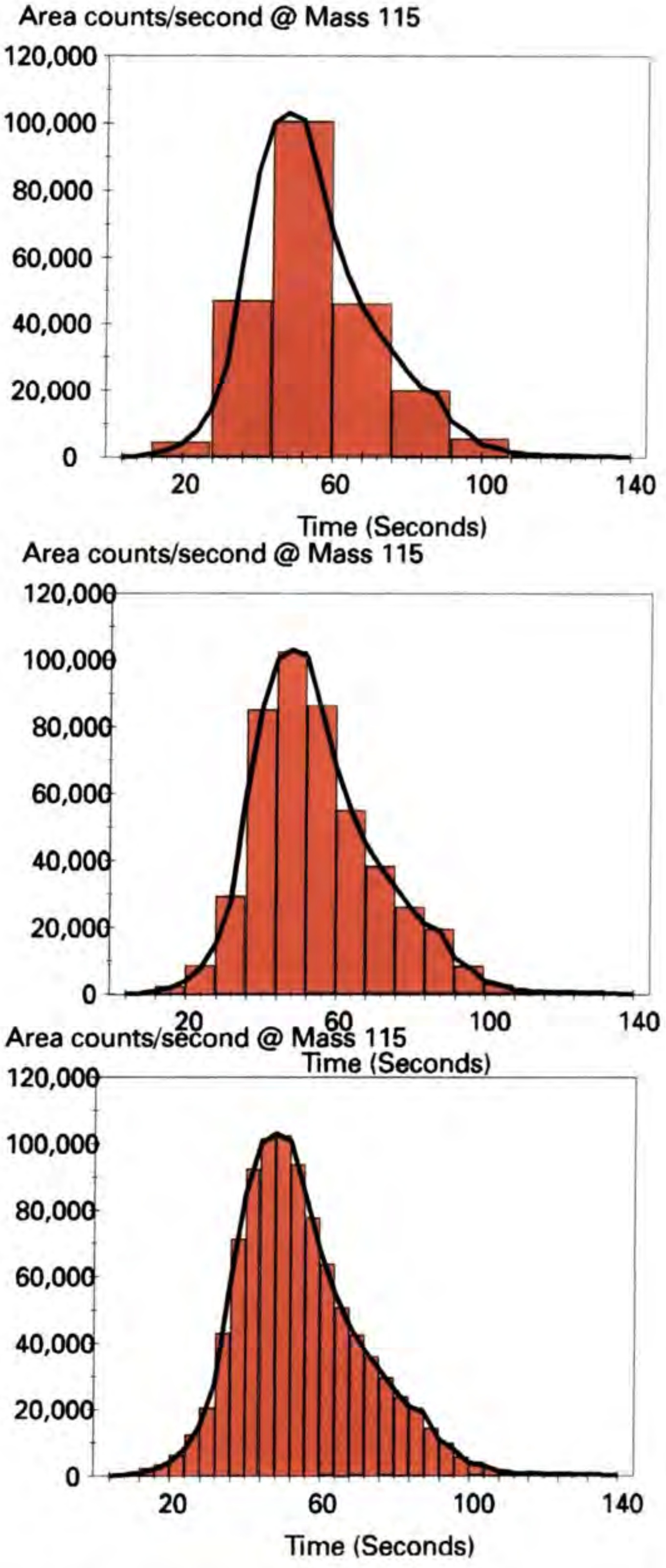


Figure 5-8: Time profile of signal at mass 115, with representations of 6, 12, and 24 sweep per scan with acquisitions overlayed

As this proved to be a sensible minimum scanning rate, the effect of increasing the scanning rate, whilst keeping the acquisition duration constant, was investigated. A series of acquisitions were performed wherein the number of sweeps was increased and the dwell time per channel decreased. The number of channels used was not varied because this would have an effect upon the quality of the peak shapes.

A solution containing 50 ng.ml^{-1} of beryllium, magnesium, cobalt, indium lead and uranium was used so that, once corrections had been applied for isotopic abundances, the variation of response with mass could be plotted.

Acquisitions were performed on this solution, for both continuous nebulization and flow injection, using the acquisition parameters shown in table 5-5.

Number of sweeps	Dwell time (μσ)	Scanning Rate (amu/s)
100	640	176.8
200	320	353.7
400	160	707.3
800	80	1,414.7
1,600	40	2,829.3
3,200	20	5,658.7

Table 5-5: Acquisition parameters used to investigate the effect of scanning rate on mass response.

The mass response plots obtained are shown in Fig. 5- 9. The continuous nebulization (Fig. 5-9a) show much greater sensitivity, as was expected, than the corresponding ones for flow injection, and also proved to be a different shape, but no significant differences were found for either sampling technique by changing the rate of scanning. It was assumed therefore that even the lowest acquisition rate used in the experiment was fast enough to eliminate the undesirable effects caused by the signal's transience.

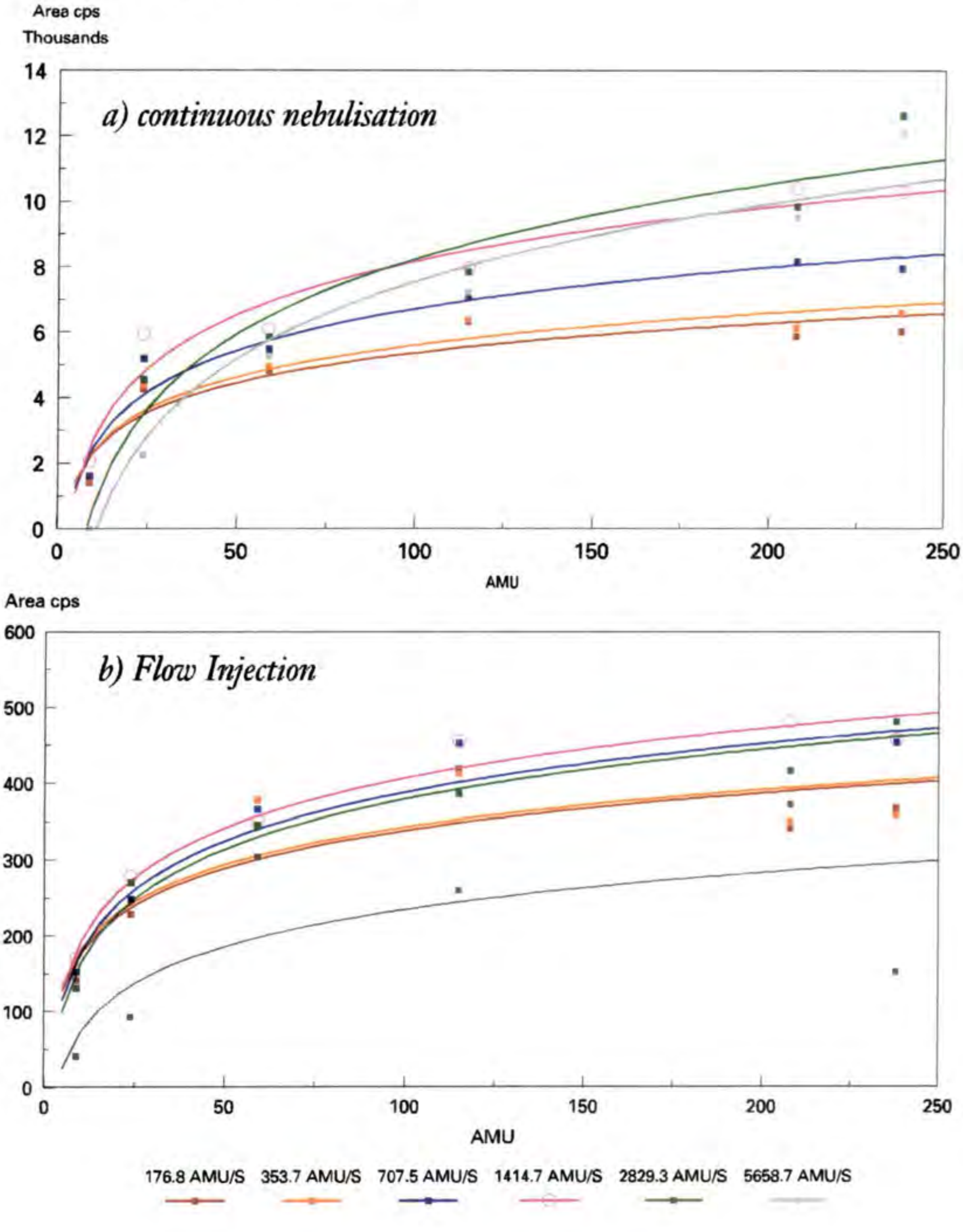


Figure 5-9. Variation in mass response with scanning speed for continuous nebulisation and flow injection

5-6.4 Dispersion

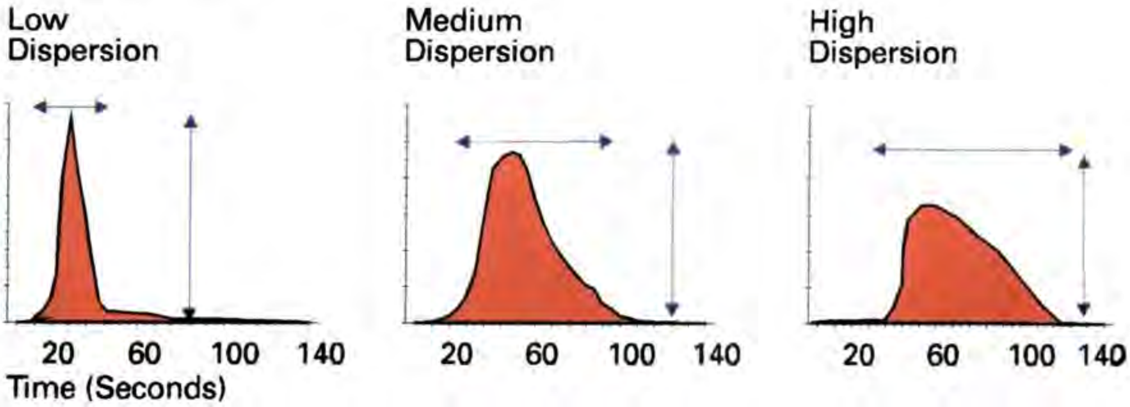


Figure 5-10: The effect of dispersion on signal profile shape

Ruzicka and Hansen[38] consider the dispersion of a system to be of paramount importance in the design of a flow injection system. Dispersion can be loosely described as the degree of mixing observed between the sample and the carrier stream. By changing the dispersion of the system the shape of the signal profile changes[39], the peak becoming much broader and lower at high dispersions (Fig. 5-10). The effect of this is to change both the duration and the maximum intensity (peak height) of the sample profile. This is of more importance when using flow injection with detectors based on chemical reactions, such as the determination of phosphate as a phosphomolybdate complex[40]. In such systems the dispersion has to be high enough to allow the reagents to mix with the sample and to have a sufficient length of tubing between the loop and the spectrophotometer to allow development of the blue colour, the intensity of which is measured at 660nm. It is of less importance in simple applications of flow injection ICP-MS where peak area rather than peak height measurements are used. In these instances the dispersion produced by the conditions described in previous sections of this work are adequate.

However the ability to control dispersion, inherent in flow injection[41], forms a powerful tool for the analyst. It enables much greater control over the introduction of samples to assist in particular applications, such as the analysis of very saline materials like sea and pore waters, which produce ionisation suppression in the plasma[42].

Alternative dispersions are very application specific and because of this it is proposed to delay detailed investigation of the possible effects of varying dispersion to section 5-5.3. The remainder of this section will therefore be concerned simply with the definition of terms for dispersion work when using peak area measurements.

For the single property or simultaneous measurements used by Ruzicka and Hansen dispersion[43] is defined as:

$$D = \frac{C^O}{C^{Max}} = \frac{H^O}{H} \cdot \frac{Const'}{Const''}$$

where:

D = the dispersion of the system
C^O = the concentration of analyte in the injected solution
C^{Max} = the concentration in the dispersed system
H^O = the intensity which would be produced in an undispersed system
H = the intensity actually produced (corresponding to I_{Max})
Const' = Constant
Const'' = Constant

Thus dispersion can be seen to be the ratio of the actual intensity to that which would be produced in an undispersed system, and therefore has a value greater than or equal to 1. The same equation can be used for area measurements, substituting A^O and A for H^O and H.

$$D_a = \frac{C^O}{C^{Max}} = \frac{A^O}{A} \cdot \frac{Const'}{Const''}$$

Where:

D_a = the dispersion of the system
A^O = the intensity which would be produced in an undispersed system
A = the intensity actually produced (corresponding to I_{Max})

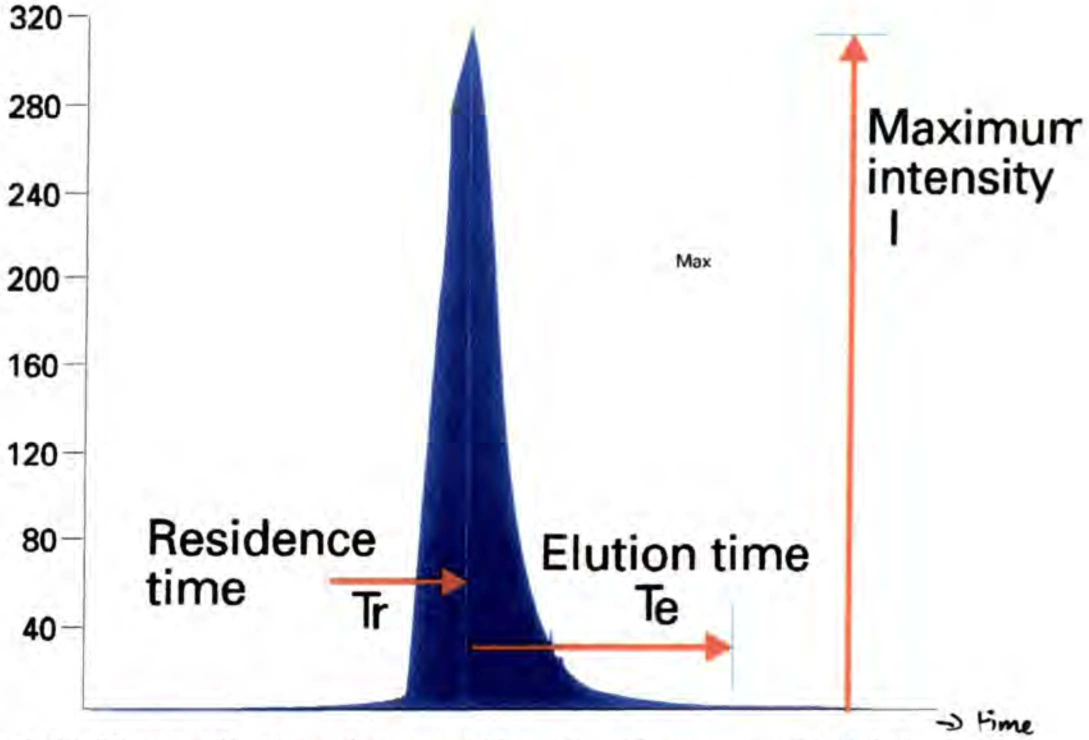


Figure 5-11. Time profile of signal at mass 115, produced by injection of 200µl of a 50ppb Indium standard solution

This formula was used to calculate the dispersion of the 200µl loop system used previously. Fig. 5-11 shows the profile obtained for the injection of a 200µl sample of 50 ng.ml^{-1} indium, monitoring mass 115. The peak height I_{Max} of a

200µl injection corresponds to the maximum height which would be obtained in an undispersed system, therefore the undispersed peak area for this acquisition, A^O, would be:

$$A^O = I_{Max} \times [T_r + T_e]$$

Where T_r is the residence time and T_e is the elution time as shown in Fig. 5-2. The dispersion, D_a, of the system is therefore given by:

$$D_a = \frac{[I_{Max} \times (T_r + T_e)]}{A} = \frac{15952902}{5926065} = 2.69$$

This value for the area determined dispersion, D_a, of 2.69 will therefore be used as a baseline in other dispersion work.

5-7. Applications of Flow Injection in Geochemistry

There are primarily four areas in which flow injection ICP-MS could potentially benefit the geochemist. The reduced sample volumes should allow shorter washout times and reduce matrix deposition on the sampling cone to give higher throughput and greater matrix tolerance, as well as facilitating the analysis of samples such as fluid inclusions where the amount of sample is limited. In addition, the ability to control dispersion may be used to reduce matrix suppression effects, thus allowing greater sensitivity for highly saline samples.

5-7.1 High Sample Throughput

The factors which control the rate of sample throughput in ICP-MS are the time required for the pumped sample to reach the plasma, the time for the signal to stabilise and the time required for the analyte signal to return to background once data acquisition is completed. With the sub ppb detection limits and wide linear working range of which ICP-MS is capable, washout times can be considerable, often over 4 minutes[44]. It is thought that because of the reduced amount of material aspirated during flow injection, it should be possible to reduce the washout period significantly and thus increase sample throughput, one of the stated objectives of this work.

Fig. 5-12 shows the variation in instrument response, which indicates the amount of material aspirated with time obtained for the signal at mass 115 for the introduction of a solution containing 50 ppb of indium by both conventional nebulization (Fig. 5-12a) and flow injection (Fig. 5-12b). Both traces represent the change in signal over the course of a typical one minute acquisition using the conditions shown in table 5-1 which could be used routinely to analyse a sample for the whole elemental range.

In conventional, continuous aspiration the total time required to perform a single acquisition is four minutes. Assuming a solution pumping speed of 1 ml.min^{-1} this corresponds to 2 ml of sample being sprayed through the introduction system. Using flow injection, this time is typically 2 minutes for a 200 µl loop. Since, in flow injection, the sample volume is fixed by the volume of the loop there is a tenfold reduction in the amount of material introduced into the system, thus giving a considerable reduction in memory and therefore washout time.

Further gains in throughput were achieved by eliminating the sample uptake period through accurate timing. Once the 'loop empty' time (Fig. 5-12b) has been reached and the signal starts to decay the valve may be switched back to the load position, because all sample material has been eluted from the loop. In fact, the loop must have been emptied before this time (calculated by the product of the volume of the tubing between the loop and nebuliser, and the pumping rate) but it would be time consuming to calculate this each time a flow injection system was set up. Using the start of the decay is an unambiguous and fast indication that the loop has in fact been emptied.

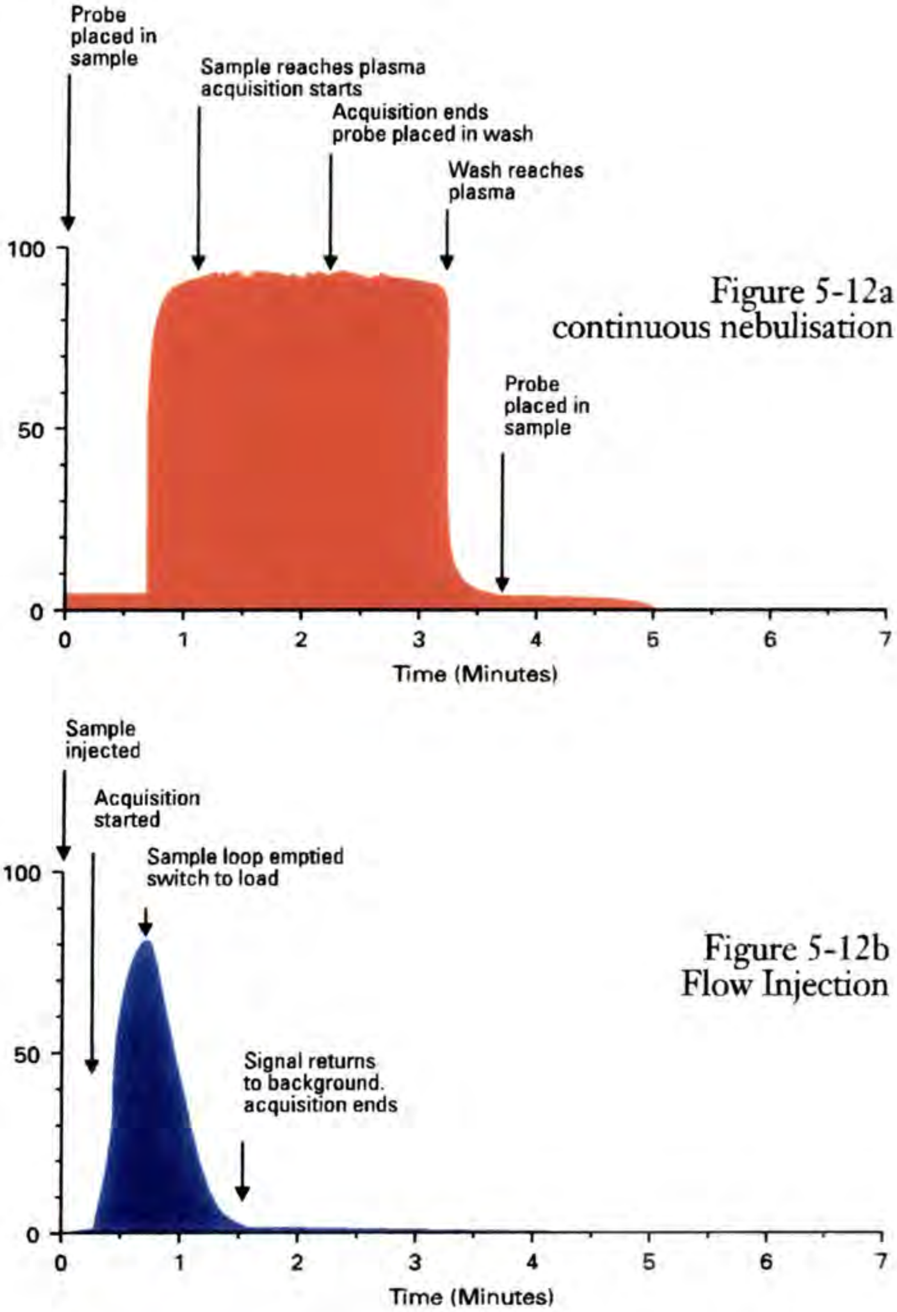


Figure 5-12a
continuous nebulisation

Figure 5-12b
Flow Injection

Figure 5-12. Instrument response vs time for continuous nebulisation and flow injection

Don't you need to wash the loop?

While the acquisition continues, the loop may be filled with the next sample. This allows the loop to be filled and ready when analysis of the first sample is complete. Because the acquisition is set up to continue until the signal has returned to background injection of the next sample may take place immediately, rather than waiting for washout to occur. Whilst this may sound complicated, and is in fact difficult to achieve manually, by programming the instrument computer to control both the valve and an autosampler it was possible to automate the system, and thus maximise the sample throughput.

A multi element analysis for the rare earth elements was performed. The run consisted of a blank, 50ppb standard and 100 ppb standard and 20 samples of the 50 ppb standard, all of which were spiked with 50ppb of indium, and was performed under the conditions shown in table 6, using ^{115}In as the internal standard. The analysis was made using both continuous nebulisation and flow injection.

	Continuous Nebulisation	Flow Injection
Number of Sweeps	100	206
Dwell time per Channel (μs)	320	320
Number of Channels	2,048	2,048
Total Acquisition time (s)	65.5	135
Uptake time (s) / Valve -> Plasma Time (s)	60	15
Washout Time (s)	120	0
Time per sample (s)	245	150
Time for blk, 2x Std's + 20 samples (min)	94 minutes	58
Relative improvement in throughput	1	1.6

Table 5-6: Acquisition parameters used in the comparison of throughput for conventional nebulization and flow injection ICP-MS

It can be seen that flow injection gives a 1.6x improvement in sample throughput, even in this simple experiment. This factor will vary depending upon the analysis in question. For example, where elements such as cadmium, mercury and bromine are to be determined, the washout time for continuous nebulisation would have to be increased to allow for the longer residence time in the system of these elements, and thus would increase the throughput factor for flow injection. Similarly, if multiple determinations were required, there would be less sample uptake time used for continuous nebulization, which would reduce the flow injection improvement factor, although the increased amount of material being aspirated may necessitate a further increase in washout time.

In conclusion, one of the stated aims of this work, the improvement of sample throughput for geological analysis, has been shown to be possible by using flow injection.

5-7.2 Small Sample Volume Handling: the Analysis of Fluid Inclusions

In flow injection, loop volumes are typically in the range 50 - 500 µl, which permit replicate analyses of total sample volumes as low as 500µl to be performed. Whilst in most geological analyses, there are plentiful amounts of sample, one area in which sample volume is the limiting factor is in the analysis of fluid inclusions.

In his classic 1858 paper, Sorby[45] argued that fluid inclusions represented trapped portions of the liquids, gases and melts from which the crystal had grown and could be used to establish the environment in which a rock or mineral might have formed. That this idea has been borne out, is proven by the vast amount of literature on the subject in the last twenty five years. (Roedder[46,47,48,49] Spooner[50], Crawford[51], Touret[52], Weisbrod[53]).

Shepherd *et al*[54], describe the contribution made by fluid inclusion studies to the understanding of the character, origin and evolution of hydrothermal ore-forming fluids and ultimately ore genesis. From this arose an increased awareness of the role of fluid phases in sedimentary, diagenetic, metamorphic and magmatic processes.

Fluid inclusion studies have been used as geothermometers and continue to provide an important guide to the pressure and temperature conditions during mineral formation, and primary and secondary inclusions in ore and gangue minerals can be used to "fingerprint" certain types of ore forming fluids, to characterise particular ore mineral assemblages, and to define areas where these fluids are most likely to concentrate.

5-7.2.1 Chemical analysis of fluid Inclusions

In considering the chemical analysis of fluid inclusions, Shepherd *et al*[55] identify a number of considerations:

5-7.2.1.1 Sample Size

Inclusions are usually between 2 and 20 μm in size and the total volume of inclusions is typically less than 0.1% of the volume of a given crystal[56]. The need to reduce the amount of sample required for analysis is clear.

5-7.2.1.2 Concentration of Analytes

The small volumes of sample available has been the limiting factor in the analysis of fluid inclusions. The determination of cations in inclusions has been performed using a variety of techniques, including the atomic absorption spectrometric determination of Ca, Fe, Mg, Mn, Sr, Ba, cu, Pb and Zn at the ppb level, in inclusions from 5g of mineral, Rye and Haffty[57] and Poty *et al*[58]. ICP-AES determination of a wide range of elements at the ppb level, using 1ml of inclusions, has been reported by Thompson and Walsh[59], and neutron activation analysis of Na, K, Cu, Mn, As, Cs and Zn in the ppb range, again using 1ml of inclusions, by Czamanske *et al*[60], Touray[61], Grappin *et al*[62] and Puchner and Holland[63].

5-7.2.1.3 Sample : Host Mineral Ratio

In addition to the analytical difficulties there also remains the problem of extracting the samples. With a host mineral to sample ratio of typically 1000:1 direct analysis of individual inclusions becomes almost impossible and bulk extraction methods are preferred. Of these bulk extractions, there are primarily two methods described in the literature: thermal decrepitation; and the crush/leach method.

Thermal decrepitation involves heating the sample so that the pressure builds up in the inclusions until they rupture, the contents being ejected or vaporised. Thompson *et al*[64], in their 1980 exploratory work, described the decrepitation of inclusions from 0.5g samples of topaz and carbonatite apatite which were placed in a silica tube through which the nebuliser argon stream from an ICP-AES was passed. The tube was heated and, upon decrepitation, the released inclusions fluids, as vapour were carried to the plasma by the flow of argon.

The crush / leach method, as the name suggests involves crushing a sample to release the inclusions then leaching the inclusions with water and analysing the leachate[65].

Due to previous work at Durham University on the analysis of fluid inclusions in fluorite samples[66,67], a number of reasonably temperature and pressure characterised samples were available. These were analysed using the crush leach technique in accordance with the following method as described by Shepherd, Rankin and Alderton[68].

The workers described previously using AAS and ICP-AES were forced to use large leachate volumes (5ml), and thus large amounts of sample, because of the sample consumption required by conventional nebulization into an ICP. It was believed by Date[69] that using flow injection ICP-MS it would be possible to analyse <500ul leachate solutions for both major and trace elements.

5-7.2.2 Initial Study

A series of fluorite samples from different locations (table 5-7) were prepared in the following manner:

Sample Identification	Colour	Weight (g)
679 Clitheroe	Purple	0.752
5 Rookhope	Green	0.808
109 Rookhope	Green / Purple	0.568
Chiltern Quarry	Yellow	0.240
23 Rookhope	Green	0.294
328 Lake District	Yellow	0.726
386 Cornwall	Green	0.523

Table 5-7. Sample Identifiers and weights used in the initial fluid inclusion study.

The samples were cleaned by an overnight soak in 4%v/v HNO_3:HCl, 1:1, followed by overnight soaking in 18MΩ deionised water, and drying at 70°C for five hours. The samples were then crushed in a pestle and mortar which had been previously cleaned with aqua regia (c̲HCl:c̲HNO_3, 4:1). 1ml of a solution of 50ppb indium in 1%v/v HNO_3 was added, stirred with the crushed sample, and allowed to stand for 10 minutes. The slurry was centrifuged for 1 minute and the supernatant liquor pipetted off. It was observed that, despite the centrifuging, a degree of turbidity was still visible, indicating a suspension of the host mineral in the sample. Samples were flow injected into the ICP-MS using a 250µl loop. That is, approximately one quarter of the total volume of sample available was used per analysis, giving the possibility of triplicate analyses of each sample. Acquisition parameters consistent with the optimum for flow injection were used (mass range 2-255amu, 160 sweeps, 250µs dwell time, 2048 channels, skipped mass regions 12-22amu and 32-42amu). Acquisition duration was 82s and the integration time per isotope was 0.32 seconds. The 50ppb of indium in each solution was used as an internal standard, from which semi-quantitative analyses could be calculated. By estimating the volume of inclusions in the mineral to be approximately 0.1%[70] concentrations may be expressed as parts per million in the original inclusions. These concentrations are shown in table 5-8.

Identification	**679 Clitheroe**	**5 Rookhope**	**109 Rookhope**	**Chiltern Quarry**	**23 Rookhope**	**328 Lake District**	**386 Cornwall**
Colour	**Purple**	**Green**	**Green / Purple**	**Yellow**	**Green**	**Yellow**	**Green**
Li	22	394	184	40	300	18	333
Be	4	27	106	32	91	91	12
B	83	72	112	197	340	57	183
Na	5,750	11,667	17,006	26,827	44,235	10,414	9,801
Mg	514	608	594	1,227	924	513	281
Al	750	753	6,554	2,345	1,626	1,250	461
P	849	838	3,527	7,335	8,693	1,961	1,324
Sc	10	29	59	24	112	18	9
Ti	3,072	4,163	4,005	5,880	4,749	5,150	5,662
V	2	2	4	8	10	<1	<1
Cr	10	9	17	59	47	9	13
Mn	15	241	202	76	260	135	197
Fe	18,513	23,536	24,409	45,800	32,475	33,188	39,316
Co	189	256	223	359	292	365	457
Ni	47	55	63	147	93	82	91
Cu	50	43	85	240	220	74	1,343
Zn	468	1,547	388	703	338	118	117
Ga	3	9	25	Int (Ba^{2+})	831	53	35
Ge	3	5	15	7	29	5	9
As	21	38	52	58	63	26	92

Table 5-8. Results expressed as concentrations in ppm of the original inclusions

Identification Colour	679 Clitheroe Purple	5 Rookhope Green	109 Rookhope Green / Purple	Chiltern Quarry Yellow	23 Rookhope Green	328 Lake District Yellow	386 Cornwall Green
Se	26	48	89	97	176	57	42
Br	134	729	434	382	885	295	111
Rb	4	50	32	13	63	6	29
Sr	937	1,158	1,527	8,706	2,056	1,003	772
Y	44	989	3,558	1,214	4,444	2,605	2,725
Zr	48	12	6	8	9	5	3
Nb	2	1	2	4	5	1	3
Mo	1	<1	2	3	9	2	1
Ru	<1	<1	<1	1	1	1	<1
Rh	<1	<1	<1	1	<1	<1	<1
Pd	2	1	2	4	7	2	2
Ag	3	4	7	11	7	1	5
Cd	8	10	21	47	61	11	13
Sn	2	2	8	8	13	4	24
Sb	1	1	18	4	7	3	7
I	5	3	5	6	14	4	6
Te	1	1	3	6	16	2	2
Cs	1	10	4	2	6	1	38
Ba	15	130	138	52,085	9,559	1,002	712
La	2	218	787	46	570	107	124
Ce	2	361	1,198	94	1,073	209	246
Pr	1	54	192	16	163	34	40
Nd	3	295	908	108	711	211	217
Sm	1	120	455	130	368	160	96
Eu	<1	93	888	114	334	144	18
Gd	2	189	805	83	622	378	218
Tb	<1	22	110	10	84	48	31
Dy	3	142	671	66	525	298	268
Ho	<1	25	101	14	93	43	55
Er	5	74	213	38	180	85	167
Tm	<1	8	22	4	20	8	21
Yb	1	39	116	17	139	38	143
Lu	<1	5	14	3	13	4	18
Hf	804	220	77	82	50	14	12
Ta	1	1	1	2	3	1	2
W	1	10	16	5	18	2	13
Re	<1	<1	<1	<1	<1	<1	<1
Os	<1	<1	<1	<1	<1	<1	<1
Ir	<1	<1	<1	<1	<1	<1	<1
Pt	4	2	2	3	6	1	2
Au	3	1	2	4	7	1	3
Hg	2	3	10	65	26	27	5
Tl	<1	1	1	1	2	<1	1
Pb	28	31	2,967	398	134	2,194	81
Bi	<1	<1	<1	1	1	<1	<1

Th	3	2	4	10	5	1	1
U	3	2	2	4	4	<1	95

Table 5-8 cont'd. Results expressed as concentrations in ppm of the original inclusions

The results for the higher concentration elements show reasonable agreement with Moore's results for these elements[71] in Northern Pennine and Derbyshire fluorites. The data shown here demonstrates notable differences between samples from different areas. An example of this is the significantly higher uranium content in the inclusions from the Cornwall fluorite, presumably due to the high solubility of the uranium fluoride which resulted in the element being concentrated in the inclusions. There is, however, evidence in the data to show that the samples were significantly contaminated by a small amount of the host mineral, the presumed cause of the turbidity observed during the sample preparation. In addition, the high concentration of barium in the Chiltern Quarry sample indicates that the samples contained significant amounts of barium, presumably as barite contamination. High lead values also suggest the presence of small traces of galena.

The concentrations of palladium, silver, platinum and gold were considerably higher than expected for all of the samples and would be indicative of ore deposits. Whilst it may be possible that one of the samples exhibited unusually high levels of these elements, it is extremely unlikely that the same should be true of all members of such a diverse set of samples. The raw data were examined and the isotope ratios for palladium, silver and platinum checked. These were found to be in reasonable agreement with natural values, indicating that the signals were produced by these elements and not by any interfering species. One possibility may be that traces of fluoride from the contaminating mineral had dissolved in the solution and was leaching these elements from the surface of the spray chamber, having been deposited there during a prior analysis.

It was decided to modify the sample preparation technique and to analyse both the inclusions and the host mineral from which the inclusions were extracted. This would hopefully show, on comparison of the two analyses, significant differences.

5-7.2.3 Follow-Up Study

Because of the problems experienced in the initial study, it was decided that rather than use valuable, well characterised samples, it would be more appropriate to use samples of uncharacterised fluorite of which there was a relatively large supply, to allow replicate determinations to be carried out and which, on visual inspection, appeared to be less contaminated by ore or other minerals than the relatively small samples which had been examined by Moore.

Hand specimens were scrubbed and washed before being broken down into chips of 2-6mm diameter. These chips were then sorted to remove any obvious non-fluorite, or ore containing chips, as indicated by opacity when illuminated from behind with a strong light. Further cleaning involved boiling the chips in 50% v/v HNO_3 for 1 hour, followed by 2 rinses in boiling deionised water. Most surface impurities, including ions, were thus removed. Final cleanup was achieved in electrolytic cells using the method described by Shepherd *et al*[72], the purpose of which was to remove ion impurities from the fracture and cleavage planes in contact with the surface and also salts from the inclusions ruptured or broken during the preliminary crushing[73]. The cells were Pyrex 'U' tubes containing de-ionised water into which were immersed platinum electrodes. A DC potential of 60V was placed across the electrodes to bring about the electrolytic cleaning process. The water was changed daily for the first week then twice weekly for the next 2-3 weeks. The process was continued until the conductivity of the solution had reached a steady value. After cleaning, the chips were dried at 70°C and one gram of sample was crushed in a mortar and leached with 10ml of deionised water in an ultrasonic bath.

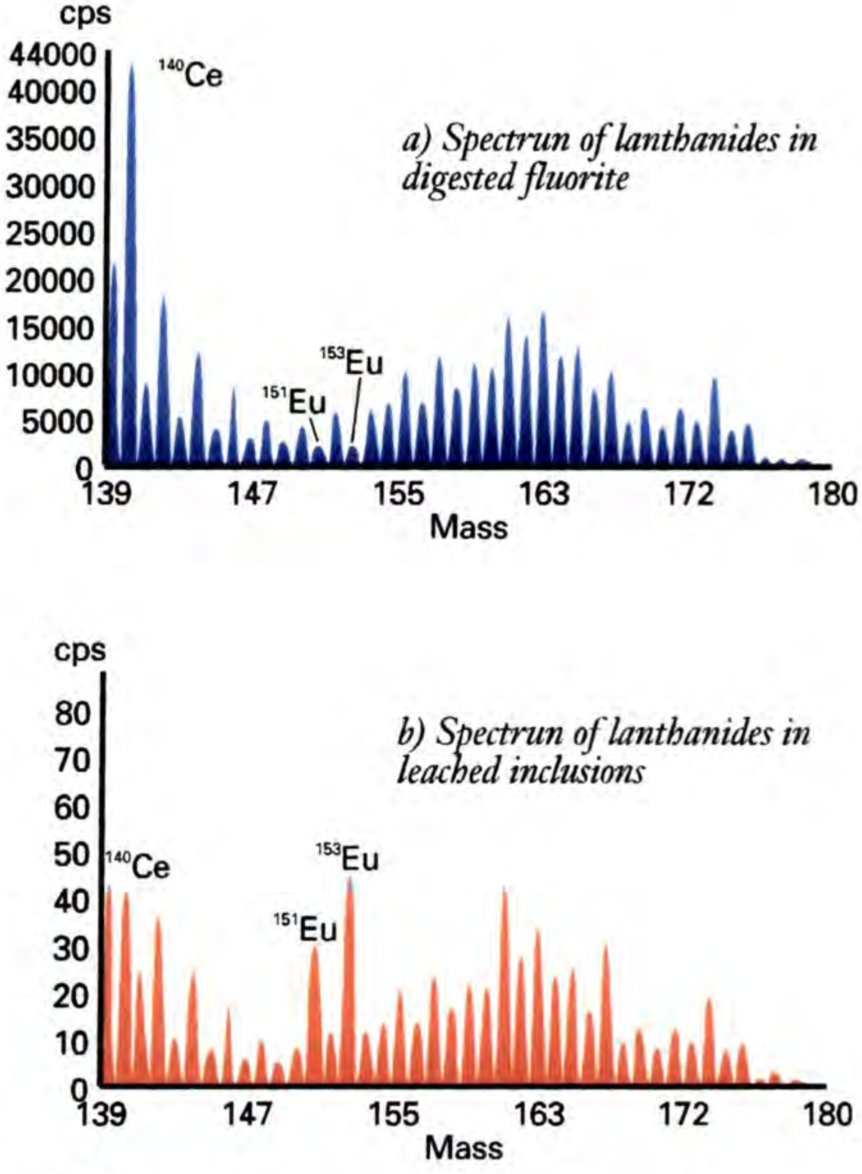
	Yellow Fluorite		Purple Fluorite	
	Inclusions (ng inclus'n/g Fluorite)	Matrix (ng/g Fluorite)	Inclusions (ng inclus'n/g Fluorite)	Matrix (ng/ g Fluorite)
Be	0.5	24.6	0.4	12.7
B	22.1	<0.1	27.8	<0.1
Na	678	<0.1	1,760	421
Mg	25.2	<0.1	55.3	ND
Al	<0.1	<0.1	<0.1	<0.1
P	<0.1	<0.1	<0.1	745
Ca	20,301	<0.1	20,285	ND
Sc	<0.1	6.9	<0.1	9.7
Ti	<0.1	25.7	<0.1	22.2
V	<0.1	0.9	<0.1	0.8
Cr	1.5	0.7	2.1	1
Mn	21.3	4.4	23.4	7.9
Fe	<0.1	2,001	<0.1	2,285
Co	0.2	0.8	<0.1	1.0
Ni	27.1	1.0	<0.1	1.5
Cu	5	1.0	<0.1	1.6
Zn	6.8	<0.1	<0.1	<0.1
Ga	<0.1	1.2	<0.1	0.9
Ge	<0.1	0.3	<0.1	0.5
As	<0.1	0.4	<0.1	0.5
Br	<0.1	5.5	<0.1	0.5
Se	<0.1	3.1	<0.1	1.7
Rb	0.5	2.6	<0.1	<0.1
Sr	12.9	76.5	<0.1	30.6
Y	3.4	3,154	6	3,793
Zr	<0.1	0.3	0.2	0.2
Nb	<0.1	0.2	<0.1	<0.1
Mo	<0.1	0.1	<0.1	<0.1
Ru	<0.1	<0.1	<0.1	<0.1
Rh	<0.1	<0.1	<0.1	<0.1
Pd	<0.1	<0.1	<0.1	<0.1
Ag	<0.1	<0.1	<0.1	<0.1
Cd	<0.1	<0.1	0.2	<0.1
Sn	<0.1	<0.1	1.3	<0.1
Sb	0.2	<0.1	<0.1	<0.1
I	0.2	<0.1	<0.1	<0.1
Te	<0.1	0.1	<0.1	<0.1
Cs	0.1	<0.1	<0.1	<0.1
Ba	10.1	2.6	<0.1	1.4
La	<0.1	3.5	<0.1	26.2
Ce	0.1	9.7	0.5	38.8
Pr	<0.1	2.0	0.1	39.8
Nd	0.2	11.4	0.5	25.8
Sm	0.1	8.7	0.2	34.5
Eu	0.2	12.1	0.5	16.4
Gd	0.3	19.9	0.5	35.5
Tb	<0.1	2.9	0.1	38.8
Dy	0.3	18.8	0.7	21.6
Ho	<0.1	2.9	0.1	5.6
Er	0.1	6.1	0.2	11.3
Tm	<0.1	1.3	<0.1	1.1
Yb	<0.1	2.4	<0.1	2.8
Lu	<0.1	<0.1	<0.1	1
Hf	<0.1	<0.1	<0.1	0.5
Ta	<0.1	<0.1	<0.1	<0.1
W	0.1	<0.1	0.4	0.1
Re	<0.1	<0.1	<0.1	0.1
Os	<0.1	<0.1	<0.1	<0.1
Ir	<0.1	<0.1	<0.1	<0.1
Pt	<0.1	<0.1	<0.1	<0.1
Au	<0.1	<0.1	<0.1	<0.1
Hg	<0.1	<0.1	<0.1	<0.1
Tl	<0.1	<0.1	<0.1	0.1
Pb	0.3	<0.1	0.2	<0.1
Bi	<0.1	<0.1	<0.1	<0.1
Th	<0.1	<0.1	<0.1	<0.1
U	<0.1	<0.1	<0.1	<0.1

Table 5.8. Elemental concentrations of the inclusions and fluorite matrix investigated in the follow up study, (ppm).

The solutions were filtered through 0.22 µm Millipore membrane filters to remove any suspended particles of fluorite. Analysis was performed using a 200 µl loop, with the same instrument conditions as described in section 5-6.2.2.

The residual fluorite was digested by heating 0.1g of sample with 0.5g of Aristar grade H_3BO_3 and 5ml "semiconductor grade" concentrated HNO_3. This method was derived from a method used by Bernas[74] for the analysis of insoluble fluorides. The method was adapted because Bernas used hydrochloric acid which, as outlined in chapter 2, produces significant signal suppression and also produces molecular interferences on isotopes of vanadium, arsenic and selenium. As described in chapter 2, nitric acid causes the least suppression and results in the least amount of interfering species and was therefore used in place of hydrochloric acid. The digested fluorite was spiked with a 50ppb indium internal standard and analysed using the same instrument conditions as those for the analysis of the inclusions.

Of particular interest are the rare earth elements, because these are not exclusively partitioned into either phase. The concentrations in the inclusions are very close to the detection limit of the method, which constrains both the precision and the accuracy of the work. In order to improve the accuracy, the analysis for both inclusions and matrix of the yellow fluorite was repeated, using the same acquisition parameters, but limiting the scanned mass range to 138-180amu, so that only the lanthanides were scanned. Fig. 5-13 shows the mass spectra of the lanthanide elements in both the inclusion (Fig. 5-13a) and the host mineral (Fig. 5-13b). It can be seen that, while the overall pattern of the lanthanides is similar in both spectra, as was found with the previous, whole mass range investigation, the Ce/La ratio is significantly higher in the mineral than in the inclusions ($Ce/La_{mineral} = 1.97$, $Ce/La_{inclusions} = 0.97$) suggesting partial substitution of cerium for calcium in the fluorite lattice. Conversely, the Eu/La ratio is significantly higher in the inclusions than in the mineral ($Eu/La_{mineral}$ = 0.27, $Eu/La_{inclusions}$ = 0.72), suggesting an incompatibility with the mineral phase.


a) Spectrun of lanthanides in digested fluorite

b) Spectrun of lanthanides in leached inclusions

Figure 5-13: ICP-MS spectrun for lanthanides in digested fluorite and leached inclusions

Although the results from these studies are of limited usefulness on their own, they do show that by using flow injection a great deal of information can be obtained. Had time permitted, a further investigation of temperature / pressure calibrated fluorite samples would have been undertaken to investigate the effect of formation temperature and pressure on the partitioning of elements such as the rare earths.

5-7.3 Reduction of Matrix Suppression Effects

The analysis of solutions containing high concentrations of matrix elements, for example (NaCl) brine solutions, is problematical for both ICP-AES and ICP-MS. Such solutions cause a suppression of the analyte signal, which is directly related to the concentration of the matrix elements and is believed to arise from a combination of ionisation suppression[75] and space charge effects[76]. As discussed in chapter 3, it has been found that this effect is negligible at salt (matrix element) concentrations <0.1% w/v, but becomes progressively more significant as the salt concentration is increased, so that at 5% NaCl (the maximum salt content which may be aspirated before matrix depositions at the sampling interface becomes significant) the analyte signal is suppressed such that only 30% of the corresponding aqueous signal remains. This is obviously detrimental to the detection limits which can be achieved in such solutions. Whilst dilution of the sample reduces the salt content and thus also the suppression, the detection limits are then compromised by the dilution factor. Ion exchange techniques which could be used to remove the sodium would be likely to remove analyte elements as well. Fig 5-14 shows the time profile of an aqueous signal for In at 115 amu with the corresponding signal in a 27% NaCl solution overlaid.

It can be seen that when, injecting the brine solution, the signal initially follows the aqueous profile, but when the salt concentration in the plasma exceeds a certain level, the signal is suppressed and the signal diminishes. When the salt level falls below the level at which suppression occurs, the signal then starts to rise and again and follow the aqueous profile until all of the sample has passed out of the system.

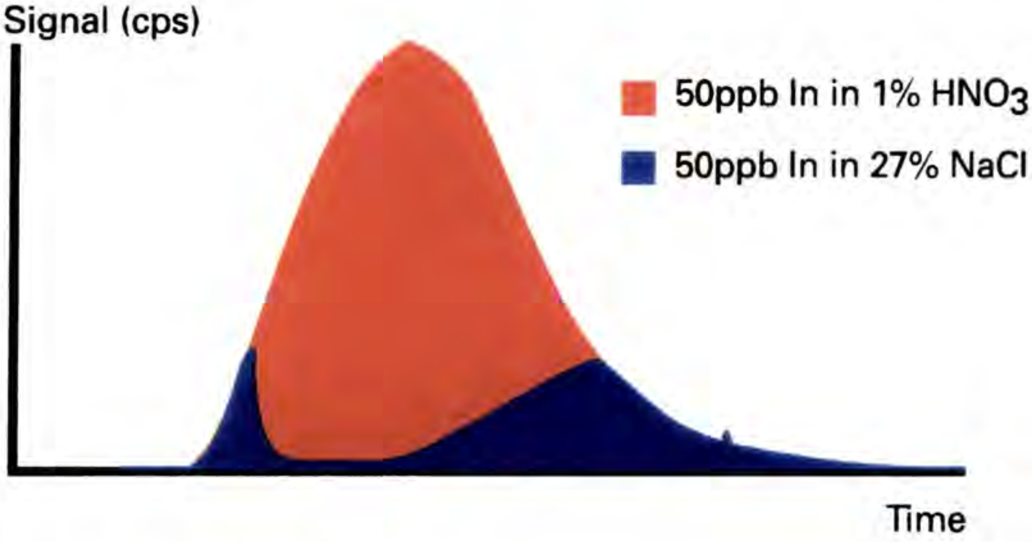


Figure 5-14: Time profiles obtained for 50ppb In in dilute HNO_3 *and 27% NaCl*

In order to maximise the signal it is possible to change the shape of the signal profile so that, while maintaining the same area, the peak height is reduced, hence more of the signal is kept below the suppression threshold, Fig. 5-15. This may be achieved by altering the dispersion of the system, a technique used since the very early days of flow injection[77]. Because the sample is continuous with the carrier flow, there is inevitably a certain amount of mixing, termed dispersion, between the two. One of the important advantages of flow injection is the fact that this dispersion is both reproducible and adjustable. Dispersion is affected by such parameters as pumping rate and sample / carrier viscosity ratios, but is primarily controlled by the diameter of the tubing used, or by the inclusion of a mixing chamber[78]. By increasing the diameter of a portion of the tubing between the injection loop and the ICP-MS the dispersion of the system may be increased. The effect of changing the level of dispersion on the signal / time profile is shown graphically in Fig. 5-15. Although the area of the signal peak for each dispersion is constant, the maximum height of the peak is inversely proportional to the dispersion. It can be seen that, by scanning longer on a higher dispersion system, most of the signal is kept below the suppression threshold and therefore a greater signal to noise, or reduction in the level of signal suppression, could be achieved.

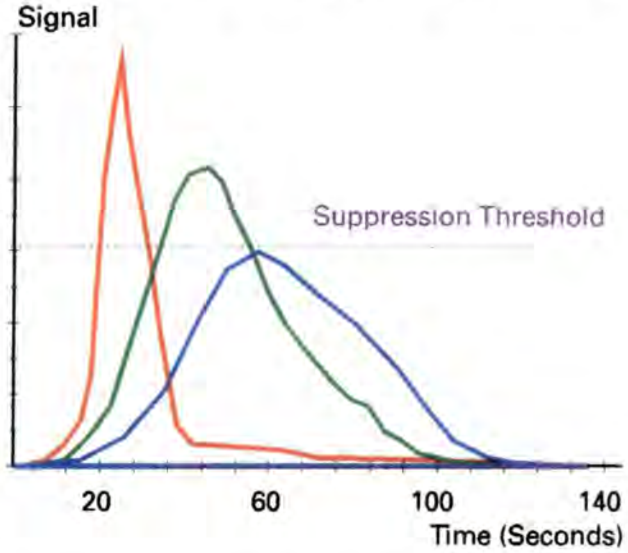


Figure 15: The effect of dispersion on maximum signal intensity

The effect of dispersion on the suppression produced for various concentrations of brine solution was investigated. Solutions were prepared containing 5, 10 and 27% w/v NaCl, acidified with 1% HNO_3. These, and a blank acid solution, were spiked with 100ppb of cobalt, indium and uranium.

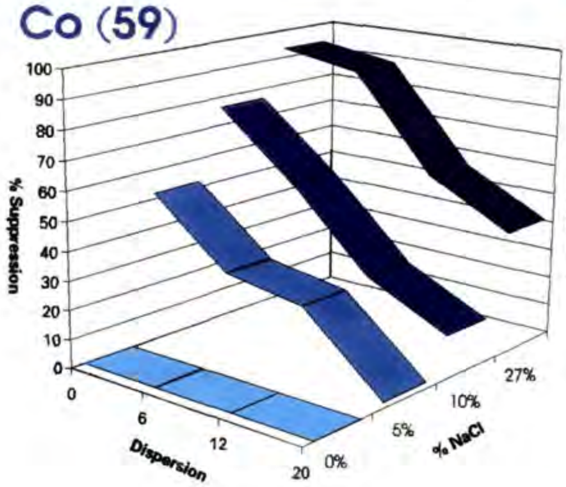
Dispersion was varied by the inclusion of a section of tubing of wider diameter than the 1/16"o.d. tubing used in the rest of the system. Although it would have been possible to use varying coiled lengths of the standard tubing this approach was rejected on account of the delay which would have been introduced in the analysis. Three mixing chambers were prepared, using various diameter tubing, and these were inserted into the line between the injection loop and the peristaltic pump. The time profile for mass 115 (indium) was obtained for injection of the aqueous solution with each of the mixing chambers. In addition, the time profile for continuously aspirated indium was measured.

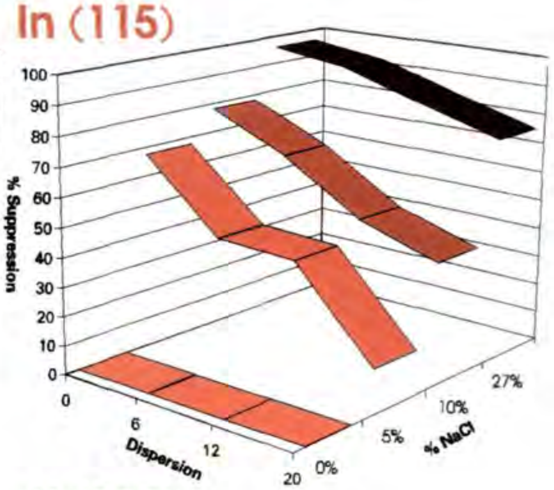
In order to determine the dispersion for each system the area of the signal under each time profile was measured. Because the width of the signal varied, that is became greater with greater dispersion, this value was ratioed to the average height of the continuous signal multiplied by the width of the time profile signal (in number of channels). It was found that the mixing chambers resulted in dispersions, D_A of approximately 6, 12 and 20.

The experiment was repeated, but with the instrument in scanning mode, (58-238amu), using a 2 minute acquisition, (100 sweeps, 1024 channels and a dwell per channel of 1024µS). This was slightly longer than the duration of the profile for D_A=20, and considerably longer than the duration of the low dispersion signal, but because the background in ICP-MS is relatively stable this would not appreciably reduce signal to noise and was therefore felt to be an acceptable compromise. The aqueous solution and the three brine solutions were injected into each of the systems, and the percentage supression, relative to the unsuppressed aqueous solution, was calculated.

Fig. 5-16 shows a plot of degree of suppression, expressed as a percentage of the unsuppressed aqueous equivalent, versus dispersion for the three elements, (Co, In & U), at each of the three brine concentrations. Since the background level is relatively unchanged detection limits are improved because the degree of suppression is reduced.

The ability to control dispersion using flow injection may therefore be used to reduce matrix induced signal suppression, such as that created by high salt concentration in samples such as fluid inclusions and hydrology studies.





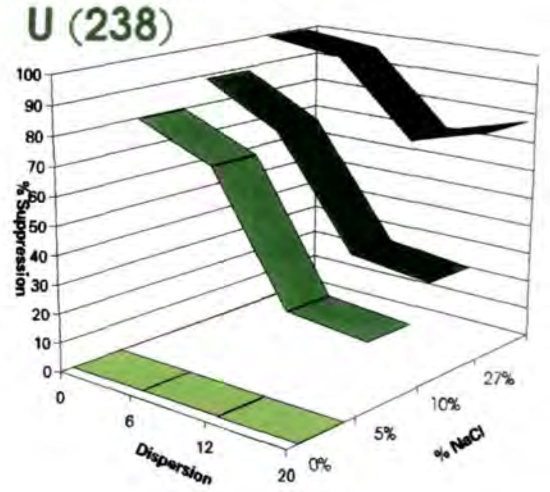


Figure 5-16: Percentage suppression at various dispersions for 0, 5%, 10% and 27% brine solutions, for the elements Co, In and U

5-7.4 Increased Matrix Tolerance

Perhaps the most significant advantage to coupling flow injection to ICP-MS is in the reduction of the amount of sample transported through the sample introduction system. The constraints on sample matrix in ICP-MS have been described by Hutton and Eaton[79]. As concluded in chapter 3, if a way could be found to alleviate these restrictions, it would be possible to determine directly elements such as the platinum group which are present at very low concentrations.

As was demonstrated in section 5-5.1, and shown graphically in Fig. 5-12, considerably less sample is introduced when using flow injection compared to conventional aspiration. This results in less material reaching, and thus able to deposit, on the sampling interface. A conservative estimate is that less than one fifth to one tenth of the material is deposited. In theory therefore a five times greater concentration could be aspirated without significant cone blockage There would, however, be some reduction in the sensitivity of the instrument for flow injection relative to continuous nebulization due to the shape of the response profile produced by flow injection (Gaussian) having a smaller area than the corresponding 'flat topped' integration area produced by continuous nebulization typically by a factor of 2-3. Average crustal abundances for the PGM's have been estimated by Taylor[80] at typically <10 $ng.g^{-1}$ in the solid sample and should thus be detectable by ICP-MS in unseparated whole rock solutions containing around 10% dissolved solids.

The samples were prepared by a modified version of the digestion described in chapter 3, section 3-5.5. The sample weight was increased from the 0.1g used in chapter 3, to 1g, reagent volumes being increased proportionally. In order to avoid losses due to the instability of platinum group metals and gold in nitric acid solution, once the solution had been evaporated until evolution of fumes of perchloric acid the residue was taken up in 4ml of Aqua Regia (3:1 HCl:HNO3) and diluted to 10ml, giving a final solids content of 10%w/v. Solutions were spiked with a 50ppb indium internal standard. Silver and osmium were not determined because of the likelihood of their being lost during sample preparation (silver by precipitation as AgCl and osmium volatilised as OsO_4). Calibration was performed relative to external aqueous standards of concentrations 0, 10, 20 and 50 ng.ml-1. Injections were made on a low dispersion system, using a 200µl loop.

Acquisition was performed in scanning mode from 95-200 amu, skipping masses 116-184 amu. 2048 channels were used with a dwell time of 500µs. The instrument software calculated the number of sweeps, based on the duration of the injection of a 50ppb indium time profile for mass 115, and hence the duration of the acquisition. The required number of sweeps was calculated at 149, giving a total acquisition time of 152 seconds. Five determinations were performed for each sample and a digestion blank.

Table 5-9 shows the mean concentrations, precisions and detection limits for PGM's for the geochemical standards G1 and PCC-1. These standard were chosen because they are well characterised for the plantinum group and gold, and the likelihood of having few polyatomic overlaps on the PGM's or gold.

Element	3σ Detection Limits (ng/g)	G1			PCC-1		
		Reference Value (ng/g)	Mean Value (ng/g)	Standard Error (n=5)	Reference Value (ng/g)	Mean Value (ng/g)	Standard Error (n=5)
Ru	0.2	-	1.12	0.09	10	8.6	0.77
Rh	0.07	-	0.76	0.07	1.4	0.8	0.03
Pd	0.03	1.9	9.5	0.57	5.4	8.7	0.57
Ag	0.2	44	37	2.98	(8)	13.3	0.94
Re	0.04	0.63	0.53	0.04	(0.058)	0.88	0.04
Ir	0.04	2	1.26	0.04	4.8	1.76	0.06
Pt	0.09	8	5.9	0.27	8	6.77	0.34
Au	0.03	3.2	3.9	0.25	0.79	1.21	0.08

Table 5-9: Results obtained by flow injection analysis of 10%w/v solutions of G1 and PCC-1

When using flow injection, precisions are typically better than 5% RSD. Acceptable accuracy's are obtained, compared to working values with the exception of Pd which gave a considerably higher value than the reference. This may have been due to the presence of an $^{40}Ar^{65}Cu^+$ polyatomic, since the digestion blank showed no significant contamination with Pd. This species was thought to arise due to the presence of around 10 ppm of copper in the original rock in both standards (Govindaraju[81]) which corresponded to a Cu concentration in the solution of 1 ppm.

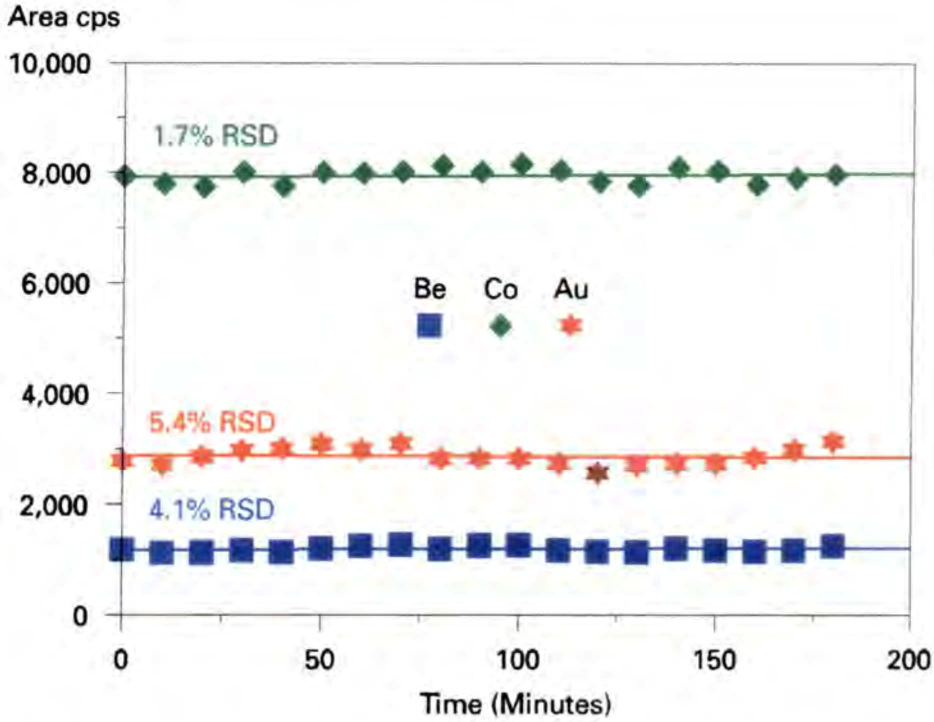


Figure 5-17: Stability over 3 hours for a spiked 10% w/v granite solutior

The excellent standard errors and accuracy tended to suggest that no significant cone blockage was evident throughout the duration of the experiment, although this was still a major concern. Therefore the stability of the signal signal over an extended period was investigated. Fig. 5-17 shows the stability over four hours when analysing a 10% w/v granite solution spiked with beryllium, cobalt and gold to 100ppb. A 200 µl sample was injected every 10 minutes for 4 hours. It can be seen that absence of any discernable downward trend in the signals confirms the view that no significant cone blockage occurred. The percentage relative standard deviations for the measurements were in the range 4-6%. Under the same conditions, continuous nebulization of this sample, with the introduction of a 1% nitric acid wash solution between samples, was found to block the sampling orifice after only 3 acquisitions (20 minutes).

5-8. Conclusion

In the field of geochemical analysis, FI-ICP-MS has the potential to:

- Increase sample throughput
- Facilitate small sample handling
- Reduce matrix suppression effects
- Increase matrix tolerance and thus allow lower detection limits to be achieved where, as in the case of geological analysis, the levels are limited by the matrix tolerance of the system

Purely on its merits of alleviating matrix effects, flow injection will almost certainly become an important addition to ICP-MS instruments in the future. Other techniques have used flow injection to perform such activities as on-line pre-concentrations, automatic calibrations by standard addition, and automatic sampling for industrial processes. As more users of ICP-MS become familiar with the capabilities and potential of flow injection, this rapidly growing technique will become commonplace in geochemistry laboratories world-wide.

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Chapter 6

Electrothermal Vaporisation ICP-MS

6-1 Introduction

Electrothermal vaporisation, in the form of a graphite furnace, was first used by L'Vov[1] to introduce microlitre amounts of sample into an atomic absorption spectrophotometer. Although slow, subject to many matrix effects and requiring a lot of skill on the part of the operator, the technique of graphite furnace atomic absorption spectrometry (GFAAS) soon found favour, due simply to the fact that it improved detection limits by up to 4 orders of magnitude.

In graphite furnace atomic absorption spectrometry, the sample is injected into a graphite tube which is then heated resistively. The heating is controlled through drying, ashing and finally atomisation to produce a vapour of sample atoms which absorb light of a characteristic wavelength which is specific to the element of interest. The improvement in detection limit arises largely from the fact that the furnace gives almost 100% transport efficiency, compared to the typically 1% efficiency of nebuliser systems.

When ICP-AES was developed, the furnace was again seen as a way to improve detection limits. Nixon *et al*[2] were the first group, in 1974, to describe the use of the furnace technique with ICP-AES, although Kleinman and Svoboda[3] had also reported the use of electrothermal vaporisation in atomic emission with a low power and frequency electrodeless discharge in 1969. The design of the furnace used for ICP-AES differed from that used with graphite furnace atomic absorption spectrometry. In the latter, the furnace was being used to vaporise and atomise the sample, hence the primary consideration was to retain the vaporised sample in the optical path of the instrument for as long as possible. For ICP-AES, however, the furnace acts simply to vaporise the sample, so that it could be carried into the plasma along the nebuliser argon flow.

Materials other than graphite have been used. A tantalum strip furnace used by Nixon *et al*[4] gave detection limits 1-2 orders of magnitude better than continuous nebulisation. Kitazume used platinum and tungsten filaments[5]. A graphite cup coated with pyrolytic graphite or tantalum carbide was used by Ng and Caruso[6,7,8,9] who obtained detection limits in the ppb range with a dynamic range of 4 orders of magnitude.

The first studies into the use of electrothermal vaporisation in ICP-MS were by Gray and Date[10], and Gray[11] who reported absolute detection limits of about 10pg and, more importantly, a reduction in the observed levels of oxide species in the spectrum. This was predictable since the water, the source of the oxygen, was removed prior to analysis during the drying stage. Such a reduction in oxide levels was found to extend the range of possible applications of ICP-MS. Whittaker *et al*[12] used ETV ICP-MS to measure iron isotope ratios in blood for a stable isotope study of iron uptake in pregnant women.

6-2 Hardware

Early research which coupled furnaces with ICP-AES and ICP-MS (Gray and Date[13], Gunn *et al*[14], Darke *et al*[15], Date and Cheung[16], Whittaker *et al*[17]) used a design of furnace based around a modified GFAAS furnace in which the furnace was enclosed in a glass chamber approximately 1 litre in volume. However, this caused problems because of the very large dead volume present in the jar. The first furnace designed specifically for ICP-MS, by Park *et al* [18], also used a glass chamber, but reduced in volume to 5ml.

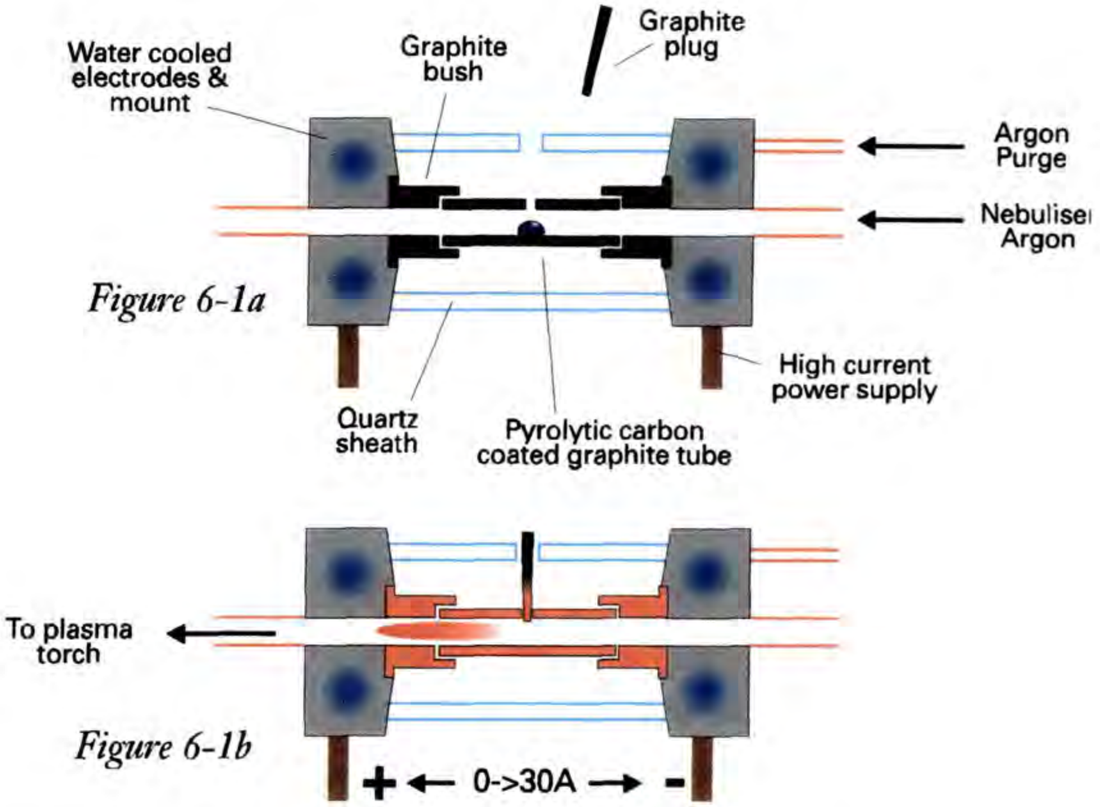

Figure 6-1: Schematic of the electrothermal vaporisation ICP-MS system (a) loading sample (b) vaporising

A schematic of the electrothermal vaporisation ICP-MS system used in this work is shown in Figs. 6-1 & 6.2. The furnace is a tube of high purity graphite coated with a layer of pyrolytic graphite to prevent adsorption of sample elements onto the tube and thus minimise crossover contamination. The tube is surrounded by a quartz tube through which passes a flow of argon to exclude air and thus prevent oxidation of the graphite when heated. The nebuliser argon passes through the graphite tube and on to the plasma torch. A major difference between the designs for AAS and ICP work is that the hole at the top of the tube, through which the sample is introduced, must be sealed to prevent loss of analyte and nebuliser gas. This is achieved with a graphite plug, of the same purity as the furnace tube. Electrical connection at either end of the tube is achieved by means of water cooled, spring loaded electrodes, the water cooling being required to cool down the furnace in a reasonable timescale. This assembly also forms the mounting for the furnace and is therefore covered both to prevent contact with the live terminal, and also to protect the user from the ultraviolet radiation produced when the furnace is operated at high temperatures.

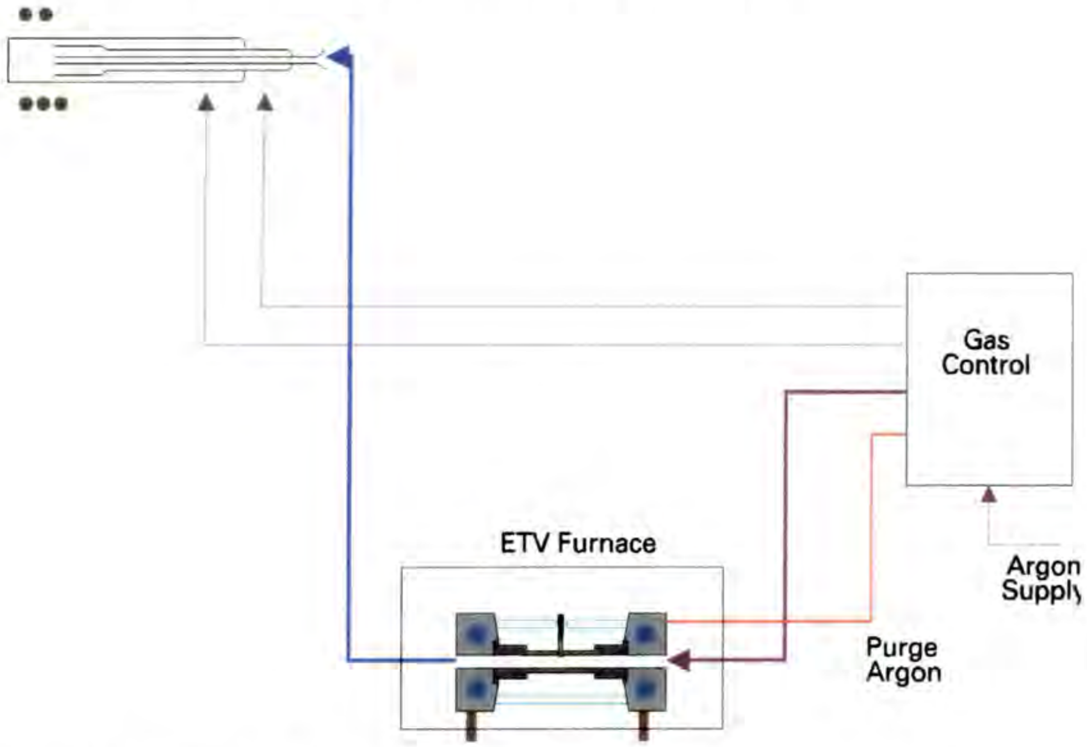

Figure 6-2: Schematic of the ETV ICP-MS system

The power supply is capable of handling up to 30Amps, the output being set by computer control. Temperature feedback is provided by resistance measurement at low temperature and an optical pyrometer fed via a fibre optic bundle at high temperatures. In this way the heating rate and absolute temperature of the furnace is controlled precisely and can be changed rapidly to allow fast heating cycles if required by the analytical methodology.

6-3 Optimisation

Park *et al*[19], optimised the system by first tuning on a solution introduced by conventional nebulisation and by then switching to electrothermal vaporisation. This is however not valid because the optimum conditions differ strongly for a 'wet' and a 'dry' plasma[20,21]. A more appropriate method (Date and Cheung[22], Whittaker *et al*[23], Gregoire[24], Hall *et al*[25]) is to slowly vaporise a volatile element, such as cadmium or mercury, and optimise on the resulting signal.

In this work advantage was taken of a gaseous inlet system originally designed to allow small amounts of oxygen to be introduced reproducibly into the nebuliser flow when aspirating organic solvents. The system comprised a second mass flow controller which was ratioed to the primary (nebuliser) mass flow controller so that an exact ratio between 0 and 1% of the two gases could be achieved. This was used to introduce 0.05% gaseous methyl iodide into the system. The advantage of this approach was that the resulting signal was continuous and did not require the furnace to be operated, thus allowing time for a more accurate optimisation to be achieved.

6-3.1 Heating Profile

The type of heating profile used in electrothermal vaporisation work is dependent upon the type of samples being analysed as well as the nature of the analyte elements. This work concentrated on the platinum group metals and gold because of the additional detection limit requirement. Solutions of digested geological material, unlike biological samples, do not require complex ashing procedures to remove the organic content of the sample. The heating profile used therefore consisted simply of three stages: drying at 125°C for 40 seconds; a slow heating to 400°C and maintenance at this temperature for 30 seconds;

followed by rapid heating in 2 seconds to a temperature of 2300°C and maintenance at this temperature for 7 seconds. The heating profile is shown graphically in Fig. 6-3. This vaporisation temperature was also used by Hall *et al*[26] for GFAAS determination of gold, palladium and platinum in ashed vegetation.

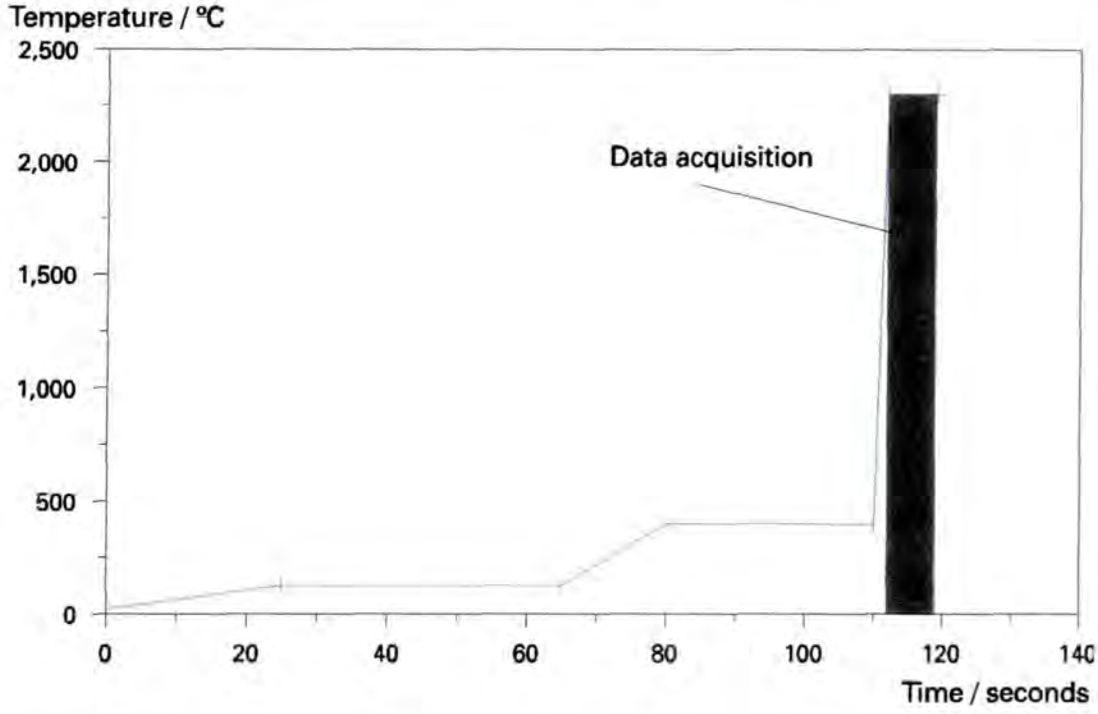

Figure 6-3: ETV-ICP-MS heating profile for the PGM's and gold

6-4 Element Profiles

In order to ensure that the proposed heating profile was appropriate for the analyte elements a series of time profiles were obtained, one for each element.

A solution of 10ppb of Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au in 5% v/v HCl was prepared and 20µl injected onto the furnace. Instead of acquiring multiple scans during the vaporisation phase, a time profile for a single element was measured throughout the entire duration of the heating cycle. The profiles obtained are shown in Fig 6-4., with the temperature profile overlaid. Profiles for rhodium and ruthenium have been omitted from Fig 6-4 for the sake of clarity, but are very similar to those obtained for silver and platinum respectively.

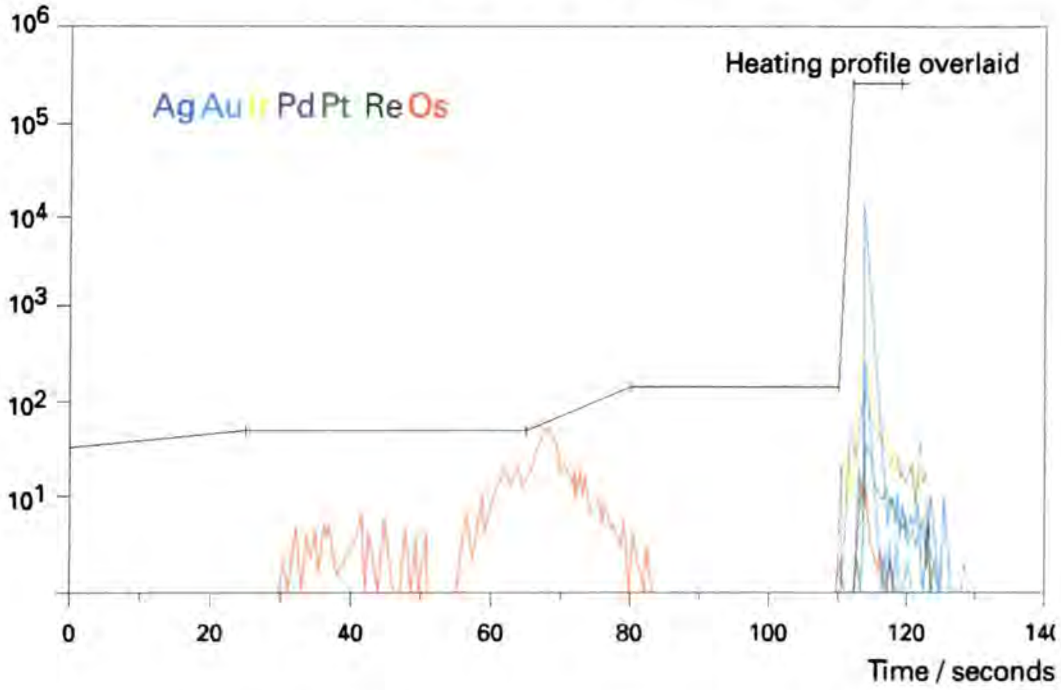

Figure 6-4: Single element profiles for the PGM's and gold

It can be seen that, with the exception of osmium, the analytes vaporised during the high temperature stage. Osmium was found to vaporise when the furnace reached 400°C, with only a small residue vaporising at the high temperature stage. Had this experiment not been performed, it would have been assumed that the low osmium figures were due to loss of the element at some stage during the sample preparation.

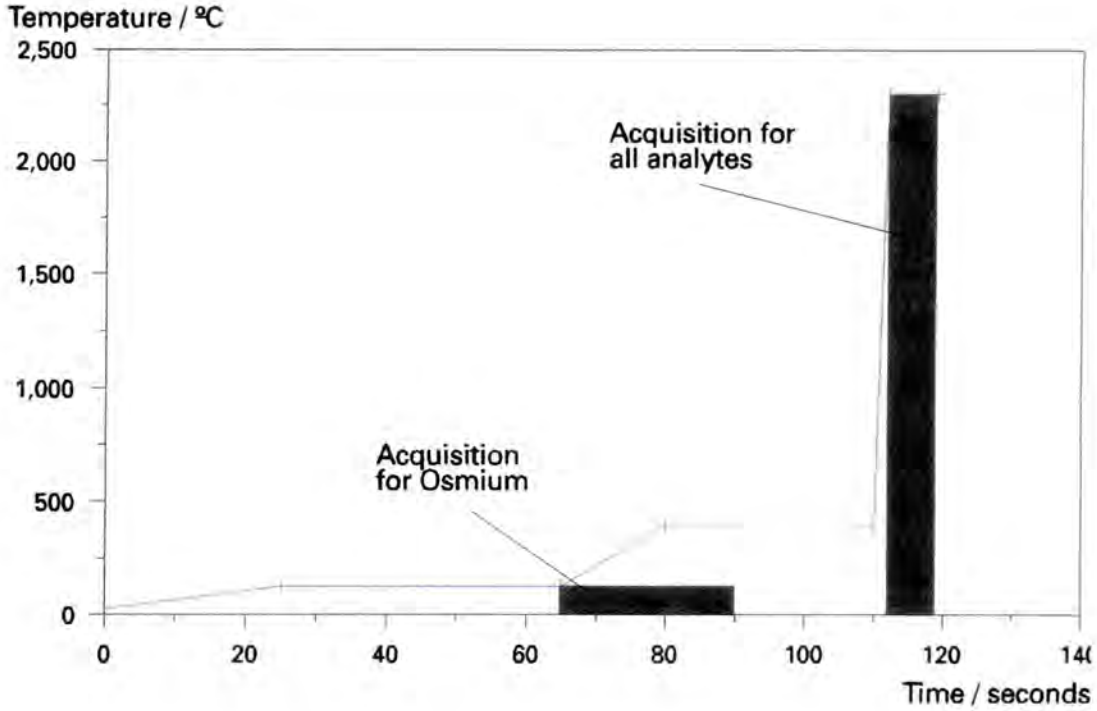

Figure 6-5: Modified ETV-ICP-MS heating profile for the PGM's and gold

As a result of this experiment, the heating profile was changed (Fig. 6-5). The instrument software allows for multiple acquisitions to be performed during a vaporisation cycle, thus another acquisition was set at the start of the 400°C stage in order to determine osmium.

Mass range	97.9-200.95 amu
Skipped mass regions	117-183 amu
Number of sweeps	110
Dwell time per channel	80μ s
Number of sweeps	1,024

Table 6-1 Instrument operating conditions for the ETV ICP-MS detection limit experiment

6-5 Instrument Detection Limits and Calibration Graphs

Detection limits for the platinum group metals and gold were determined using the heating profile shown in Fig. 6-5, and the instrument operating conditions are given in table 6-1. A series of blank solutions and standards of concentrations: 1, 10, 30 and 50 ppb of the analyte elements were run. 12 determinations of the blank and three determinations of each standard were made. The calculated detection limits are shown in table 6-2 and the calibration graphs Were linear

	Blank (n=10)		1ppb Std		LOD (ppt)
	Mean	Std Dev.	Mean	% RSD	3σ
Ru	4	1.83	465	8.2	11.8
Rh	51	23.24	5160	3.8	13.5
Pd	12	1.52	1605	2.2	2.8
Ag	36	36.39	9237	10	11.8
Re	15	10.09	768	17.4	39.4
Os	6	4.31	612	14	21.1
Ir	9	6.22	2322	9.7	8.0
Pt	4	1.83	1902	5	2.9
Au	16	12.08	3561	22.4	10.2

Table 6-2. Solution detection limits by ETV ICP-MS

The detection limits are typically 10ppt in solution which, assuming no matrix effects and a dilution factor of 1000 (0.1g in 100ml), corresponds to 10ppb in the original rock. This is still too high for the routine determination of the pgm's in most rocks, being approximately equal to the average crustal abundances of these elements[27].

Precisions for the high concentration solutions (50ppb) were found to be between 2 and 22% relative standard deviation. Although poor by the standards of other techniques, this is typical for manually injected electrothermal vaporisation work, Park and Hall having reported precisions of 20%[28], although the use of an isotope dilution calibration strategy ultimately resulted in analytical precisions of 1-2%.

6-6 Application to the Determination of the PGM's

The international standards G1, G2, AVG-1, GSP-1 and PCC-1 were prepared using the acid digestion method described in section 3-5.5, but the amount of sample was increased to 2g and the reagent quantities similarly increased to give a final solution containing 2% dissolved solids. This was because such a small amount of solution (20μl) was aspirated, there would be much less chance of causing cone blockage. Acquisition was performed using furnace and acquisition parameters identical to those described in section 6-5. Calibration was performed relative to aqueous standards of concentrations 0, 20 and 50 ppb. Both samples and standards were spiked with an indium internal standard to a concntration of 20ppb.

When running the 2% solution samples it was found that a rapid decrease in internal standard countrate was observed after the first two injections. Acquisition was halted and the cone examined. Significant deposition of sample material on the cone was observed. Although the injected amount of sample was significantly less than for conventional solution nebulisation, in electrothermal vaporisation all of the sample is vaporised whereas nebuliser systems are inefficient and perhaps only 1% of the sample actually reaches the plasma. Additional sensitivity could not be gained from running a more concentrated solution. Therefore, the samples were diluted to the more normal 0.2% dissolved solids and the acquisition was repeated. The results are shown in table 6-3.

Results above the detection limit were only obtained for silver which was present at relatively high concentrations, although the palladium concentration in PCC-1 was determined, but with significant error.

	G1		G2		AGV-1		GSP-1		PCC-1	
	Granite		Granite		Andesite		Granodiorite		Peridotite	
	Ref	*ETV*	*Ref*	*ETV*	*Ref*	*ETV*	*Ref*	*ETV*	*Ref*	*ETV*
Ru	NV	<10	NV	<10	NV	<10	NV	<10	10	<10
Rh	NV	<10	NV	<10	NV	<10	NV	<10	1.4	<10
Pd	1.9	<5	0.25	<5	2.2	<5	1.2	<5	5.4	11
Ag	43	46	31	57	104	99	86	103	3.5	<10
Re	0.63	<10	NV	<10	0.4	<10	NV	<10	0.058	<10
Os	0.11	<10		<10		<10		<10	7	<10
Ir	2	<10	0.4	<10	0.4	<10	0.3	<10	4.8	<10
Pt	8	<10	5.9	<10	1.1	<10	NV	<10	8	<10
Au	3.2	<10	1.03	<10	0.6	<10	0.1	<10	0.79	<10

Table 6-3. Results (ppb) obained by ETV. NV=no reference value

Though disappointing, these results are consistent with other workers in this field who have published data on low concentration elements in geological samples using electrothermal vaporisation ICP-MS. Amongst these the most notable is Gregoire[29,30] at the Canadian Geological Survey who used the nickel sulphide fire assay to preconcentrate the platinum group metals and gold prior to analysis followed by isotope dilution to obtain accurate results with the use of a 500ppm nickel matrix modifier to increase sensitivity.

Park and Hall[31], also of the Canadian Geological Survey, reported the use of electrothermal vaporisation ICP-MS for the determination of thallium in geological materials, and recorded a detection limit of 9 ppb.

6-7 Conclusions

Whilst the technique of electrothermal vaporisation in ICP-MS has the potential for useful application to the determination of low concentration elements in geological materials, as demonstrated in this research and by other workers a great deal more work is required to refine the method.

The primary concern lies in the detection limits that can be achieved. Whilst other workers have reported incredible detection limits for elements such as plutonium in biological matrices[32], the matrix tolerance difficulties experienced in determining such levels of elements in refractory matrices such as rocks are likely to prevent any significant improvement in the technique, necessitating a recourse to sample preconcentration methods such as fire assay and ion exchange versus solvent extraction processes.

Another particular concern is the precision which can be attained by the technique. Although an automated sample injection system would no doubt remove some of the operator induced irreproducibility, precisions are still likely to be poor, especially when detection limits are being pushed to the extreme.

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Chapter 7

Laser Ablation ICP-MS

7-1 Introduction

The primary method of introducing a sample into an ICP-MS is in the form of a solution. This represents a limitation in terms of geochemical analysis since very few of the samples to be analysed are naturally liquids, nor are they readily dissolved to form a liquid. Thus the geochemist must invest considerable time and resources in the dissolution or other forms of sample preparation prior to analysis. In the commercial world this is acceptable only whilst there is no more cost effective method. In accordance with the objectives of this work, as described in Chapter 1, to minimise the time required to prepare samples for ICP-MS, the potential in applied geochemistry of a solids analysis technique which can achieve the detection limits of ICP-MS is very high.

Other techniques such as slurry nebulisation (Chapter 4) represent an attempt to eliminate the time consuming digestion and dissolution procedure but achieves only limited success because of the extended period of time spent reducing the mean particle size. Although this process can in some respects be automated, it still means long sample preparation times and thus limits the throughput of the laboratory.

Spark source mass spectrometry is a direct solids analysis technique but, as described in Chapter 1, considerable time is taken up in processing and reading the photographic plates. Electrothermal vaporisation can also be used to introduce small amounts of solid sample, but again the mean particle size needs to be small to ensure uniform heating, and in addition, because of the small sample size used, the inhomogeneity of most geological samples means that several replicates must be run for each sample to ensure that a true representation of the sample is obtained, thus causing poor precision in the final results.

True solids analysis must be applicable to samples with limited preparation. Bulk sampling of pressed disks or briquettes formed by fusion with a flux such as lithium metaborate used for XRF analysis can be prepared very quickly and since XRF would in all probability continue to be used for the analysis of major components due to its high precision, the ability to use the same disks for ICP-MS analysis would be clearly advantageous.

In addition to the bulk sampling of solids, there exists the possibility to analyse the composition of individual features in an inhomogeneous sample as described in the aims of this work. For example, in the field of geochemical and petrological research, there is a need to determine the concentrations of trace elements in individual mineral grains to examine the partitioning of elements during the formation of a rock.

In this chapter, the requirements and potential of both bulk and feature analysis are investigated

7-2 History of Laser Ablation ICP-MS

Laser ablation has for many years been used as a method for introducing samples into an ICP-AES, one of the earliest references being Abercrombie *et al*[1] in 1978. Other authors who have made significant reports of work in this field include Thompson *et al*[2], and Horlick[3]. The first major investigation into laser ablation ICP-MS was by Gray[4] in 1985, using a 1J ruby laser to analyse pressed pellets of rock powder. Whilst good detection limits were reported, typically 10ppb, poor precision was obtained. This was attributed to the low repetition rate of the ruby laser and further work using a fast repetition rate such as the neodymium-yttrium aluminium garnet laser (Nd:YAG) which was subsequently used by Arrowsmith[5] who analysed pressed rocks and lithium metaborate disks, reporting detection limits in the 0.2-2ppm range, and Tye *et al*[6] who also used a Nd:YAG for the analysis of uranium oxide. Mochizuki *et al*[7] used a ruby laser and reported detection limits in pressed rocks of 0.1-1 ppm but again poor precision was reported with relative standard deviations in the range 10-30%.

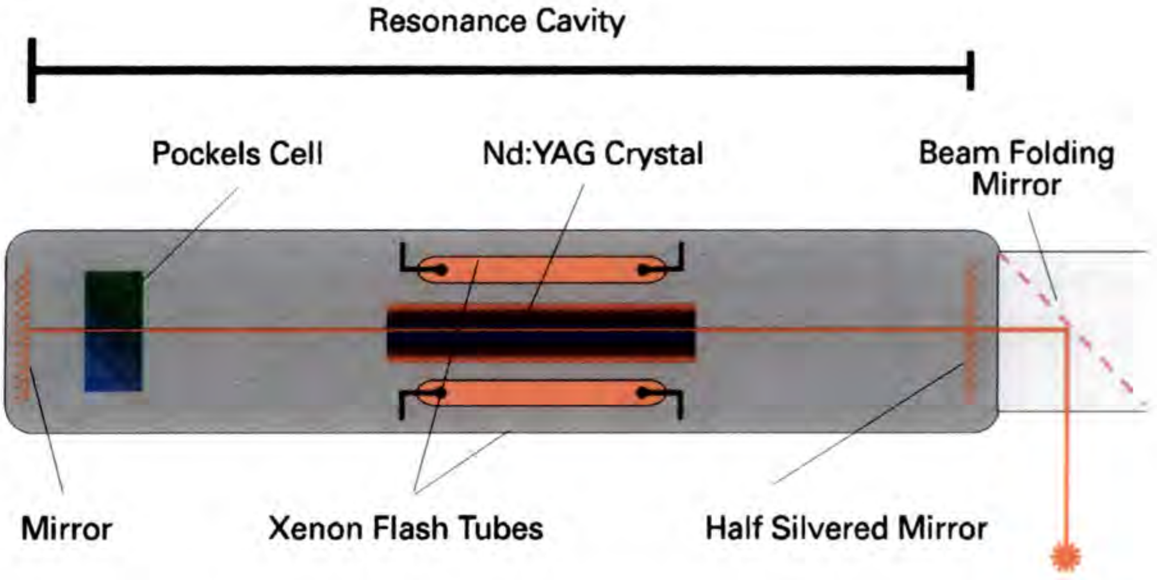

Figure 7-1: schematic of a Nd:YAG laser

7-3 Technique of Laser Ablation

For laser ablation work, a pulsed laser, such as the ruby or Nd:YAG is used and in this research a 500mJ Nd:YAG laser with a wavelength of 1064 nm was preferred. The schematic of a typical laser ablation system is shown in figure 7-1.

The optical medium, a rod of neodymium doped YAG, is contained in a resonance cavity, composed of two mirrors at either end of the rod, one of which is half silvered to allow emission of the laser light. Xenon flash tubes parallel to the rod act as an optical pump. The mirrors are placed such that the distance between them is an integral multiple of a half wavelength. This results in a system of standing waves being set up between them. Any light of a different wavelength is lost from the system within a few reflections therefore the resonator is essentially monochromatic.

7-3.1 Firing Modes

In its simplest mode of operation, the laser is pumped by the flash tubes and the light is emitted through the half silvered mirror when the threshold conditions for laser operation are reached which results in a relatively long pulse, typically 100μs, of low energy (Fig. 7-2). Such operation is termed "fixed Q" where Q is the quality of the resonance cavity.

The second mode of operating such lasers is termed "Q switching". Here the quality of the resonant cavity is changed by means of an electro-optical switch, such as a Pockells cell. This is a deuterium doped potassium dihydrogen phosphate or ammonium dihydrogen phosphate crystal which, when a voltage of typically 5kV is applied across it, becomes opaque. By placing the Pockells cell inside the resonant cavity, when opaque, resonance cannot occur thus the population of excited atoms builds up until the voltage is removed from the Pockells cell, at which point resonance occurs rapidly, resulting in the emission of a very short, typically 20ns, high intensity pulse of light. This has important implications and is discussed further in the section dealing with firing modes.

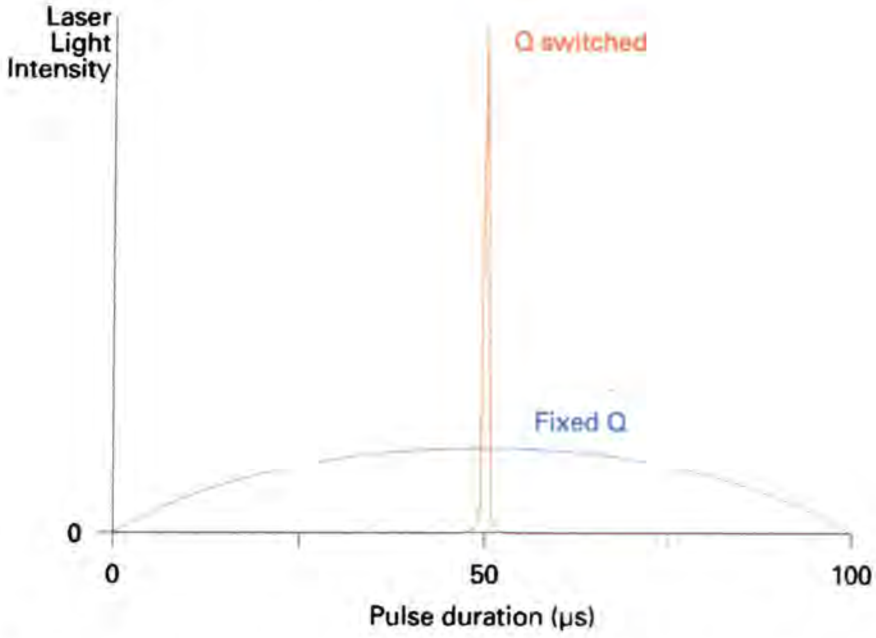

Figure 7-2: Diagram to show the duration of laser light emitted in fixed Q and Q switching modes.

7-3.2 Hardware

In laser ablation, the purpose of the laser is to vaporise a portion of the sample to form a microparticulate dust which is then carried to the plasma on the nebuliser gas flow. A schematic of the laser ablation ICP-MS system is shown in Fig. 7-3.

The sample is mounted on a small stage covered with a quartz cell. The top of the cell is inclined at an angle of 45°, to prevent the laser from reflecting back and damaging the expensive focusing optics. The nebuliser argon flow passes through the cell and on to the plasma torch, the cell effectively replacing the spray chamber used in solution nebulisation. In order to mount the sample in the cell the nebuliser gas had to be stopped as air entrained in the cell destabilises the plasma to the extent of extinguishing it. In the commercial version of the laser ablation system this was achieved by diverting the nebuliser flow away from the torch until the cell had been purged with argon using a motorised valve. This, however, caused problems because the ablated sample material had to pass through the valve causing deposition which resulted in contamination necessitating frequent cleaning of the valve.

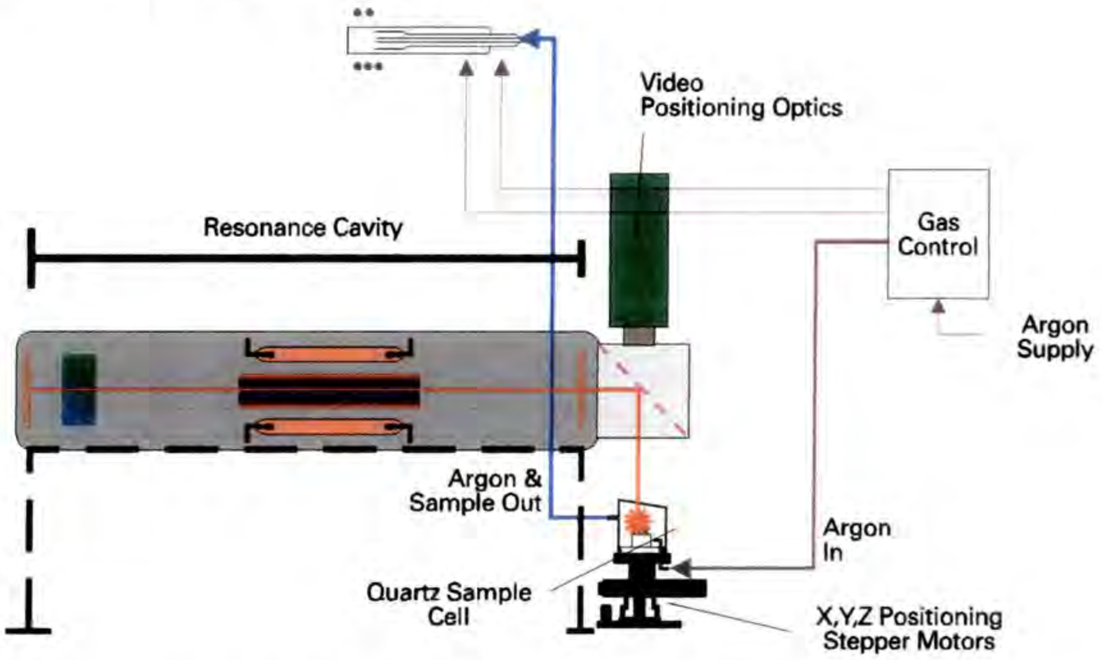

Figure 7-3: Scematic of the laser ablation ICP-MS system

The stage on which the sample was mounted could be moved in all three dimensions - either manually or by computer control. The Z axis was used primarily for focusing the beam onto the surface of the sample, while relative motion in the X and Y directions were used to position a particular portion of the sample under the beam. Accurate positioning of the sample and focusing required a magnified view of the sample. This is achieved by means of a low magnification optical system linked to either a binocular head, or a video camera and monitor. For the earlier bulk sampling work the sample was illuminated by reflected light from above using a fibre optic illumination system. For the later thin section work, a transmitted lighting system was constructed by placing the sample on a glass mount under which a mirror was located to reflect light from a side mounted fibre optic through the sample. The video monitor was fitted with an electronic cross hatch generator which was aligned with the firing position of the laser.

7-3.3 Firing Pattern

It is possible either to fire repeated shots at a single point, or to use the computer controlled stage to fire at a different point on the sample with each shot or series of shots, thus taking a more representative sampling, a feature which is particularly advantageous with inhomogeneous samples such as geological materials.

7-3.4 Effect of Firing Mode on Analysis and Cratering

The ablation of material from the sample results in the formation of a small pit or crater, the size of which depends upon the type and number of laser shots used.

The two firing modes, fixed Q and Q switching, were found to produce very different craters. A range of pressed geological materials were ablated, using the laser at 75% power, and the resulting craters examined microscopically. The quadrupole was set at mass 139 during this preliminary investigation and the signal produced by the ablated material was observed on the instrument ratemeter. Representations of the characteristics of the craters produced by each of the two firing mode are shown in figure 7-4.

7-3.4.1 Fixed Q

Fixed Q shots were found to produce a narrow crater of diameter <50μm. It was not possible to measure the depth of such craters although this was estimated to be in the range 50-200µm. The depth of fixed Q craters was found to vary depending upon the nature of the sample and, if a pressed powder, upon the binding agent and compression conditions used. This was an important observation since variation in crater depth indicated that a varying amount of sample material was being ablated each time, thus affecting the precision of an analysis.

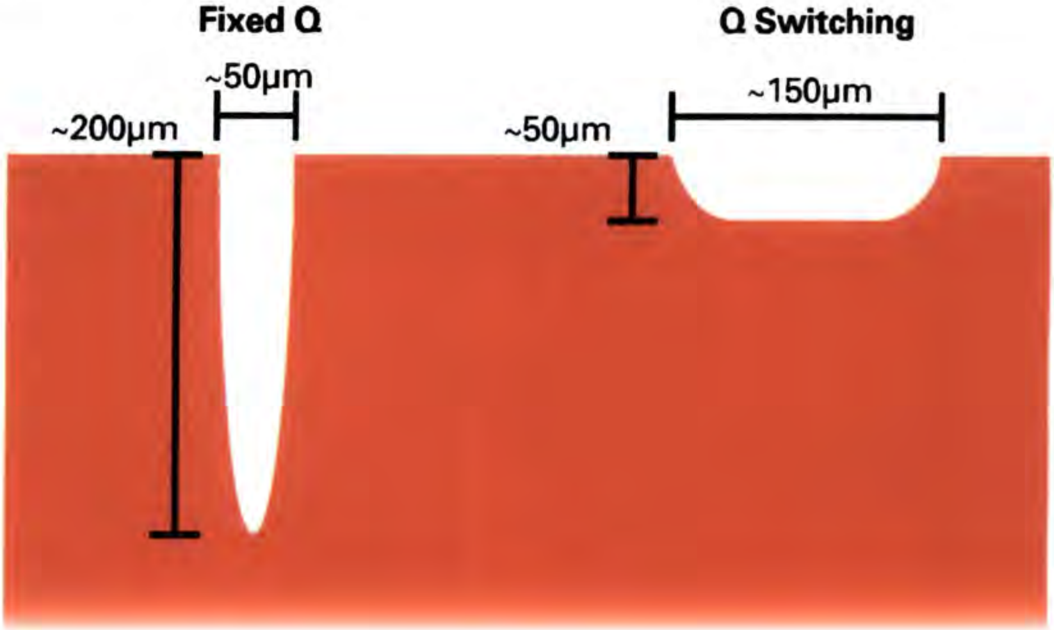

Figure 7-4: Representation of laser ablation craters produced by fixed Q and Q switching

The mouth of the fixed Q crater was jagged, suggesting that some of the material had been shaken loose, rather than been ablated. A fine dust of pieces of sample material, individual grains being observable with the naked eye, was found on the base of the sample cell, and in the tubing which connected the cell to the plasma torch. This further supports the theory of its removal by mechanical shock, and provides evidence for the existence of some particle size dependent fractionation occurring in the transport process. In addition, some evidence of molten material around the edge was observed.

Repeated fixed Q shots fired at the same point on a sample did not produce any discernible change in crater dimensions, and, furthermore, the maximum signal shown on the ratemeter was four orders of magnitude lower than that produced by the first ablation at that spot. It is likely that, due to the relative depth of the crater, the beam was not focused by the time it hit the sample and therefore did not have enough energy to produce a further ablation.

7-3.4.2 Q Switched

Q switched shots were found to produce a much wider and shallower crater of typically 150μm diameter and 50μm depth. "Burn" Marks were observed round the outside of the crater, but no molten material. Due to the high intensity, short duration pulse produced by Q switching, ablation is achieved, in part, by ionisation of the argon gas above the surface of the sample[8]. This is why the resulting crater is so much larger than the diameter of the focused beam, which is typically 30-50μm.

Repeated shots at the same point gave consistent maxima on the instrument ratemeter suggesting that comparable amounts of material were being ablated each time, permitting the use of repeated sampling from the same point.

The precision of sampling five shots at the same point and five shots at different points on the sample was investigated. The ICP-MS was set up to continuously monitor the signal for mass 139 (lanthanum) and to record the variation in signal with time (as was used in the flow injection work described in chapter 5). The results are shown in figure 7-5.

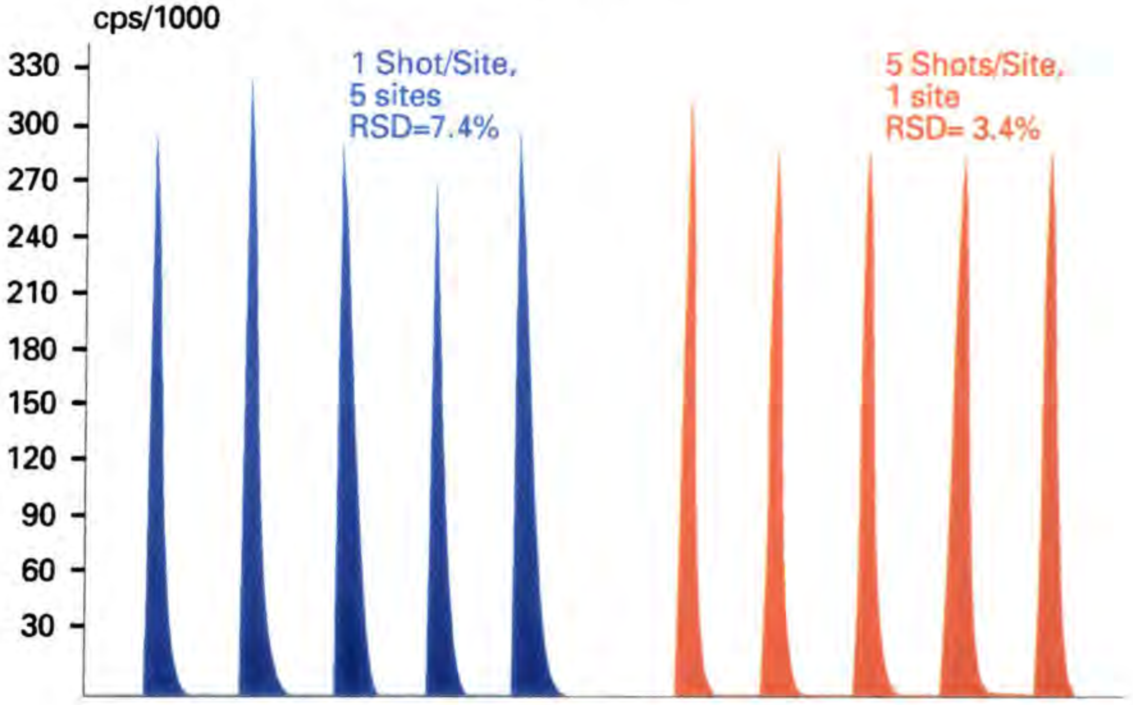

Figure 7-5. Reproducibility of Q switched shots at the same and at different sampling points

The relative standard deviation was found to be better for repeated shots at the same site, than for single shots at different sites. This may have been in part due to inhomogeneity in the sample, but more likely is the result of surface contamination introduced during handling or pressing. It can be seen that, for the repeated sampling of a single point, the first shot gave a high result whilst subsequent shots gave very similar responses, suggesting that the first shot removed any surface contamination which was present. Therefore, when analysing in Q switching mode, pre-ablation of the sample was felt to be advantageous to remove surface contamination. Due to the single shot per sampling point nature, this is not possible in fixed Q mode.

7-4 Sample Preparation

Samples of powdered rock were placed in a 25mm die and a pressure of 10 tons/cm^2 applied for 1 minute. In the initial work, in an attempt to minimise the possibility of contamination, no binder was used. However, the resulting disks were very fragile and collapsed after only a single laser shot.

50μl of a 5% solution of Moviol (a polyvinyl alcohol) in water was mixed with the powder before pressing. This resulted in a robust disk, although such disks had to be dried in a vacuum oven to remove water prior to analysis. This method was used for all of the pressed sample work in this research.

7-5 Bulk Analysis

Bulk analysis of whole rock is the mainstay of geochemical analysis. The major constituents of a sample are usually determined by XRF[9] from powdered rock samples, either pressed into disk or fused with lithium metaborate. If minor or trace elements which would be below the detection limits of XRF need to be determined, a solution technique is usually employed. This necessitates expensive and time consuming digestion and dissolution. If, instead, a solid sampling technique such as laser ablation could be used, considerable improvements in sample throughput and major cost reduction could be made.

7-5.1 Detection Limits

A prime consideration for any analytical technique is the detection limits which can be achieved. For laser ablation ICP-MS to be worthwhile it must at least be capable of detecting the levels of elements which can be determined by solution ICP-MS.

Firing mode	Q Switched
Firing frequency	50Hz
Laser power	375J (75%)
Ablation duration	60s
Mass Range	2-255amu
Number of Sweeps	50
Dwell time	500µs
Number of channels	2,048
Total acquisition time	60s

Table 7-1. Laser ablation and acquisition parameters for the detection limit experiment

An experiment was devised to compare detection limits by the laser ablation technique. One difficulty in comparing laser ablation with solution nebulisation is that there is no equivalent to a reagent blank in laser ablation. Simply acquiring data without firing the laser yielded unrealistically low data - the only signal noise presumably being electronic. A synthetic blank was prepared by pressing a sample of high purity silica powder. Calibration was performed relative to a pressed sample of the international standard G1.

Surface contamination of the sampling sites was removed by a pre-ablation period of 15 seconds, during which the laser was fired at a rate of 50Hz in the Q switching mode. Five acquisitions were performed at the pre-ablated site using the conditions shown in table 7-1.

The results are shown in table 7-2. The detection limits obtained for solution nebulisation in chapter 3 (table 3-3) have been used to calculate detection limits in the original rock using the 1000 times dilution factor and are included for comparison. It can be seen that laser ablation results are 2-15 times worse than those obtained for solution. Jarvis *et al* obtained similar results[10]. They calculated, on the assumption that 12µg of sample is removed from the sample, that the absolute detection limit in pg is higher for laser ablation but, due to the small amount of sample actually removed, the laser ablation system gave poorer practical detection limits. The possibility exists therefore either to ablate for longer periods, or to analyse a reduced mass range. By spending more time on each of the selected elements better detection limits would be achieved.

		Abundance	Laser LOD's (ppm)
Y	89	100	0.05
Zr	90	51.46	0.10
Nb	93	100	0.05
Ru	101	16.98	0.29
Rh	103	100	0.05
Pd	105	22.6	0.22
Ag	107	51.35	0.10
Cd	110	12.43	0.40
Sn	118	24.01	0.21
La	139	99.911	0.05
Ce	140	88.48	0.60
Pr	141	100	0.05
Nd	146	27	0.31
Sm	147	15.07	0.33
Eu	151	47.77	0.10
Gd	157	15.68	0.32
Hf	178	27.23	0.18
Ta	181	99.98	0.05
W	182	26.31	0.19
Re	185	37.07	0.13
Ir	193	61.5	0.08
Pt	195	33.7	0.15
Au	197	100	0.29
Hg	202	29.8	0.56
Tl	205	70.5	0.07
Pb	208	52.38	0.10
Th	232	100	0.05
U	238	99.28	0.05

Table 7-2. Detection limits by laser ablation

7-5.2 Analysis of Geochemical Standards

The international geochemical standards G1, AGV-1 and PCC-1 were analysed by laser ablation. The samples were pressed into disks and analysed using the laser and instrument conditions described in section 7-5.1.

	G 1		AGV-1		BCR-1		PCC-1	
	Ref	LA ICP-MS	Ref	LA ICP-MS	Ref	LA ICP-MS	Ref	LA ICP-MS
Si	337933	458868	274255	340840	252190	313417	194391	263957
Al	75266	67152	90722	86499	72197	65027	3546	3164
Mn	217	253	713	767	1371	1529	922	999
Mg	2160	2056	9178	8998	20877	20028	260537	243547
Ca	9785	10268	35281	39635	49637	52760	3714	4181
Na	24705	24502	31605	35027	24260	24061	200	222
K	45634	59001	24144	33404	14022	33962	58	248
Ti	1619	1495	6298	6012	13436	11875	78	71
P	362	1022	2139	3356	1571	2879	9	203
Fe	13576	12567	47306	42425	93843	84160	57734	53444
Ag	0.044	<0.2	0.078	<0.2	0.027	<.2	0.008	<0.2
As	0.7	0.5	880	724.0	650	601	56	49
Au	0.00320	<0.2	0.00062	<0.2	0.00066	<0.2	0.00079	<0.2
B	1.6		7.8	5.9	3.0	2.5	1.7	1.3
Ba	1080	1084	1226	1201	681	680	1.2	2
Be	3	1.9	2	1.9	2	2	0.05	<0.2
Bi	50	52	57	60	47	51	8.0	8
Br	0.14	<0.2	0.3	<0.2	0.07	<0.2	0.4	<0.2
Cd	0.06	<0.2	0.07	<0.2	0.1	<0.2	0.02	<0.2
Ce	173	156	67	59	54	41	0.1	<0.2
Co	2	2	15	14	37	40	112	121
Cr	20	22	10	11	16	18	2730	3028
Cs	2	1.7	1.3	1.5	1	1	0.006	<0.2
Cu	12	11	60	57	19	18	10	8
Dy	2	2	4	4	6.3	5	0.01	0
Er	1	1	2	2	3.6	3.8	0.01	<0.2
Eu	1.2	1.2	1.6	1.7	2.0	1.7	0.002	<0.2
Ga	20	20	20	19	22	23	0.7	1.2
Gd	5	5	5	4	7	6	0.01	<0.2
Ge	1.1	1.3	1.3	1.4	1.5	1.75	0.94	1.17
Hf	5.4	4.9	5.1	4.8	5.0	3.9	0.04	<0.2
Hg	0.0850	<0.2	0.0200	<0.2	0.0079	<0.2	0.0060	<0.2
Ho	0.3900	<0.2	0.6700	<0.2	1.26	1.4600	0.0025	<0.2
I	0.0350	<0.2	0.2700	<0.2	0.18	<0.2	0.1850	0.4000
In	0.0252	<0.2	0.0410	<0.2	0.092	<0.2	0.0037	<0.2
Ir	0.0020	<0.2	0.0002	<0.2	0.000004	<0.2	0.0048	<0.2
La	105	*105	38	*38	25	*25	0.0520	<0.2
Li	21	19	12	11	13	12	2	2
Lu	0.16	<0.2	0.27	0.3	0.51	0.44	0.006	<0.2
Mo	6.8	6.7	2.7	2.7	1.6	1.6	2.0	1.8
Nb	23	20	15	12	14	9	1	0.7

Table 7-3. Results obtained by laser ablation of pressed powder, (ppm).

	G 1		AGV-1		BCR-1		PCC-1	
	Ref	LA ICP-MS	Ref	LA ICP-MS	Ref	LA ICP-MS	Ref	LA ICP-MS
Nd	57	55	33	32	29	26	0.04	<0.2
Ni	3	3	16	14	13	15	2380	2973
Os	0.0001	<0.2		<0.2	0.000009	<0.2	0.0007	<0.2
Pb	46	46	36	36	14	12	10	10
Pd	0.0019	<0.2	0.0022	<0.2		<0.2	0.0054	<0.2
Pr	17.0	17.7	8	8.4	7	7.8	0.013	<0.2
Pt	0.008	<0.2	0.0011	<0.2	0.002	<0.2	0.008	<0.2
Rb	214	220	67	68	47	47	0.066	<0.2
Re	0.0006	<0.2	0.00038	<0.2	0.0008	<0.2	0.000058	<0.2
Rh		<0.2		<0.2	0.0002	<0.2	0.0014	<0.2
Ru		<0.2		<0.2	0.001	<0.2	0.01	<0.2
Sb	0.3	<0.2	4	3.2	0.6	0.4	1.3	1.0
Sc	3	2.7	12	15	33	34	8.4	7
Se	0.007	<0.2	0.0005	<0.2	0.0001	<0.2	0.027	<0.2
Sm	8.3	8.1	5.9	4.7	6.6	5.2	0.007	<0.2
Sn	3	3	4	4	3	3	1.6	2
Sr	248	256	662	676	330	328	0.4	<0.2
Ta	1.5	1.5	0.9	1.1	0.8	0.9	1.2	1.7
Tb	0.6	0.7	0.7	0.8	1.1	0.9	0.0015	<0.2
Te		<0.2	0.0019	<0.2	0.005	<0.2	0.003	<0.2
Th	51	50	7	6.4	6	5	0.013	<0.2
Tl	1.2	1.1	0.3	<0.2	0.3	<0.2	0.002	<0.2
Tm	0.2	<0.2	0.3	<0.2	0.6	0.4	0.003	<0.2
U	3.4	3.4	1.9	2	1.8	1.6	0.005	<0.2
V	18	15	121	117	407	358	31	28
W	0.4	<0.2	0.6	0.3	0.4	<0.2	0.02	<0.2
Y	13	13	20	17	38	35	0.1	0
Yb	1.0	1.0	1.7	1.8	3.4	3.6	0.02	<0.2
Zn	45	48	88	92	129	140	42	56
Zr	201	190	227	210	190	177	10	*10

Table 7-3 cont'd. Results obtained by laser ablation of pressed powder, (ppm).

Semiquantitative calibration was performed relative to lanthanum for G1, AGV-1 and BCR-1. The lanthanum concentration in PCC-1 was below the detection limit, making it unusable as an internal standard so zirconium, present in PCC-1 at 10ppm, was used instead.

It can be seen from the results (Table 7-3) that in general, good agreement with reference values is achieved. Results for the major elements silicon and potassium are consistently high. This is due to a high background at the analyte masses. The inability to use background subtraction means that these cannot be corrected as in solution work. The high silicon figures are due to a polyatomic interference, $^{14}N_2{}^1H^+$, on ^{29}Si. Potassium results are high because the only analytically valid isotope of potassium, ^{39}K, is overlapped by an argon hydride species, $^{38}Ar^1H^+$. Although the abundance of ^{38}Ar is only 0.06%, the high argon concentration of the ion beam makes this polyatomic species significant enough to register a substantial background.

The platinum group metals and gold were below the detection limits of the method. A separate experiment was devised to determine these elements.

7-5.3 Analysis of SARM-7

Firing mode	Q Switched
Firing frequency	50Hz
Laser power	375J (75%)
Ablation duration	120s
Mass Range	89-120, 138-140, 180-200amu
Number of Sweeps	120
Dwell time	512.ms
Number of channels	2046
Total acquisition time	123s

Table 7-4. Laser ablation and acquisition parameters for the determination of platinum group metals and gold in SARM-7

SARM-7 is a South African platinum ore standard which has elevated levels of all of the platinum group and gold. The laser ablation experiment was repeated, but a restricted mass range and longer ablation and acquisition times (table 7-4) were used in order to improve the detection limits achievable and thus be able to determine the PGM's and gold. Mass 139 was included in the acquisition to allow the use of lanthanum as an internal standard. Two samples of

SARM-7 were prepared. Sampling was performed at two sites on each sample.

	SARM 7	Sample 1		Sample 2		Average		
	Ref	Spot 1	Spot 2	Spot 1	Spot 2	Mean	t=.90	% RSD
Ru	0.43	0.368	0.358	0.358	0.354	0.36	0.010	1.7
Rh	0.24	0.268	0.302	0.269	0.302	0.29	0.032	6.8
Pd	1.53	1.132	1.235	1.104	1.23	1.18	0.110	5.7
Ag	0.42	0.41	0.394	0.434	0.402	0.41	0.028	4.2
La	5	*5	*5	*5	*5			
Re		0.03	0.02	0.04	0.03	0.03	0.013	27.2
Os	0.063	0.103	0.099	0.111	0.124	0.11	0.018	10.1
Ir	0.074	0.078	0.053	0.088	0.078	0.07	0.024	20.1
Pt	3.74	3.37	3.94	3.52	3.76	3.65	0.414	6.9
Au	0.31	0.215	0.189	0.204	0.250	0.21	0.043	12.1

Table 7-5. Results obtained by laser ablation of SARM-7 as a pressed powder, (ppm).

The results (table 7-5) show reasonable agreement with certified values except for palladium and gold. Gold has a high first ionisation potential and requires a Saha correction in order to obtain good semiquantitative results[11]. Unlike solution nebulisation, where Saha corrections can be determined simply by running a solution of all analyte elements, it is difficult to find an appropriate solid sample with a sufficiently high level of gold and platinum group metals, with which to calibrate the Saha factors. The instrument response for a 'dry' plasma, as in laser ablation, and a 'wet' plasma, as in solution work, is markedly different[12]. For this reason, it is not valid to use a solution instrument response, and it's associated Saha factors, to calibrate results obtained by laser ablation. It is therefore likely that the low result is due to insufficient Saha correction.

Palladium has a first ionisation potential of 8.3V[13], which is sufficiently lower than argon (15.8V) to suggest that the low value is unlikely to arise due to an imperfect Saha correction. Interferences in ICP-MS which affect individual elements are always additive, rather than subtractive, and therefore the low palladium result cannot have been caused this way. The fact that similar values are obtained from different sampling sites suggests that the results are not due to homogeneity problems. In the absence of any other explanation to the contrary, it is concluded therefore that the results for palladium are correct.

Precision for the results is poor, particularly for those elements which are close to the limit of detection of the method (Re, Os, Ir). SARM-7 is an ore sample and thus has higher levels of the platinum group metals and gold than the normal crustal abundance. In order for the method to become applicable for routine analysis of these elements, the limits of detection would need to be improved.

7-6 Feature Analysis

One area in which low detection limits can be of considerable benefit is in the analysis of individual features in a sample, such as the analysis of minor and trace elements in individual minerals in a rock.

The principle technique for analysing individual minerals is by electron microprobe. As discussed in chapter 1, this technique offers very good spatial resolution, 20µm spot sizes being typical, but only for elements at concentrations of 100ppm or more. The lack of a technique capable of determining elements at the ppm level means that in order to determine lower concentrations the sample had to be crushed and the individual minerals picked out manually or separated mechanically and the bulk compositions determined for each collection of minerals.

In its present form the craters produced by laser ablation are too large to allow such analysis to be performed on any but the largest phenocrysts.

For microprobe work, thin sections, approximately 200µm in thickness, are mounted onto glass slides and coated with a conductive layer of graphite. Such samples required only that the slide be cut down in order to fit into the ablation cell.

If laser ablation ICP-MS could be applied to the analysis of these minor and trace elements in individual minerals it would be possible to investigate their partitioning in, for example, the crystallisation of minerals from a magma and thus contribute to our understanding of both the mechanisms of petrogenesis and the origins of specific geological features. In determining partition coefficients, it is necessary to ablate areas of both the mineral (e.g. olivine, Mg_2SiO_4/Fe_2SiO_4), and the surrounding glass melt from which the minerals crystallised. Although fixed Q ablation gives the smallest spot sizes, it does not satisfactorily couple to glass and therefore cannot be used for this application. Q switching couples equally well to both mineral and glass, but produces a much larger spot size, typically 120µm, limiting the analysis to large phenocrysts.

The choice of material for this type of work is further restricted by the geochemistry of the minerals themselves. The purpose of the analysis is to determine partition coefficients (K_D) for a range of minor and trace elements. These indicate the extent to which an element is partitioned between a mineral and the liquid melt from which it formed. However, the range of partition coefficients which can be measured will be restricted by the sensitivity of the laser ablation technique.

For example, olivine would not be a suitable choice because partition coefficients in the order of 10^{-5} are common. To determine such a partition coefficient, analytical determinations spanning this range (10^5 orders of magnitude) must be made, necessitating either the use of a major element, or an exceptionally high analytical sensitivity; certainly greater than that which could be achieved by laser ablation ICP-MS.

For this work a pyroxene was chosen. This mineral has given partition coefficients in the range 10-0.1 for major elements, suggesting scope for the determination of the minor and trace element partition coefficients. Other possible minerals include epidote and mica which also exhibit a similar range.

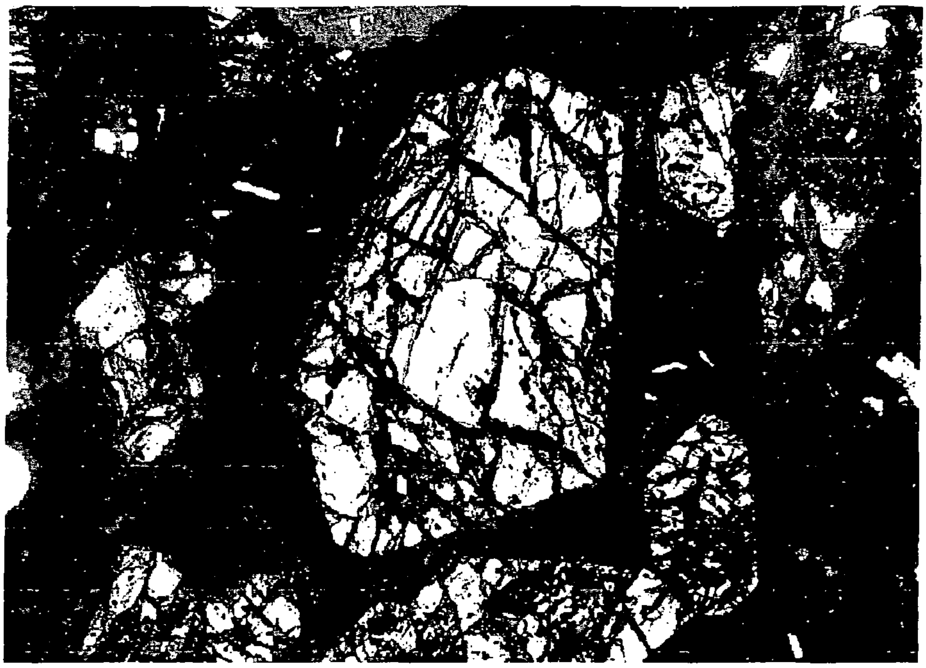

Figure 7-6. Photomicrograph of zoned pyroxene crystal and surrounding melt

A thin section taken from a porphyritic olivine-pyroxene alkali basalt (University of Durham sample number DU24814) from Tenerife in the Canary Islands was chosen because of the coarse grained aspect of the fresh clinopyroxene grains. A single large pyroxene, approximately 4mm, was identified in the sample (Fig. 7-6). This phenocryst was chosen firstly because it was sufficiently large to allow a number of Q switched craters of typically 120μm to be made, and secondly because it exhibited clear zoning, with a definite boundary between the middle and rim of the crystal.

The most likely cause of such zoning is that there was a change in the composition of the liquid magma, resulting in the rim having a different composition from the middle.

Sampling was made from three areas; corresponding to the middle of the crystal, the rim and the surrounding glass melt. These are shown in Fig. 7-7. Firing of the laser was carried out manually. Five 75% power Q switched shots were fired in rapid sequence. Acquisition was performed using 60 sweeps, 2048 channels and a dwell time of 500μs. The mass range was 5-250amu. Calibration was performed using semiquantitative analysis.

Since it was not possible to use an internal standard, a fixed response of 135 counts/ppm was used, this having been determined by ablating a sample of NBS 614 (Trace elements in glass)[14], which was assumed to have a similar ablation response to the three sampling sites. The absolute values thus calculated may therefore be subject to some error, especially for low concentration elements where instrument background may represent a large proportion of the counts obtained for that element. However, this should not affect the relative concentrations, or the partition coefficients.

The results for the analysis of the three sites are shown in table 7-6. The glass was designated "Liquid 2", because this represented the second liquid composition which resulted in the formation of the zoned rim of the crystal, the middle of the crystal forming from a presumed "Liquid 1".

As a consistency check the zirconium/hafnium ratios for each sample were calculated. Hafnium has a very similar geochemistry to zirconium and thus the ratio of these two elements should be almost constant in all phases of the sample. The ratios were found to be 22.2 for the middle of the crystal, 23.1 for the rim or edge and 27.9 for the liquid melt. These are sufficiently close to indicate that ablation efficiencies were similar for all three samples and justify the assumption made in the calibration that the three sites were ablated with similar efficiency.

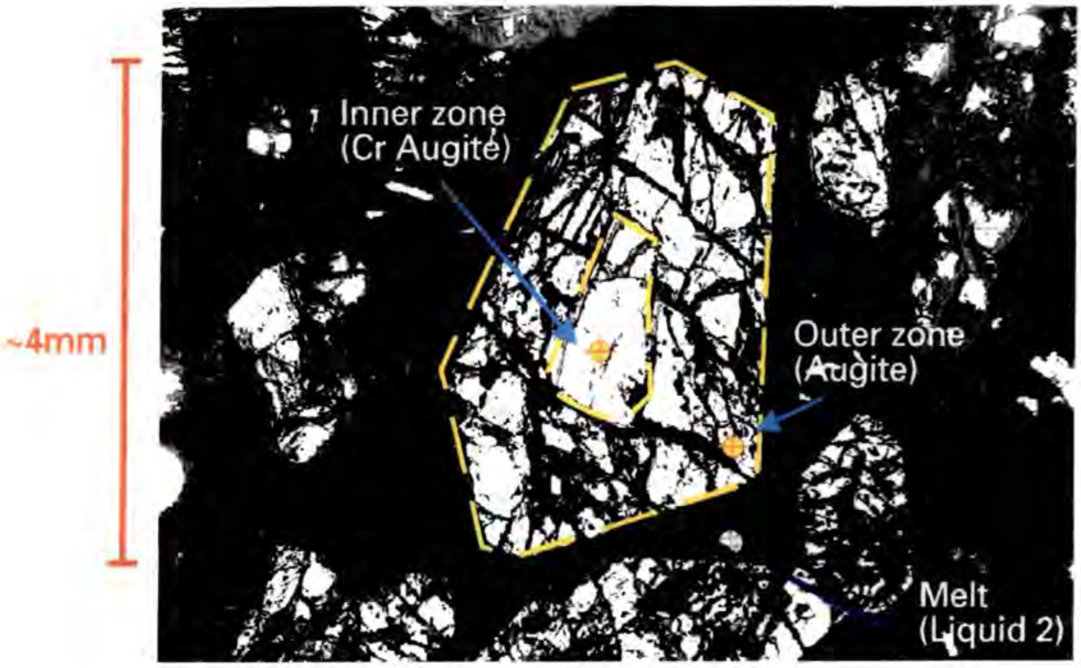

Figure 7-7. Photomicrograph of zoned pyroxene crystal with laser ablation sites indicated

The partition coefficients (K_D) for the analyte elements between the rim of the crystal and liquid 2 were determined and are also given in table 7-6. As predicted for a pyroxene, these were generally in the range 10-0.1, the exception being chromium at 18.8.

		Middle ppm	Rim ppm	Liquid 2 ppm	Kd	Liquid 1 ppm	Liquid 2 ppm
Li	7	0.664	1.087	1.752	0.620	1.070	1.752
Be	9	1.402	0.785	0.785	1.000	1.402	0.785
B	11	9.93	10.76	10.62	1.013	9.799	10.62
Mg	25	39801	28219	22417	1.259	31618	22417
Al	27	7590	17326	46496	0.373	20368	46496
Sc	45	57.68	45.21	29.37	1.540	37.46	29.37
Ti	49	3715	7937	37638	0.211	17618	37638
V	51	133.8	219.6	690.7	0.318	421.0	690.7
Cr	52	6699.2	839.3	44.70	18.775	356.8	44.70
Mn	55	612.9	883.9	2918	0.303	2024	2918
Fe	57	14632	19847	84402	0.235	62227	84402
Co	59	30.63	95.86	86.12	1.113	27.51	86.12
Ni	60	173.7	108.3	92.40	1.172	148.2	92.40
Zn	68	29.25	33.92	93.58	0.362	80.68	93.58
Ga	69	5.636	11.50	28.86	0.398	14.15	28.86
Ge	72	3.060	1.127	3.704	0.304	10.06	3.704
As	75	14.44	11.21	9.266	1.209	11.94	9.266
Se	77	87.59	45.21	67.81	0.667	131.4	67.81
Br	81	1003	26.51	1084	0.024	40986	1084
Rb	85	0.767	4.930	31.28	0.158	4.866	31.28
Sr	88	48.43	196.0	757.1	0.259	187.1	757.1
Y	89	4.002	7.013	20.54	0.341	11.72	20.54
Zr	90	16.00	62.46	241.3	0.259	61.82	241.3
Nb	93	0.367	6.831	67.69	0.101	3.637	67.69
Mo	98	0.567	0.850	3.118	0.273	2.080	3.118
Ru	102	1.291	0.861	0.215	4.005	0.322	0.215
Rh	103	0.234	0.234	0.167	1.401	0.167	0.167
Pd	108	1.192	1.073	0.477	2.249	0.530	0.477
Ag	109	12.96	2.591	12.31	0.211	61.54	12.31
Cd	111	3.328	1.479	1.849	0.800	4.161	1.849
In	115	0.372	0.372	0.589	0.632	0.589	0.589
Sn	120	11.16	31.19	18.31	1.703	6.552	18.31
Sb	121	42.10	35.62	26.19	1.360	30.96	26.19
I	127	2.379	1.586	0.925	1.715	1.388	0.925
Te	128	2.058	0.412	1.441	0.286	7.198	1.441
Cs	133	0.174	0.125	0.100	1.250	0.139	0.100
Ba	138	1.155	120.4	256.1	0.470	2.457	256.1

Table 7-6. Individual mineral and melt results obtained for pyroxene

		Middle ppm	Edge ppm	Liquid 2 ppm	Kd	Liquid 1 ppm	Liquid 2 ppm
La	**139**	1.718	8.592	44.33	0.194	8.864	44.33
Ce	**140**	6.977	25.88	109.9	0.235	29.63	109.9
Pr	**141**	1.269	3.760	14.51	0.259	4.897	14.51
Nd	**146**	6.497	15.03	55.29	0.272	23.90	55.29
Sm	**152**	0.936	4.134	10.14	0.408	2.296	10.14
Eu	**153**	0.827	1.339	2.954	0.453	1.824	2.954
Gd	**158**	1.737	2.842	9.157	0.310	5.597	9.157
Tb	**159**	0.389	0.467	1.031	0.453	0.859	1.031
Dy	**163**	2.252	1.726	7.055	0.245	9.205	7.055
Ho	**165**	0.423	0.552	1.141	0.484	0.874	1.141
Er	**166**	0.655	0.928	2.947	0.315	2.080	2.947
Tm	**169**	0.071	0.177	0.319	0.555	0.128	0.319
Yb	**172**	1.029	1.345	2.136	0.630	1.634	2.136
Lu	**175**	0.173	0.173	0.155	1.116	0.155	0.155
Hf	**178**	0.721	2.704	8.651	0.313	2.307	8.651
Ta	**181**	0.064	0.749	5.162	0.145	0.441	5.162
W	**182**	0.420	0.480	0.720	0.667	0.630	0.720
Re	**187**	0.024	0.168	0.096	1.750	0.014	0.096
Os	**192**	0.226	0.272	0.181	1.503	0.150	0.181
Ir	**193**	0.163	0.163	0.117	1.393	0.117	0.117
Pt	**195**	0.135	0.540	0.338	1.598	0.085	0.338
Au	**197**	0.315	0.757	0.315	2.403	0.131	0.315
Hg	**202**	3.525	2.233	2.585	0.864	4.081	2.585
Tl	**205**	0.243	0.101	0.121	0.835	0.291	0.121
Pb	**208**	3.191	4.981	4.570	1.090	2.928	4.570
Bi	**209**	0.452	0.126	0.226	0.558	0.811	0.226
Th	**232**	0.073	0.346	2.273	0.152	0.480	2.273
U	**238**	0.040	0.222	0.655	0.339	0.118	0.655

Table 7-6 Cont'd. Individual mineral and melt results obtained for pyroxene

By assuming that the partition coefficients would not change significantly from the rim and its associated magma to the middle and its magma, the composition of the presumed original magma (Liquid 1) was calculated by multiplying the composition of an element in the middle by the partition coefficient for that element. The calculated composition of Liquid 1 is also shown in table 7-6. From these results it can be seen that there are significant differences in composition between the two liquids.

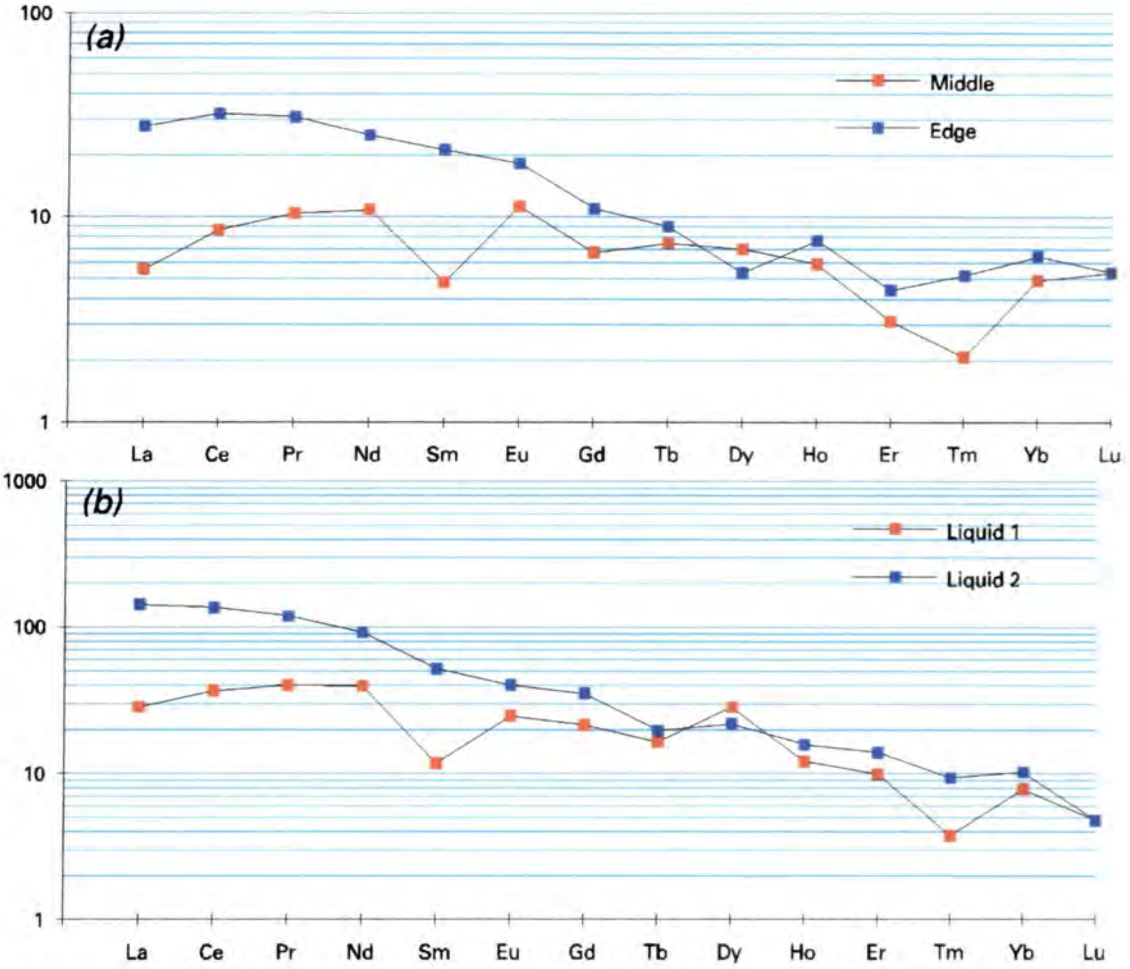

Figure 7-8. Chondrite normalised plots of the rare earth elements in the mineral (a) and the liquid melts (b)

It is clear that the early magmatic liquid had a more primative chemistry than the liquid that was at equilibrium with the outer edge of the pyroxene: it is enriched in magnesium, chromium and nickel; but strongly impoverished in the 'alkali' elements rubidium, strontium, zirconium, niobium and barium, and is also impoverished in iron and the transition metals as well as the rare earth elements. These rare earth element concentrations were chondrite normalised, using values obtained by Nakamura[15], and are plotted in Fig.7-8. The plots show that, compared to the chondrite norm, both magmas were enriched in the rare earth elements but that the later magma (Liquid 2) was more strongly enriched, especially in the light rare earth elements. The marked absence of a europium anomaly suggests that plagioclase was not involved in the primary magma generation process which was probably dominated by an upper mantle garnet-pyroxene lherzolite source. The different rare earth element profiles between the two magmas suggests either greater partial melting of this matrix during the formation of the earlier magma, or a more refined and mature melting process for the later magma. This second option is given support by the strong increase in the 'alkali' elements such as rubidium, barium, niobium and zirconium, and by the marked increase in the iron / magnesium ratio from 1.97 in the earlier liquid to 3.77 in the final liquid.

Despite the limitations of the technique, these results show considerable potential for the analysis of specific features for geochemical and petrogenetic studies.

7-7 Reduction of Ablation 'Spot' Size

As discussed in section 7-1, the applicability of the laser ablation technique is limited to large crystals by the size of the resulting crater. Q switching produces a crater which is larger than many crystals which it would be desirable to analyse. A Nd:YAG laser fired in fixed Q mode produces a much smaller crater but does not couple sufficiently to glass. By using a laser of higher energy, for example an ultraviolet laser, it should be possible to ablate the glass in fixed Q mode, therefore producing a small enough crater.

A 1J Nd:YAG laser was used with two frequency doubling crystals in the optical path. As the name suggests, when correctly aligned, these crystals double the frequency of the beam so that by using two, a wavelength of 266nm could be achieved. To test this approach a set of samples from Iceland containing small crystals of pyroxene, 30μm across, set in a basaltic glass matrix were targeted. However, in practice, this procedure was complicated by the fact that the alignment of the frequency doubling crystals is temperature dependent. As the ambient temperature inside the laser casing changed, due in part to the firing of the laser, the alignment changed so that it was impossible to be certain what frequency the laser would have from one shot to the next. The resulting data was therefore judged to be meaningless.

The principle of using a laser of higher frequency than a YAG is however still valid and an alternative type of laser such as a hydrogen fluoride excimer laser, which has a frequency in the ultraviolet region, may be a possibility.

7-8 Conclusions

At the outset of this work it was hoped that laser ablation would show advantages over the solution sampling techniques in terms of reduced sample preparation and increased sample throughput.

It has been demonstrated in this work that laser ablation ICP-MS is capable of achieving good semi-quantitative results for bulk analysis, provided that laser firing is carried out in the Q switching mode. It is likely that such fast bulk analysis will be applied as a screening technique in many applications in the future.

Fully quantitative analysis has not been investigated in this work although Jarvis *et al*[16] report that despite achieving linear calibrations, the samples and standards must be matrix matched, thus limiting the applicability of the technique. This, coupled with the lack of additional sensitivity over the solution techniques, is likely to ensure that, for bulk analysis, laser ablation ICP-MS will probably remain a screening technique for the foreseeable future.

The really exciting results arose from the feature analysis and this promises to be a very important tool in the study of geochemistry and petrogenesis in particular. Pearce *et al*[17] have already used a modified Nd:YAG laser with reduced beam divergence, beam energy attenuation and a compound focusing optic, to achieve Q Switched craters of 20-30μm diameter and have applied it to the analysis of carbonates, zircon, olivine and feldspars. This is an area of significant potential and further research should be rewarding.

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Chapter 8

Conclusions & Future Directions

8-1 Review of aims

At the start of this research, the following aims were identified from a review of the needs of geochemists and the status of current analytical techniques

To determine the optimum methods, sample preparation and sample introduction systems for a variety of geochemical analytical problems to give

- High sample throughput
- Reduced sample preparation
- High sensitivity (low minimum determinable concentration)

To develop the technique of ICP-MS to meet the requirement for future needs in geochemistry, in particular the ability to determine minor and trace concentrations of individual areas of a sample.

8-2 Comparison of sample introduction techniques

8-2.1 Solution nebulisation

Although more suited to the analysis of simple materials such as water[1] or single element matrices such as uranium oxide[2] or low alloy metals[3,4], the solution nebulisation technique has been proved to be effective for a range of geochemical analysis.

The requirement to perform long and often difficult sample preparation tends to limit sample throughput more than the actual analysis and the level of dissolved solids which can be aspirated is ultimately the limiting factor in solution nebulisation.

Of the two commonly used types of digestion method available, fusion of the sample was found to produce too high a level of dissolved solids to permit the determination of elements at low concentration and is therefore restricted to specialist applications such as, for example, fire assay enrichment of the platinum group elements, although even this is subject to unacceptably large losses and uncertainties, rendering it unsuitable for accurate quantitative work.

Acid digestion is more applicable to ICP-MS, since it does not add significantly to the level of dissolved solids in the sample. In fact, due to loss of silicon as volatile SiF_4, it actually reduces the amount of dissolved material in the final solution. Both conventional 'open' digestions and the more recent microwave 'closed' digestion methods are applicable for geological work and both yied results of acceptable precision, even at low levels, provided care is taken at all stages of the preparation.

This research and others[5] have shown that the maximum dissolved content for a refractory matrix such as a digested igneous rock is typically 0.1-0.2% w/v. If by some means this could be increased by a factor of 10, then the direct determination of such low concentration elements as the platinum group metals and gold could bebrought within the range of the technique. As it stands, most of the periodic table can be determined in geological materials by ICP-MS, although for the major constituents, ICP-MS is far from being as precise as techniques such as XRF.

A final problem which must be considered for all low level solution ICP-MS work is in fact caused by the high sensitivity of the technique. Deionised water and all acids and other reagents must be of the highest achievable purity in order to keep background contamination to an acceptably low level. The instrument tubing, glassware (plasma torch, spray chamber and nebulisers) and sampling cone must be regularly cleaned to prevent cross contamination from previous samples and standards.

8-2.2 Slurry nebulisation

Slurry nebulisation was initially viewed as a way to eliminate the skilled and time consuming sample digestion and preparation required by solution nebulisation ICP-MS. Although it was found to be possible to obtain good results for geochemical standards using slurry nebulisation, a number of practical difficulties were encountered.

Standardisation is a problem for slurry nebulisation. The difference in response for aqueous and slurried analyte elements poses a limitation to the technique. Matrix matching is the only practical answer, but this presupposes that suitably characterised standards are available and that the matching with an unknown sample is accurate.

Of greater significance is the inability to add an internal standard. Without this ability, the analyst is restricted to running reference materials with at least one, and preferably more than one, known elemental concentration. There will be instances where the concentrations of some elements in a sample, usually major and minor elements, will be known from XRF and other techniques which can be used as a variable internal standard.

Sample preparation for slurry nebulisation is a highly skilled task and is felt to be too complex to be reliable on a routine basis. It is not easy to see how this procedure could be automated and therefore is likely to remain time consuming and labour intensive, making its routine adoption even more unlikely.

Given the potential advantages in terms of sample throughput which it was originally thought could have been achieved by slurry nebulisation, the fact that there have been so few papers on the subject tends to support the conclusions drawn from this work, that the practical difficulties outweigh the potential benefits.

8-2.3 Flow injection

Of all the sample introduction systems investigated in this research, flow injection appears to offer the most benefit to the geochemical analyst.

By reducing the amount of material aspirated, flow injection was found to increase sample throughput by reducing washout and uptake times. More importantly, by improving matrix tolerance by a factor of 10x, it allows direct determination of the platinum group elements and gold in geological materials without pretreatment, and uses the same sample preparation procedure as conventional solution nebulisation.

Small samples, such as fluid inclusion leachates, can be analysed without requirement for dilution which would reduce many elements below their detection limit. In addition, the matrix effects experienced when analysing samples which contain a high salt concentration can be reduced by careful control of dispersion.

These advantages are of sufficient importance to ensure that flow injection ICP-MS is certain to become widely used in geochemical laboratories.

8-2.4 Electrothermal vaporisation

Whilst the technique of electrothermal vaporisation into ICP-MS has the potential for useful application to the determination of low level elements in geological materials, a great deal more work needs to be done in refining the method.

The main advantage of electrothermal vaporisation lies in the increased detection capability which has been demonstrated for other applications, such as the determination of femtogram levels (ppq) of plutonium in biological matrices[6]. Such an improvement in the detection of ultratrace elements in geological materials was not obtained in this research. The same matrix tolerance problems which limit solution nebulisation were found to be limiting the performance of electrothermal vaporisation, and although more work in this area is both necessary and desirable, at present it would seem unlikely to result in any significant improvement in the technique, and sample preconcentration methods, such as fire assay and ion exchange / solvent extraction processes, will continue to be necessary with this technique.

8-2.5 Laser ablation.

At the outset of this work it was hoped that, by direct analysis of the solid sample, the requirement for extensive sample preparation could be eliminated, resulting in greater sample throughput. In this research it has been shown that laser ablation ICP-MS is capable of achieving good semiquantitative results for bulk analysis, provided that laser firing is carried out in the Q switching mode. It is likely that such fast bulk analysis will be applied as a screening technique in many applications in the future.

Although no fully quantitative analysis was performed, other workers[7] report that despite achieving linear calibrations, the samples and standards must be matrix matched, thus limiting the applicability of the technique. This, coupled with the lack of additional sensitivity over the solution techniques, means that, for bulk analysis, laser ablation ICP-MS is likely to remain as a screening technique for the foreseeable future.

The use of laser ablation to analyse trace element concentrations in individual mineral grains opens up a particularly important and exciting avenue for the geochemist. Although microprobe techniques have been available for many years, they are limited to the determination of major elements. Now by using laser ablation ICP-MS, the minor and trace elements may be dirctly determined as well.

8-2.6 Summary of sample introduction techniques and their application in geochemistry

Table 8-1 shows a summary of the applicability and potential applications of the various sample introduction techniques investigated in this research.

8-3 Future development of the technique of ICP-MS

Although the majority of work has been dirrected at sample introduction, in the twelve years since this technique was developed, ICP-MS has been continually evolved resulting in a number of small and gradual enhancements to performance such as dynamic range and detection limits. With the exception of the introduction of high resolution ICP-MS (section 8-3.1.1) there have been no major "revolutionary" developments in the technique.

In this final section, developments in other fields of mass spectrometry are reviewed and their likely applicability to ICP-MS is considered.

Technique	**Application**
Solution Nebulisation	General geochemical analysis of minor and trace elements where good accuracy and precision are a primary requirment. eg. mineral exploration and academic investigations of large areas.
Slurry Nebulisation	Limited academic research. Not suited to routine work where a large number of samples need to be determined
Flow Injection	General geochemical analysis of minor and trace elements where good accuracy and precision are a primary requirment. eg. mineral exploration and academic investigations of large areas.
	Analysis of minerals such as halite or saline solutions such as sea or pore waters where the final solution would have a high salt content
	Analysis of fluid inclusion leachates
Electrothermal Vaporisation	Limited academic research. Not suited to routine work where a large number of samples need to be determined. Not recommended until further development of both the method and the technology is carried out.
Laser Ablation	Fast screening (i.e. semiquantitative) of bulk compositions, eg. mineral exploration
	Feature analysis of individual grains for petrogenetic and other such investigations
	Feature analysis of sedimentary materials todetermine trends in elemental composition

Table 8-1. Summary of the applicability and potential applications of the various sample introduction techniques for ICP-MS

8-4.1 Plasma

Several workers have investigated the posibility of using gases other than argon to form the plasma. Choot and Horlick[8] used an argon plasma mixed with other gases and found that the presence of a molecular gas changes the fundamental properties of the plasma and that the addition of a few percent of hydrogen or nitrogen was found to enhance ionisation. This is attributed by Jarvis *et al*[9] to the higher thermal conductivity of these gases, leading to a more efficient transfer of energy within the plasma. If this is the case, it might explain the different mass versus response profiles obtained for wet and dry plasmas, the water from the solvent providing significant levels of hydrogen and oxygen in the central channel in the plasma, and may account for the relative lack of sensitivity of 'dry' introduction techniques such as laser ablation and electrothermal vaporisation, compared to solution techniques. One area for further research would be to investigate the effect on sensitivity of introducing a gas such as hydrogen into the nebuliser line for laser ablation or electrothermal vaporisation.

Most of the work performed on mixed gases has been with the intention of removing interferences. Evans and Ebdon[10,11] examined the effect of oxygen and nitrogen additions to a plasma and reported a reduction in the levels of the chlorine polyatomic species $ArCl^+$ and the argon dimer Ar_2^+. Beauchemin and Craig[12] also demonstrated a reduction in the argon dimer by the introduction of hydrogen and nitrogen. Both these groups reported reduced sensitivity for the mixed gas system.

The ultimate way to remove argon induced interferences is to use a gas other than argon to form the plasma, the most likely replacement being helium. However, a number of lower mass alternative interferences have been reported by Koppenaal and Quinton[13]. The helium ICP was found to be difficult to ignite and showed poorer matrix tolerance and greater matrix suppression than the argon ICP, although sensitivity for elements in simple matrices were of the order of 100 times greater.

Other workers have investigated the possibility of using a microwave induced plasma instread of an ICP. Brown *et al*[14] used a helium microwave induced plasma (MIP) while Wilson *et al*[15] used a nitrogen only plasma. The helium and nitrogen MIP's were found to be as unstable and intolerant of real samples as the helium MIP.

The lack of recent published work suggests that the practical difficulties were such that this area is unlikely to produce any significant advances.

8-4.2 Mass analysers

With any mass spectrometry technique, the principle component of the system is the mass analyser. Since Gray[16] used a quadrupole mass analyser in the initial development of the technique, the quadrupole has become the standard analyser for the technique. Although it has advatages in terms of being relatively inexpensive and simple, the quadrupole suffers from only being capable of unit mass resolution, which is not sufficient to resolve overlaps of analyte elements and polyatomic species. In addition, because it is effectively a bandpass mass filter, its transmission efficiency is low. The quadrupole, however, is only one of a number of possible analysers which could potentially be used in ICP-MS.

8-4.2.1 High resolution & multicollector ICP-MS

Magnetic and electrostatic sector analysers are what most people visualise as being mass spectrometers, largely due to historical precedent. They are capable of resolutions up to 10,000[17]. Bradshaw *et al*[18] and Morita *et al*[19] both reported the development of an ICP-MS system based on double focussing magnetic sector analysers. In both cases the ICP used is a standard system but has been electrically isolated from the vacuum system and is given a high positive potential to provide the required ion accelerating voltage for the ion beam. Having passed through the interface, electrostatic lenses are used to change the beam shape from essentially circular to a slit like profile, in order to gain maximum transmission.

These systems are now commercially available and in addition to the high resolution, are capable of detection limits of the order of ppq (pg.l^{-1}) for conventional nebulisation. Although such performance is ideally suited to the determination of ultratrace levels of elements, such as the determination of the platinum group metals and gold in geological materials, both the high cost and amount of operator skill required are likely to limit such instrumentation to extremely well funded research establishments.

Although outside the scope of this work, the traditional use of mass spectrometry in geochemistry has been the determination of isotope ratios for geochronology studies[20]. This work has traditionally been carried out using thermal ionisation mass spectrometry, the precision necessary for such work is beyond the scope of quadrupole ICP-MS instruments. The high resolution magnetic sector instruments have been adapted by Walder *et al*[21],[22] to use a multicollector detection system to allow the simultaneous determination of a number of isotops. Using this system, Walder's group have reported a precision for the ratio ^{206}Pb:^{204}Pb in NIST SRM Pb-981 of 0.02-0.04% RSD. Such precision is comparable to those obtained by thermal ionisation mass spctrometry[21] but analysis times for the ICP-MS multicollector were typically 100 seconds compared to 25 minutes by thermal ionisation mass spectrometry. This, combined with the relative ease of sample preparation compared to thermal ionisation, suggests that multicollector ICP-MS is likely to lead to significant advances in this field of research.

8-4.2.2 Time of flight ICP-MS

Through advances in fast electronics, the technique of time of flight mass spectrometry has recently generated considerable interest in the field of organic mass spectrometry, especially when coupled to laser desorption ionisation techniques. The time of flight mass spectrometer is very simple to manufacture and capable of both high resolution and high sensitivity. Falk *et al*[23] and Myers and Hieftje[24] have both presented work on the design of an ICP-MS based around a time of flight mass spectrometer. Although no data have as yet been presented, it seems likely that this is an area of great potential for gaining improvements in sensitivity. At present the cost of the fast electronics is quite high, but once its usefulness has been proved and demand grows, the ICP-TOFMS will probably be the first low cost benchtop ICP-MS. More important, the time of flight offers the potential for increased sensitivity and resolution over current quadrupole based systems. Whilst unlikely to achieve the performance of the magnetic sector instruments, time of flight based ICP-MS has the greatest potential for improving the sensitivity and resolution of the technique.

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