

**SAMPLE MANIPULATION AND SAMPLE INTRODUCTION
TECHNIQUES FOR INDUCTIVELY COUPLED PLASMA-
ATOMIC EMISSION SPECTROMETRY AND INDUCTIVELY
COUPLED PLASMA-MASS SPECTROMETRY**

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ABSTRACT

Alternative sample manipulation and sample introduction methods for inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) have been investigated. The broad objectives of the study were to broaden the scope and improve the analytical performance of the techniques. The methods which were investigated were :

1) Laser ablation. This technique was used only in combination with ICP-MS. The technique was not applied to ICP-AES because the laser ablation system is dedicated to the ICP-MS instrument. The laser ablation system was applied to the direct analysis of solid refractory materials, without dissolution of the sample. The main advantages of avoiding the dissolution step are that the sample preparation is rapid, there is no dilution or contamination of the sample, and no loss of volatile analyte elements. The problems which were encountered with the use of laser ablation were firstly, poor precision of measurement relative to solution analysis due to sample particles of widely varying size entering the plasma, and secondly, memory effects when changing from one sample type to another.

2) Flow injection. This sample manipulation method was used in combination with pneumatic nebulization for ICP-AES and ICP-MS. The technique was applied to a number of different analytical problems, with the objectives of

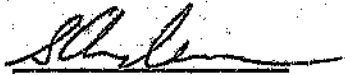
speeding up analysis times, increasing the matrix tolerance of the instruments, and automating a variety of sample preparation processes.

3) Hydride generation. This technique was applied to the determination of arsenic and selenium by ICP-AES and ICP-MS, using a novel type of gas liquid separator. The advantages of the technique were the separation of the analyte elements from interfering matrix species, and increased analyte sensitivity due to the excellent transport efficiency of hydride generation relative to solution nebulization.

Numerous advantages have been obtained from the application of these sample manipulation and sample introduction techniques. Methods have been developed for the analysis of materials which are not suited to conventional solution nebulization, and the techniques have been used to improve the efficiency of analysis, to achieve lower detection limits, and to eliminate interferences.

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



S.T.G. Anderson

7th day of February, 1994.

In memory of my Parents

Stanley Anderson

1921-1978

and Joyce Anderson

1927-1992

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Chapter 1. Introduction and Theory

1.1 Introduction

The inductively coupled plasma (ICP) is well established as an excitation source for optical emission spectrometry and as a source of ions for mass spectrometry. Inductively coupled plasma-optical emission spectrometry (ICP-AES) has been in use for almost thirty years and is widely accepted as a technique for elemental analysis. Inductively coupled plasma-mass spectrometry (ICP-MS) is a much newer technique, but in the ten years that ICP-MS instruments have been available, the technique has rapidly become established as a complementary technique to ICP-AES. Both techniques are capable of rapid, multielement analysis with good accuracy and precision. The two techniques dovetail with each other, since the detection systems are quite different and therefore many of the problems experienced with one technique are not experienced with the other. However, the introduction of the sample into the plasma is a problem which is common to both techniques.

ICPs can not tolerate the introduction of large quantities of foreign material, which has a tendency to extinguish the plasma or at least cause it to become unstable and

thus degrade precision of measurement. To ensure efficient excitation or ionisation, the sample must be in a form which is easily dissociated, i.e. a vapour or a finely dispersed solid or liquid. In almost all methods of sample introduction into ICPs (an exception being direct sample introduction), a small amount of sample material is carried in a stream of argon gas (which the plasma can tolerate) and injected into the centre of the plasma. The most commonly used sample introduction method for routine applications is pneumatic nebulisation, in which a flow of liquid sample is broken up into small droplets by a high-velocity stream of argon. The dispersed sample is then carried in the argon stream, via a spray chamber which removes all but the smallest droplets, to the plasma.

The main advantages of pneumatic nebulisation are simplicity, ease of use and good analytical performance. These advantages have made pneumatic nebulisation the most widely used sample introduction technique. However, there are many disadvantages to pneumatic nebulisation. The greatest disadvantage is the requirement that the sample be in solution form. This implies that solid samples must be dissolved prior to analysis, which is time consuming and in some cases virtually impossible. There is also the problem of contamination of the sample or loss of volatile analytes in the dissolution process, as well as degradation of detection limits due to dilution of the sample. There are also disadvantages inherent in the nebulisation process. Firstly, sample transport efficiency is only of the order of one to two per cent, which degrades absolute detection limits. Secondly, nebulisation efficiency is dependent on the viscosity of the solution.

Thirdly, the spray chamber is a source of memory effects, particularly of volatile species such as elemental mercury and osmium tetroxide.

Although pneumatic nebulisation remains the sample introduction method of choice for most applications, a wide variety of alternative methods have been explored for applications where dissolution or pneumatic nebulisation present problems. Alternative solution nebulisation methods include ultrasonic, thermospray and direct injection nebulisers which provide better sample transport efficiency than pneumatic nebulisers, although each has problems associated with it. The introduction of solids without prior dissolution has obvious advantages, and several methods of solid sample introduction have been investigated, including spark and laser ablation, slurry nebulisation, direct sample introduction, and electrothermal vaporization. Electrothermal vaporization has also been used for solution introduction.

A certain amount of sample manipulation is generally necessary prior to introduction of the sample into the plasma. Samples in solution must be diluted to appropriate acid and dissolved solid concentrations, and in most cases an internal standard may be added to correct for matrix effects. In addition to these steps it is sometimes necessary to preconcentrate the elements of interest to improve detection limits, or to separate these elements from interferences in the sample matrix. In many cases the manipulation is done in the laboratory prior to analysis, but significant reductions in analysis time can be achieved by doing the

sample manipulation on-line. Flow injection is a technique which lends itself to on-line sample manipulation and which can be used in conjunction with many other techniques. Techniques which can be used to preconcentrate or separate analyte elements include various chromatographic methods, hydride generation and electrothermal vaporization.

Pneumatic nebulisation is likely to remain the method of choice for most routine applications of ICP-AES and ICP-MS. However, when sample dissolution or pneumatic nebulisation present problems for a particular application, it is necessary to investigate alternative methods. This work describes the investigation of a variety of alternative sample introduction techniques and their application to specific problems in ICP-AES and ICP-MS. The use of on-line sample manipulation prior to introduction of the sample into the plasma is also described.

The sample introduction and sample manipulation techniques investigated in this work were selected on the basis that each technique should be potentially applicable to specific analytical problems at Mintek. The selected techniques were:

- 1) Laser ablation, which enables direct analysis of solid materials. The laser ablation unit is dedicated to the ICP-MS instrument and was therefore not applicable to ICP-AES.
- 2) Flow injection, which lends itself to on-line sample manipulation and was applied to both ICP-MS and ICP-AES.

3) Hydride generation, which confers greatly increased analytical sensitivity for the hydride-forming elements as well as, in some cases, elimination of interferences. This technique was applied to both ICP-MS and ICP-AES.

Wherever possible the sample manipulation and introduction systems were assembled from readily available, inexpensive materials or by adaptation of existing equipment.

1.2 Aim of the Investigation

The investigation of alternative sample introduction techniques and on-line sample manipulation for ICP-MS and ICP-AES was undertaken with two main objectives. The first was to extend the applicability of the techniques to sample types which are not suited to conventional sample introduction. The second was to improve the quality of analyses by improving the speed and efficiency of analysis, lowering detection limits, and eliminating interferences.

1.3 Inductively coupled plasma-atomic emission spectrometry¹⁻⁴

1.3.1 Principles of atomic emission

When sufficient energy is supplied to an atom, an electron of the atom absorbs a discrete quantum of energy and is raised to a higher energy level. This process is termed excitation. The excited atom is unstable and the excited electron rapidly returns to the ground state. This process may involve more than one energy level step, and at each step the atom emits energy in the form of a photon. This process is called atomic emission. Each emitted photon has an energy equal to (and therefore a wavelength proportional to) the difference between the atomic energy levels.

The dispersion of elemental atomic emission by means of a spectrometer results in a "fingerprint" of spectral emission lines which is useful for element identification. The intensity of the lines is proportional to the number of emitting atoms and can therefore be used to determine elemental concentrations.

The emission spectrum of each element consists of a large number of lines, due to the large number of possible electronic transitions. The number of lines in elemental spectra tends to increase with the complexity of electron configuration, and hence with atomic number. Since the total emission spectrum of a sample is a composite of all the elements present, complex sample matrices have

correspondingly complex spectra, which gives rise to the problem of interelemental line coincidence. This problem is made more severe by the fact that spectral lines are not truly monochromatic, and are in fact broadened to an approximately Gaussian shape about the emission wavelength. The main reason for this broadening is the Doppler effect, due to the emitting species moving randomly at high speed in the emission source, towards or away from the entrance slit. The problem of line overlap can be overcome by ensuring that the degree of dispersion of the spectrum is sufficient to resolve the overlapping lines, and where this is not attainable, by careful selection of analyte lines which are free of interference in a particular sample matrix. This approach has made ICP-AES widely applicable despite interference problems, but there are applications where the complexity of the matrix spectrum makes ICP-AES analysis practically impossible.

"Atomic emission" is something of a misnomer when an ICP is the excitation source, since the majority of emitting species are ions rather than atoms. Since emission occurs in the optical region of the spectrum, which is bounded by the x- and gamma-ray region and the microwave region at the high and low energy ends, there is an argument for using the term "optical emission" rather than "atomic emission". However, inductively coupled plasma-atomic emission spectrometry is the term recommended by IUPAC and is unlikely to be changed.

1.3.2 Origins

The use of the inductively coupled plasma as an excitation source for emission spectrometry was first described by Greenfield *et al*⁵ and Wendt and Fassel⁶ in 1964 and 1965. It was soon established that the capabilities of the ICP were superior to any other excitation source for the analysis of solutions. This was partially attributable to the high temperature and good stability of the plasma, but the main advantage which the ICP has over other discharges is the annular channel through which the sample is injected. This channel ensures efficient vaporisation, atomization, ionisation and excitation of the sample, thereby reducing the severity of matrix effects.

The first ICP-AES instruments consisted of 'home-built' excitation sources and single-channel monochromators, but it was only when multi-channel spectrometers were employed that the multi-elemental capability of the technique could be fully exploited. This led to a greater acceptance of the technique, and by the mid-1970s purpose-built ICP-AES systems became available. Today ICP-AES is a standard technique in a wide variety of applications and there are many thousands of instruments in operation world-wide.



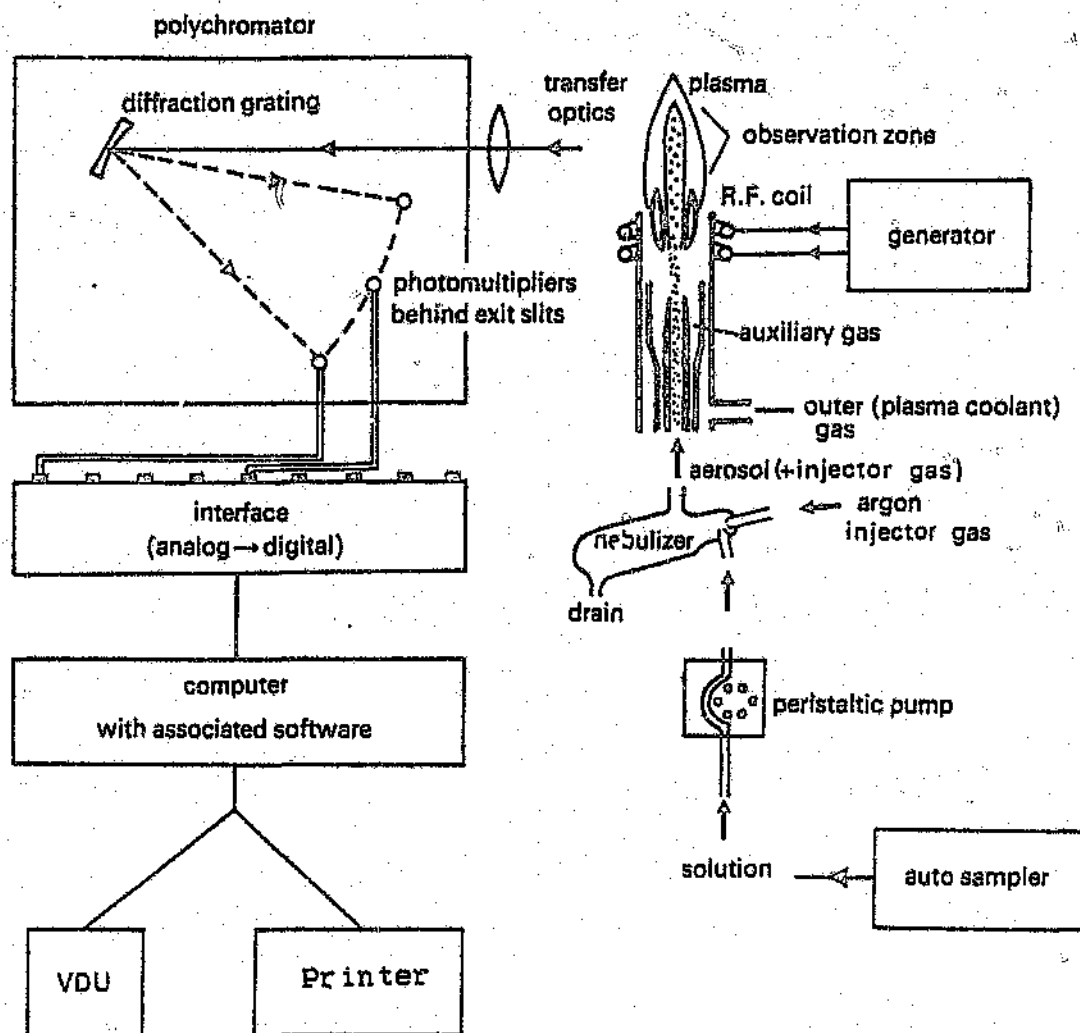
1.3.3 The ICP-AES instrument

An ICP-AES instrument consists of four main components: the sample introduction system, the inductively coupled plasma, optics and spectrometers, and the data processing system. A diagram of a typical ICP-AES system is shown in *Fig. 1.1*. In an instrument utilising conventional sample introduction, a liquid sample is pumped through a nebuliser in which the sample stream is dispersed into small droplets by a stream of argon. The sample aerosol passes through a spray chamber which removes all but the smallest droplets. The remaining aerosol is injected into the plasma where the processes of atomization, ionisation, excitation and emission occur. The emitted light is dispersed by means of a diffraction grating and detected at element-specific wavelengths. The measured intensity is then related to the concentration of the analyte elements.

1.3.3.1 Sample introduction

Conventional ICP-AES analysis is performed on solutions which are injected into the plasma in the form of an aerosol carried in a stream of gas. The sample introduction system which generates the aerosol consists of a peristaltic pump, a nebuliser and a spray chamber. The peristaltic pump draws the sample solution up and pumps it to the nebuliser. In some systems the pump is also used to drain the waste solution which collects in the spray chamber.

Fig. 1.1. Overview of a typical ICP-AES instrument
(Thompson and Walsh 1983)



The most commonly used nebuliser types on ICP-AES systems are the Meinhard concentric and Babington V-groove types. Both are based on the principle of a high velocity stream of the carrier gas (generally argon) passing through a narrow orifice, which is used to break up the solution stream into small droplets. However, the implementation is different in each type.

The Meinhard nebuliser consists of two concentric tubes: an inner capillary tube through which the sample is pumped, and an outer carrier gas tube which narrows at the tip. The sample is drawn through the orifice by the Venturi effect of the carrier gas, and is dispersed into droplets. It is therefore not essential to use a peristaltic pump to supply solution to a Meinhard system, but it is recommended since this counters capillary blockages by solid matter.

The Babington nebuliser consists of a v-shaped groove with two orifices at the apex, the solution orifice positioned above the narrower carrier gas orifice. The solution is pumped through the upper orifice and runs down the groove until it reaches the gas orifice, where it is dispersed. The peristaltic pump is essential in the Babington system as there is no inherent solution uptake. The Babington nebuliser is particularly suited to situations where there may be particulate matter in the sample solutions, as the diameter of the sample orifice is relatively large in comparison to the narrow capillary tube of the Meinhard nebuliser. It is therefore less prone to blockage. Diagrams of Meinhard and Babington nebulisers are shown in *Fig. 1.2*.

Fig. 1.2. Nebulisers for sample introduction into the ICP

(Moore 1989)

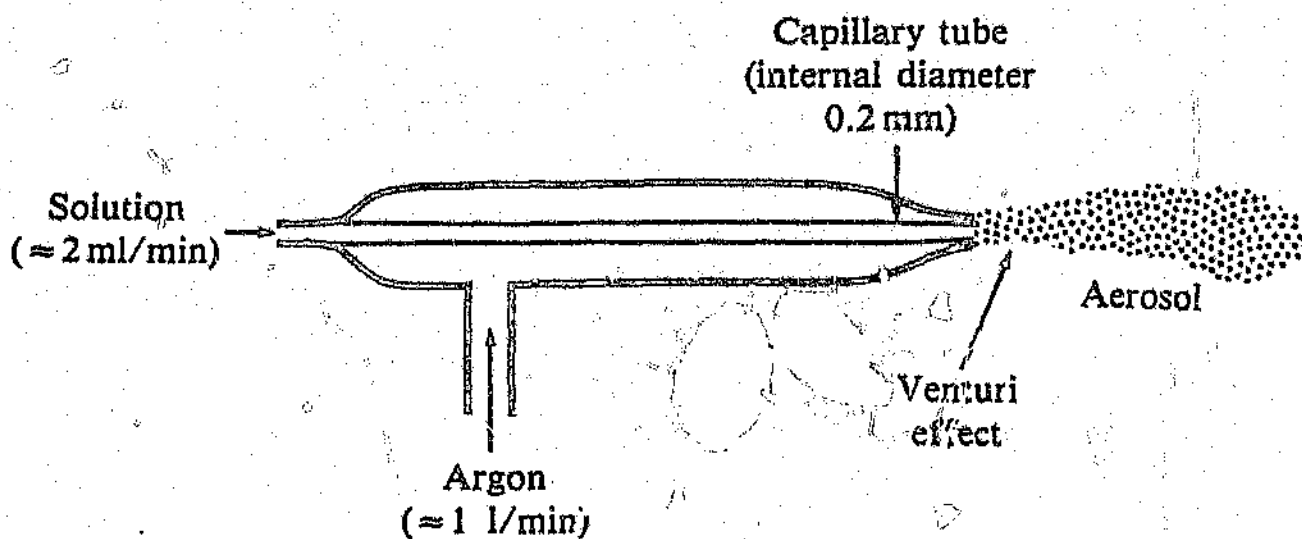


Fig. 1.2a. Meinhard concentric nebuliser

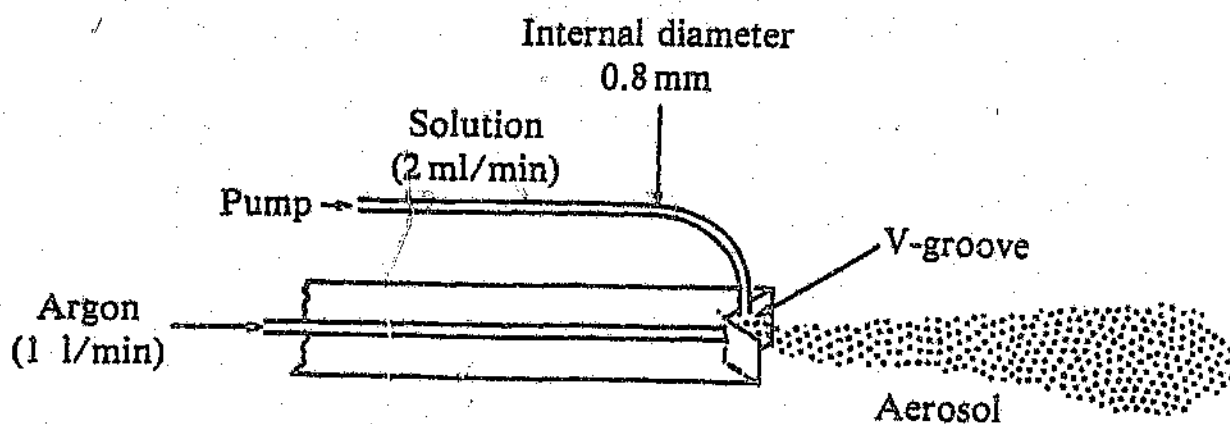


Fig. 1.2b. Babington V-Groove nebuliser

Nebulisers generally do not generate aerosols of even droplet size. If large droplets ($> 10 \mu\text{m}$ in diameter) are allowed to enter the plasma they cause instability of analyte signals due to fluctuations in the plasma temperature. The aerosol is therefore not sprayed directly into the plasma, but into a spray chamber. This is a glass chamber consisting of a baffle system which causes the larger droplets to collect on the sides of the chamber and allows only the smaller droplets to be transported to the plasma. The larger droplets collect in the bottom of the spray chamber and are pumped to waste.

1.3.3.2 The inductively coupled plasma

The ICP system consists of the plasma radio frequency (RF) generator, the torch stand and the gas supply system.

During the development of the ICP as an emission source, many different torch sizes, incident power levels and frequencies were investigated. However, these parameters have to a large extent been standardised in modern instruments and similar sets of conditions are used on both ICP-AES and ICP-MS systems. These are: an 18 mm diameter Fassel-type torch, and a plasma operating at an incident power of between 1 and 2 Kw and a frequency of 27 or 40 MHz. This frequency was chosen to comply with regulations controlling interference to radio traffic.

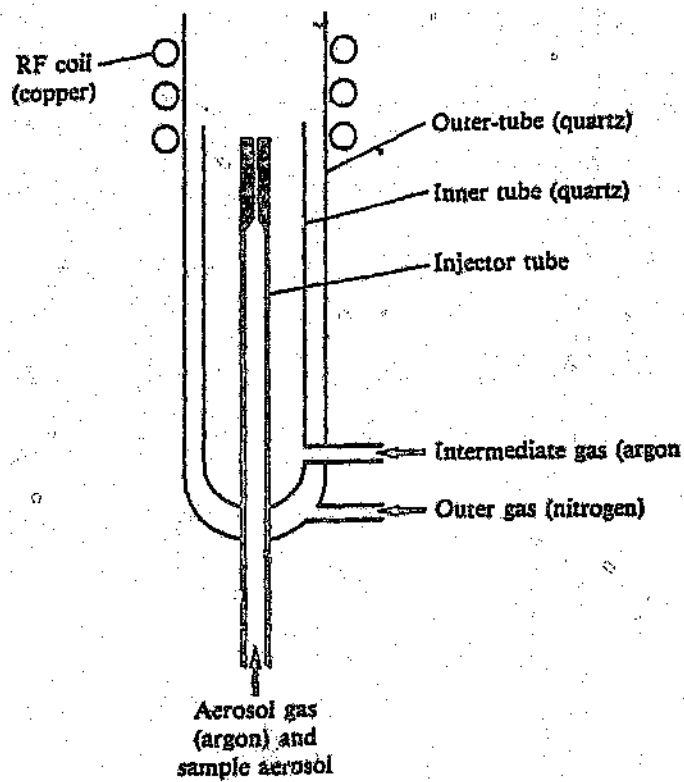


Fig. 1.3. The ICP torch

(Moore 1989)

To achieve a stable plasma, an RF source with a stable frequency and power output is required. The frequency of the RF generator is kept constant by a quartz crystal. However, this implies that any change in the impedance of the plasma results in a loss of power. This is countered by automatic tuning of the plasma based on a feedback system, which reduces power fluctuations to below 0.1 %. Older RF generators are based on high power triode valves, but most new instruments are supplied with solid state generators.

The plasma torch consists of two concentric tubes with independent gas inlets, and an innermost tube through which the sample is injected (*Fig. 1.3*). The outer tubes are made of quartz to withstand the high temperatures near the plasma. The injector tube is usually also quartz, but tubes made of other materials (for example alumina) may be used to handle corrosive samples.

Argon is generally used as the plasma gas, although other inert gases can also be used in special circumstances. There are three streams of gas through the plasma torch. The innermost stream carries the sample through the injector tube and into the plasma, the middle stream provides the argon to sustain the plasma, and the outermost or coolant gas prevents the plasma from impinging on and melting the torch tube. Each of these gas flows is independently controlled by rotameters.

The torch is positioned inside a water-cooled induction coil, typically with three turns. Energy is transferred to the plasma in a manner analogous to the operation

of a transformer. When an alternating current flows in the coil, the fluctuating magnetic field couples with the gas, accelerating the ions and electrons in the gas. These charged particles collide with other particles, transferring energy and causing further ionisation. In this way the plasma is sustained. However, the inert gas does not contain enough charged particles at room temperature to initiate the plasma. It is therefore necessary to seed the gas with electrons of sufficient energy to ionise the gas. This is done by generating a spark from a Tesla coil in the gas stream. The ionised gas is then able to couple with the magnetic field from the RF coil and the plasma is generated. Since the rate of collisions in the plasma is high, energy transfer to particles is very efficient, and the plasma reaches temperatures of between 6000 and 8000 K.

The high velocity injection of the carrier gas stream along the axis of the torch results in the characteristic 'doughnut' shape of the plasma (*Fig. 1.4*). This ensures efficient and rapid energy transfer to the sample droplets, and in rapid succession the sample is desolvated, volatilised and dissociated. The majority of sample atoms are ionised, both atoms and ions are excited and emission occurs. All of these processes occur in the few milliseconds in which each sample atom is resident in the plasma.

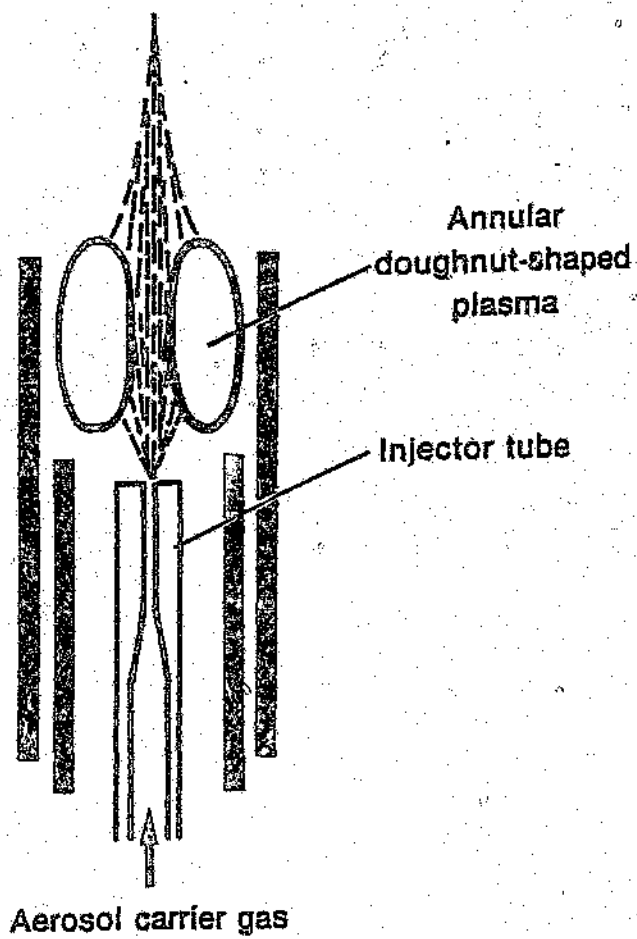


Fig. 1.4. The "doughnut-shaped" plasma

(Moore 1989)

1.3.3.3 Optics and spectrometers

The optical system serves to direct light from the plasma to one or more spectrometers. It usually consists of a series of mirrors and lenses, although a recent innovation uses optical fibres as light guides. The spectrometer consists of a dispersion system and a means of signal detection. The dispersion system spatially resolves the polychromatic light emitted from the plasma into its component wavelengths. The dispersion device that is most commonly used is the diffraction grating. Light from the plasma is directed through a narrow (20 μ m) entrance slit and dispersed by the grating. The dispersed light passes through an exit slit to the detector. There are two basic types of spectrometer, sequential and simultaneous (*Fig. 1.5*). A sequential spectrometer (or scanning monochromator) has a single detector and a moveable diffraction grating which is rotated to direct light of a selected wavelength to the detector. The emission of each analyte element is measured in sequence. Monochromators are highly versatile, since lines can be selected over the entire spectral range of the grating. A simultaneous spectrometer (or polychromator) has a fixed grating and several detectors positioned at preselected wavelengths. This enables much faster multielement analysis than a monochromator system, since detection of all elements is simultaneous. However, simultaneous systems do not have the flexibility of sequential systems, and if a preselected line is subject to an overlap interference in a particular sample, there is no possibility of selecting another line. For this

Fig. 1.5. Optical systems of simultaneous and sequential spectrometers
(Moore 1989)

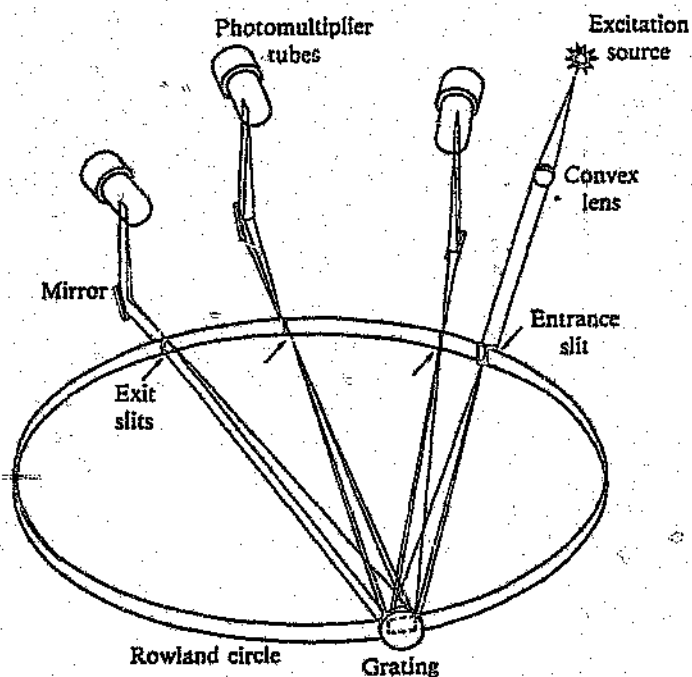


Fig. 1.5a. Polychromator system

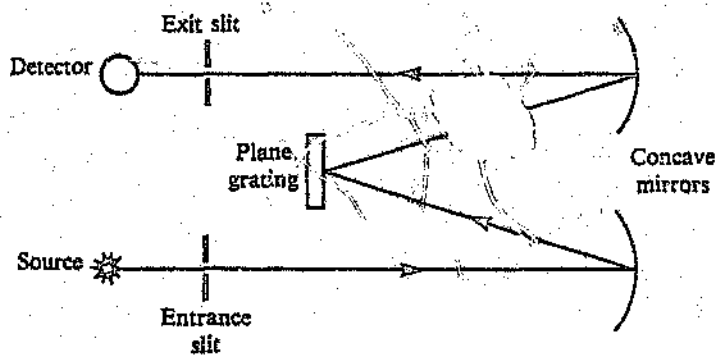


Fig. 1.5b. Monochromator system

reason, many ICP-AES instruments are now fitted with both simultaneous and sequential spectrometers to provide both speed and flexibility.

The detector most commonly used in ICP-AES systems is the photomultiplier tube, a device which, when exposed to light, generates an electric current which is proportional to the intensity of the incident light. The current is integrated and amplified to give a millivolt output signal.

1.3.3.4 Data processing

Data processing is handled by a dedicated personal computer. The interface consists of an analog-to-digital converter for data acquisition as well as digital output for control of the instrument functions and autosampler use. Software supplied by the instrument manufacturers is able to handle almost all aspects of data processing, including regression analysis, report generation and statistical evaluation of results.

1.3.4 Characteristics of ICP-AES analysis

1.3.4.1 Applicability

An ideal technique for elemental analysis would be universally applicable, i.e. it would have the capability to determine all the elements in any type of material. The usefulness of a technique can be evaluated in terms of how nearly the technique approaches this ideal.

In terms of elemental versatility, ICP-AES is very good, since the temperature of the ICP is sufficiently high to achieve efficient excitation of some seventy elements. However, in terms of applicability to materials, ICP-AES with conventional sample introduction is restricted to the analysis of aqueous solutions, which is a drawback of the technique.

1.3.4.2 Spectra and interferences

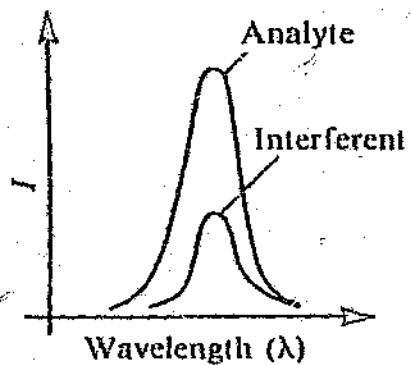
Although ICP-AES is relatively free of interferences when compared to many other spectroscopic techniques, there are interference problems which can adversely affect ICP-AES analysis. These interferences can be broadly classified as spectral interferences, matrix effects and memory effects.

Spectral interferences

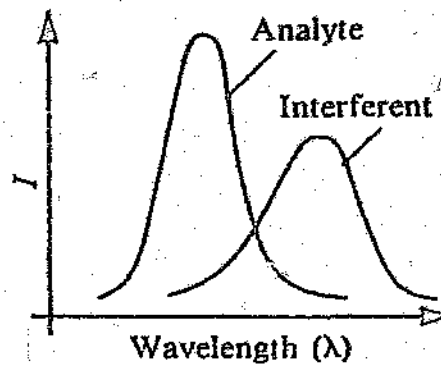
Spectral interferences or line overlap interferences have been discussed in Section 1.3.1. There are three types of spectral interference: direct overlap, 'wing' overlap and background shift. Examples of each type are shown in *Fig. 1.6*. In most instances spectral interferences can be overcome by careful selection of interference-free analyte lines. However, in cases where this approach is not possible (for example, where the instrument is a fixed-channel polychromator system), there are other ways of overcoming these problems. In the case of direct overlap, a correction factor based on the measured concentration of the interferent can be applied. This method can also be applied to wing overlaps, although it is less accurate because small changes in spectrometer profile can result in large changes in the severity of the interference. Variations in the background continuum which are spectral in origin are caused by recombination radiation, which is emission resulting from the capture of free electrons by ions in the plasma. Background shift can be corrected by measuring the background emission level on one or both sides of the analyte peak and subtracting the background signal from the analyte signal.

Matrix effects

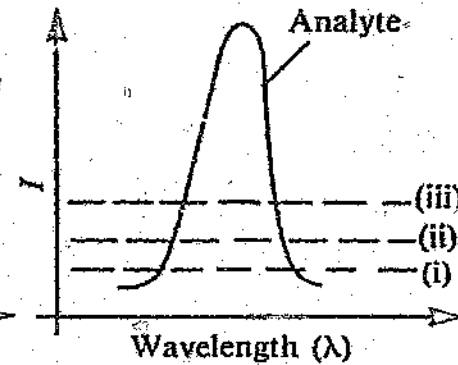
Matrix effects are variations in signal intensity which can be ascribed to the physical or chemical composition of the sample. ICP-AES is relatively free of



(a) Direct spectral overlap



(b) Wing overlap



(c) Continuum overlap

Fig. 1.6. Types of spectral interference

(Thompson and Walsh 1983)

matrix effects when compared to lower temperature emission sources. The reason for this is the total sample decomposition in the plasma, which eliminates the chemical effects due to radicals and molecular species that occur in other sources. However, ICP-AES is still subject to some matrix effects. The most significant sources of matrix interferences are nebulisation effects and ionisation effects.

Nebulisation effects are a result of variations in the nebulisation efficiency of samples due to changes in sample composition. An example of this is the observed decrease in analyte signals with increasing acid concentration. Ionisation interference is the suppression of analyte signals due to the presence of easily ionisable elements (e.g. Na, K, Ca) in the plasma. The problem of matrix effects can generally be solved by the use of internal standardisation and/or the matrix-matching of standards to samples.

Memory effects

The residual analyte signal which is observed after aspiration of the analyte solution has ceased is called the memory effect. The main source of memory effects is the spray chamber, which has a large dead volume where residual aerosol remains after aspiration. Care must be taken to ensure that adequate wash-out time is allowed between samples, so that there is no carry-over of analyte from one sample to the next. When there are large variations in analyte concentrations,

the wash-out time is generally longer than the measurement time. This inefficiency is one of the drawbacks of conventional nebulisation.

1.3.4.3 Detection limits

Detection limits are an important characteristic of any analytical technique. Conventionally these are quoted as the solution concentration equivalent to three times the standard deviation (3σ) of the blank signal. Detection limits are thus a function of the sensitivity and precision of the technique as well as the level of the background signal.

Published ICP-AES detection limits must be used with caution, since these have generally been established for ideal solutions under ideal operating conditions. Detection limits may be very much higher for real samples, and will also depend on the instrument used. However, the published values can be used as general guidelines. Detection limits for ICP-AES vary widely from one element to another: the most sensitive magnesium emission line has a quoted detection limit of $0.10 \mu\text{g.l}^{-1}$, while the most sensitive line for uranium has a detection limit of $170 \mu\text{g.l}^{-1}$. However, detection limits for most elements lie in the range of 1 to $50 \mu\text{g.l}^{-1}$. Practical limits of determination are usually set at ten times the quoted detection limit.

1.3.4.4 Accuracy and precision

The excellent stability of the ICP as an emission source enables good precision to be achieved. Reported precision values based on repeated measurements of a sample are generally around 1% for measurements which are well above the detection limit. The main contributors to measurement imprecision are fluctuations in the generator power supply and the nebuliser system. On simultaneous instruments, internal standardisation can be used to improve precision to below 0.2%, provided that the internal standard is carefully chosen.

Accuracy is dependant to an extent on precision, but more important are systematic errors. The main sources of systematic errors in ICP-AES are matrix effects and spectral interferences, both of which can be avoided by matrix matching and careful line selection.

1.3.4.5 Dynamic range

The width of the linear dynamic range is an important feature of any analytical technique. If the range is narrow, as is the case with atomic absorption spectrometry, repeated dilutions may be necessary to bring the analyte elements within the calibration range. These dilutions are time-consuming and introduce imprecision. ICP-AES has a wide linear dynamic range, and is potentially capable of linear calibration graphs ranging from below $0.010 \mu\text{g.ml}^{-1}$ to $1000 \mu\text{g.ml}^{-1}$. In

practice however, calibration ranges are limited by significant curvature in some cases, as well as unacceptably high relative errors in the low concentration range when wide calibration ranges are used. In most practical applications calibration ranges cover two to three orders of magnitude.

1.4 Inductively coupled plasma-mass spectrometry^{2,3,10,11}

1.4.1 Origins

1.4.1.1 Precursors of ICP-MS

ICP-MS is often described as a hybrid technique. This is an apt description, as it resulted from the coupling of two other multielement analytical techniques, with the objective of eliminating the worst features of each while retaining the best features. These techniques were ICP-AES and spark source-mass spectrometry (SS-MS).

As has been described in Section 1.3.4, ICP-AES is an excellent technique for the elemental analysis of solutions because of its sensitivity, precision, and relative freedom from matrix effects. These advantages are to a large extent attributable to the high temperature, good atomization and ionisation efficiency, and excellent stability of the inductively coupled plasma when compared with other emission sources. However, limitations of ICP-AES became apparent when the technique

was applied to the analysis of materials containing elements with complex emission spectra, such as the platinum group metals and the rare earths. Since there are a large number of possible electronic energy level transitions for these elements, and therefore a relatively low probability of any one particular transition occurring, their spectra are characterised by a very large number of emission lines, but the most intense lines are relatively weak. As a result of this these elements tend to have higher limits of detection than those of the first transition metal series and above (although there are exceptions), and analyses are prone to line overlap interferences. These problems are particularly severe when determining traces in a complex matrix.

The most widely used elemental mass spectrometric technique prior to the development of ICP-MS was SS-MS, in which a sample is placed in an evacuated chamber and a high energy radio frequency spark is used to volatilise, atomise and ionise the sample. These ions are analyzed according to mass/charge ratio by the mass spectrometer. Mass spectrometry has two main advantages over emission spectrometry: it is considerably more sensitive, and mass spectra are simpler than emission spectra. This is because each element, instead of producing a large number of emission lines, produces only as many peaks as there are isotopes for that element (provided that dissociation of the volatilised material is total, and all ions are singly charged). However, the limitation of SS-MS is imposed by the method of sample ionisation. Because of the low pressure in the spark chamber, transfer of energy to the sample is extremely non-uniform. As a result the sample

is not fully atomised, and the ions produced include molecular ions of varying masses as well as multiply charged ions. The mass spectra produced by this technique are therefore complex and require skilled interpretation and high-resolution spectrometers to avoid overlap interferences. This, coupled with a relatively slow sample throughput (due to the necessity for evacuating the sample chamber before each analysis) has limited the usefulness of the technique.

1.4.1.2 Plasmas as ion sources

It was evident that if the inductively coupled plasma could be used as a source of ions for mass spectrometry, this would confer several advantages. It was already apparent from the high intensities of ionic plasma emission lines by comparison to atomic lines that the ionisation efficiency of the plasma was high for most elements. It was realised that the plasma was able to transfer energy to the sample much more efficiently and uniformly than the low pressure spark, since the plasma was at atmospheric pressure, and therefore there was a much higher frequency of collisions between sample particles and plasma gas ions, which would reduce the degree of molecular ion formation. In addition to this, the plasma would also allow a considerably higher sample throughput than SS-MS. On the other hand, mass spectrometric analysis rather than emission spectrometric analysis of the plasma would have the advantages of superior detection limits and simpler spectra with fewer overlap interferences. The challenge lay in developing a means of extracting

ions from the high temperature (6000 - 8000 K), atmospheric pressure plasma into the low pressure mass spectrometer.

A solution to this problem was suggested by work which had been performed by Sugden¹⁰ and Knewstubb¹² on the mass spectrometric sampling of chemical flames, although these studies were of processes occurring in the flames themselves rather than of material introduced into the flame. The sampling system consisted of a cone with a small (≈ 70 μm diameter) orifice between the flame and the first vacuum chamber of the mass spectrometer, over which a pressure differential was maintained by a diffusion pump. Although it was realised that a chemical flame with a maximum temperature of 3000 K was not hot enough for effective ionisation of most materials, it was anticipated that this sampling system could be applied to a plasma which would be hotter and less chemically reactive, and would therefore form fewer molecular species.

The feasibility of using a plasma as an ion source for mass spectrometry was demonstrated by Gray at the University of Surrey in 1974¹³. In this study a small d.c. arc plasma (DCP) was used, which was easier to sample than an ICP because the sampling cone could be positioned impinging on the lower temperature (3500 K) tailflame of the plasma. The feasibility study showed that excellent sensitivity was possible, with counts of between 10^4 and 10^5 obtained for some elements at concentrations of $1\mu\text{g.ml}^{-1}$ and that background counts between peaks were essentially zero. However, the system was found to be prone to severe

interelement effects and insensitive for elements with high ionisation energies (above 8 eV), due to the low temperature of the area of the plasma which was sampled¹⁴. It was therefore necessary to investigate the use of other types of plasmas.

A study was performed on a microwave plasma (MIP) system by Douglas and French¹⁵ at the University of Toronto, and this was found to have the same poor response for elements with high ionisation energies as the DCP system, once again due to the insufficiently high gas temperature in the plasma. Concurrent with this work, programmes were commenced by Houk, Fassel *et al.* at the Ames Laboratory at Iowa State University, and by Date and Gray at Surrey, to develop systems for sampling ions from inductively coupled plasmas. Co-operation between these groups resulted in the successful operation of systems at the Ames Laboratory¹⁶ and at Surrey¹⁷ within a short period of each other.

1.4.1.3 Ion sampling from the ICP

Sampling the higher temperature ICP required a larger diameter (≈ 0.4 mm) sampling orifice than that used on the MIP and DCP systems. This was necessary to prevent the formation of a boundary layer of cooler gas where molecular species would form, and improved thermal contact was required to prevent melting of the orifice rim. When this had been achieved, it was found that the influx of gas was sufficient to stall the diffusion pump. This problem was solved by adopting the system, developed for the microwave plasma at Toronto¹⁸, of a

relatively high pressure (≈ 1 mbar) first stage chamber pumped down by a rotary pump from which ions were extracted into the mass spectrometer.

1.4.1.4 Development of commercial ICP-MS instruments

Once a satisfactory extraction system had been established, rapid advancement of the technique was made by the Ames and Surrey groups, as well as the Toronto group which had switched its attention from the microwave plasma to the ICP. The first successful extraction of ions from the ICP was demonstrated in 1982¹⁹, and a year later the first commercial ICP-MS instruments were launched. In the UK the Plasmaquad, based on the Surrey system, was manufactured by VG Isotopes Ltd, and in Canada the Elan, based on the work of the Toronto group, was manufactured by Sciex, Inc. These instruments rapidly established the credentials of the technique, and other instrument manufacturers have since entered the market. The description of an ICP-MS instrument given in the following section is based on the original VG and Sciex instruments. Other manufacturers have adopted different approaches to various aspects of instrument design.

1.4.2 The ICP-MS instrument^{20,21}

In a typical ICP-MS system using conventional solution nebulisation, the sample is nebulised and the resulting aerosol is injected into the plasma. In the plasma the sample is atomised and to a large extent ionised. The plasma is sampled via the cone interface over which a pressure gradient is maintained. The ion beam is directed by a series of electrostatic lenses into the quadrupole mass analyzer. The mass analyzer discriminates according to mass/charge ratio and sweeps across the mass range to produce the mass spectrum. The mass spectral data is transferred to a computer for further processing.

The ICP-MS system can therefore be divided into a number of subsystems. These subsystems are: the sample introduction system, the inductively coupled plasma, the plasma sampling interface, the ion lenses, the quadrupole mass filter, the ion detection system and the data processing system. In addition to these there are the vacuum and cooling systems. Each of these systems will be described in detail. A schematic overview of a typical instrument is shown in *Fig. 1.7*.

1.4.2.1 Sample introduction

The conventional sample introduction system for an ICP-MS instrument is very similar to that of an ICP-AES system, which was described in Section 1.3.3.1. The only difference is that in ICP-MS the spray chamber is chilled to -5°C by a

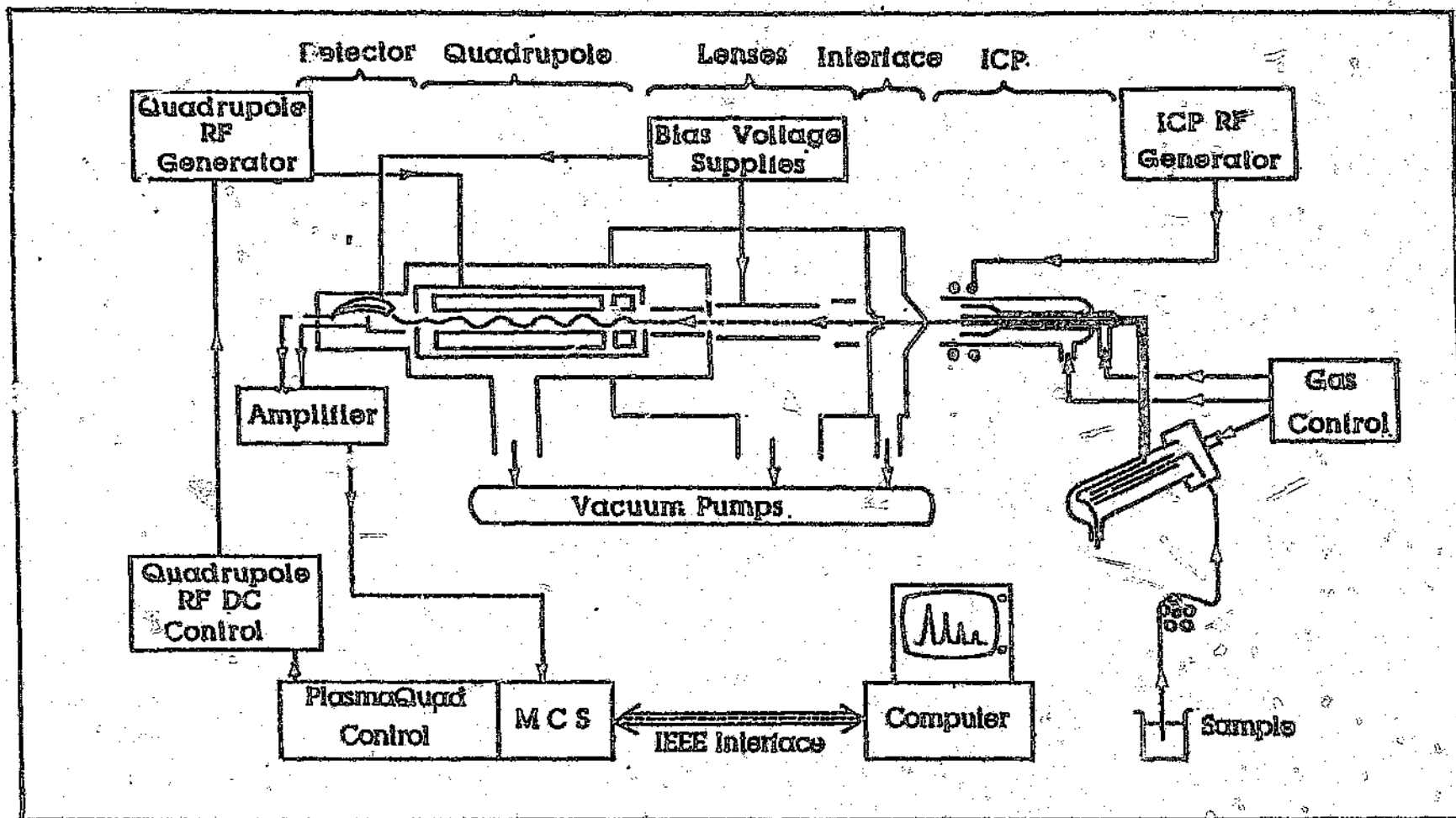


Fig. 1.7. Overview of a typical ICP-MS instrument

(VG Plasmaquad System Manual 1988)

cooling water jacket. This is done to minimise evaporation of water during nebulisation, and so decrease the water loading of the plasma. This reduces the level of undesirable oxide and hydroxide peaks in the mass spectrum²⁵.

1.4.2.2 The inductively coupled plasma

The plasma system of an ICP-MS instrument is much the same as that of an ICP-AES, which was described in Section 1.3.3.2. The only differences are the torch orientation, which is horizontal rather than vertical to facilitate ion sampling, and the use of a mass flow controller to give more accurate control the nebuliser gas flow rate.

1.4.2.3 The plasma sampling interface

As has been described in section 1.5.1, most of the work involved in the development of ICP-MS as a technique was aimed at the development of the plasma sampling interface. It is this interface that is the most important feature of the technique, since it enables the sampling of ions from the very high temperature, atmospheric pressure plasma into the high vacuum of the mass spectrometer.

The interface consists of two metal cones, each with a small aperture at the apex. The first cone (termed the sample cone) is fastened to the wall of the first vacuum chamber (or expansion chamber), which is kept at a pressure of approximately 5 mbar by a rotary pump. The wall of the chamber is water-cooled to remove heat from the cone, which impinges on the plasma. The cone aperture, which is approximately 1 mm in diameter, is aligned with the axis of the torch. The second or skimmer cone has an aperture of approximately 0.75 mm. It is positioned coaxially with the sample cone, between the relatively low vacuum first chamber and the high vacuum second chamber (*Fig. 1.8*).

- The metal used to manufacture the cones must meet several requirements. It must be a good conductor of heat, so that excessive localised heating does not occur at the aperture, it must be resistant to chemical attack by the reactive species in the plasma, and it must be physically robust, to enable easy cleaning. A number of metals have been successfully used for cone manufacture, including aluminium, copper, nickel and platinum. Of these, nickel is most commonly used, as it gives good results at low cost. The useful lifetime of a set of cones is very dependent on the acid matrix of sample solutions. When analysing samples in a 1% nitric acid matrix, a set of cones may last several months, but when analysing samples with more corrosive matrices (for example 10% sulphuric acid), the cones may only last a few days. It is therefore important to keep sample acid concentrations as low as possible. The level of dissolved solids in samples is also an important factor, since high levels of solids can cause blockage of the cone apertures with

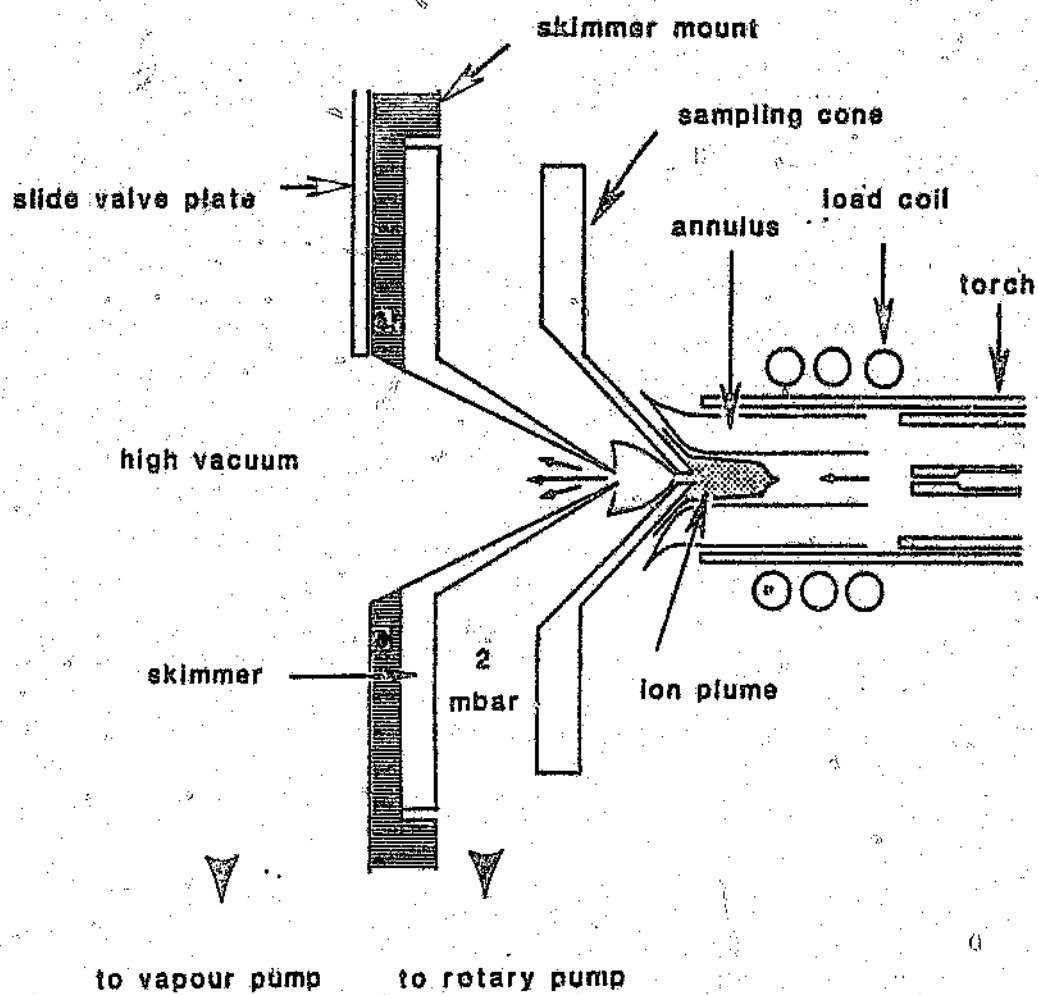


Fig. 1.8. The cone interface

(Date and Gray 1989)

resulting loss of instrumental performance. The level of dissolved solids should as a rule be kept below 0.2%, and the cones should be cleaned on a daily basis to prevent blockages.

The central portion of the plasma gas is extracted through the orifice of the sample cone due to the difference in pressure across the interface. As the gas expands into the first chamber it is rapidly cooled, which effectively prevents recombination reactions between the gas particles. The kinetic energy of the gas particles is converted into directional flow along the axis, and the gas jet reaches supersonic speed. This results in the formation of an axial shock wave termed the Mach disc, approximately 10 mm behind the aperture. Beyond this point the flow of the jet is no longer uniform, and the gas combines with the background gas in the chamber. It is consequently no longer a representative sample of the plasma. The skimmer aperture is therefore positioned between the sample aperture and the Mach disc, usually approximately 7 mm from the sample aperture. Although the temperature at the axis of the gas jet is as low as 200 K, the surrounding gas is not cooled to the same extent and in fact remains very hot. It is therefore necessary to supply cooling to the skimmer cone as well as the sample cone. Another feature of the skimmer cone interface is a slide valve, which is closed when the plasma is not operational to maintain the vacuum of the inner chamber.

The gas which has been extracted through the skimmer cone orifice is at very low pressure (approximately 10^{-6} mbar). There are few collisions between particles at this pressure, and the movement of the particles becomes random. The collection of the charged species present in the gas into a beam and the direction of the beam into the mass analyzer is achieved by the ion lens system.

1.4.2.4 The ion lens system

The ion lens system consists of a series of circular electrostatic lenses, each of which has a tunable voltage. The vacuum pump systems are different on the VG and Sciex instruments, and therefore the ion lens systems differ to suit the pumping systems. On the VG instrument where two vapour pumps are used, there are two stages to the ion lens system separated by a differential pumping aperture. On the original Sciex instrument, a single large helium cryogenic pump was used and therefore there was no need for a differential aperture. The configuration of the two systems is shown in *Fig. 1.9*. The Sciex system has since been modified and is now similar to that of the VG system.

Under normal operating circumstances the lenses are tuned to extract positive ions. The negative species are repelled and the neutral species, being unaffected by the lenses, diffuse to the pump. The system can however be specifically tuned for extraction of negative ions.

Fig. 1.9. Ion lens systems

(Date and Gray 1989)

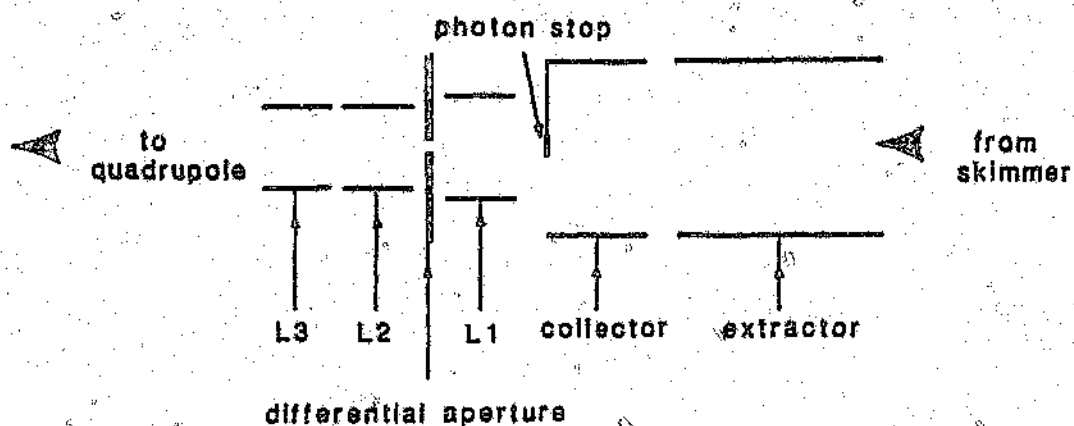


Fig. 1.9a. VG Plasmaquad type

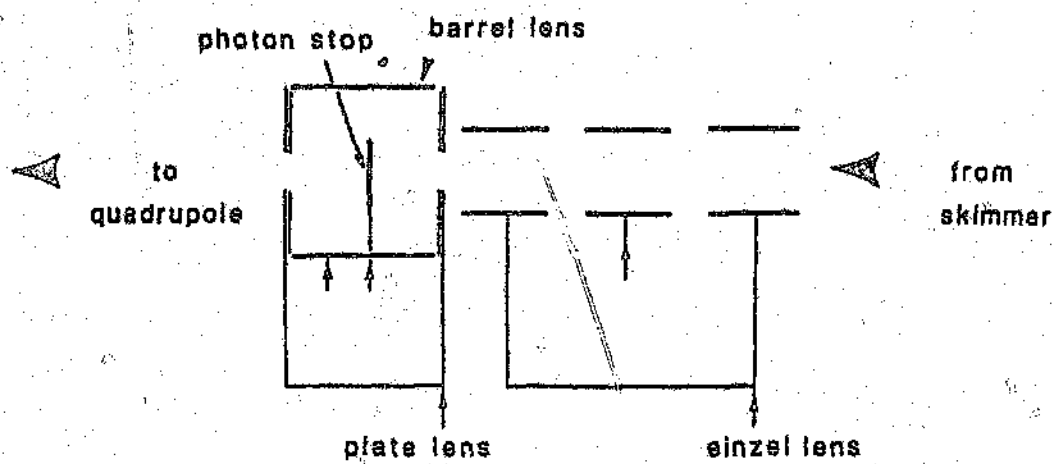


Fig. 1.9b. Sciex Elan type

In both the VG and Sciex systems a photon stop is positioned on the axis of the ion beam. The purpose of this stop is to prevent stray photons emitted by the plasma from reaching the detector, since the detector is sensitive to photons as well as ions and the stray photons would contribute to background noise. The ion lens system is used to defocus the ion beam around the photon stop and refocus it on the other side. The focused beam is then directed into the quadrupole mass analyzer.

1.4.2.5 The quadrupole mass analyzer

A typical quadrupole mass analyzer used on an ICP-MS instrument consists of a square array of molybdenum rods, 12-18 mm in diameter and approximately 200 mm long, to which an RF field is applied. The quadrupole acts as a mass filter, only allowing ions with a narrow range of mass to charge ratios to pass through at any one time.

To achieve good resolution, it is necessary for the ions to move fairly slowly through the quadrupole so that sufficient RF cycles are experienced by the ions. The ions must therefore have fairly low energies (in the low eV range). These energies are dependent on the d.c. potential drop between the plasma and the quadrupole rods. Since the potential of the plasma is dependent on the operating conditions in use, an adjustable d.c. potential is applied to the rods, also supplied by the RF generator. This potential is termed the pole bias, and is adjusted to

obtain the optimum mean ion energy. The fringing field at the end of the rods is sufficiently strong to exclude low energy ions, and to minimise this problem a pre-rod system is positioned at the entrance to the quadrupole. This consists of a set of rods, shorter than the quadrupole rods (25 mm) but of the same diameter. The RF field is applied to these rods, but the d.c. potential is not. A similar set of rods is positioned at the exit end to improve the extraction of ions (*Fig. 1.10*).

The greatest drawback of the quadrupole mass filter is its limited resolution. The resolution is less than one atomic mass unit (a.m.u.), and is sufficient to separate adjacent elemental peaks. It can also be improved to the extent that an elemental peak can be separated from a doubly charged ion peak at a half-integral charge to mass ratio, although this results in a loss of sensitivity. However, the resolution is inadequate for the separation of polyatomic ion and elemental ion peak overlaps, where the mass differences are typically between 0.02 and 0.03 a.m.u. These polyatomic ion overlaps are the major source of interference problems in ICP-MS. Magnetic sector mass analyzers are able to resolve polyatomic ion overlaps on elemental peaks, but their implementation in ICP-MS poses several problems. Magnetic sector analyzers are considerably more expensive than quadrupoles, and increase the price of what are already expensive instruments. They also require lower operating pressures and smaller ion energy distributions than quadrupoles. However, the implementation of high resolution magnetic sector mass analyzers in ICP-MS instruments appears to be the only solution to the problem of peak overlap interferences. At the time of writing, a commercial high resolution ICP-

MS has just been launched by VG Elemental²⁶. This instrument has a double focusing magnetic sector mass analyzer with a variable resolution of up to 10 000, which enables the resolution of molecular interferences.

1.4.2.6 The detector

One of the most attractive features of ICP-MS as an analytical technique is the ability to achieve very low detection limits, and this capability is due to two factors: very low background, and a detector which is able to count individual ions. Samples are usually analyzed at solution analyte concentrations below $1\mu\text{g.ml}^{-1}$. At these levels the number of analyte ions leaving the mass analyzer is very small and the beam current is less than $0.1\mu\text{A}$, (which equates to less than 10^6 ions per second. However, the instrument background is only a few ions per second. The detector which is most suited to signal measurement over this range of ion currents is the electron multiplier detector.

The electron multiplier detector consists of a curved tube 70 mm long and with a 1 mm internal diameter. The tube is flared at the input end to form a funnel, and has a resistive coating of approximately $10^5\Omega$. The funnel is positioned at the exit end of the quadrupole, slightly off the axis to reduce the possibility of stray photon noise. A high voltage (typically -3000 V) is applied to the tube, to attract ions leaving the quadrupole. When a positive ion strikes the funnel, one or more electrons are ejected from the surface, and are accelerated down the tube. Further

collisions with the walls occur and more electrons are ejected until the cascade reaches saturation at a charge of approximately 15 pC, or 5×10^8 electrons. This charge passes out of the end of the tube to a collector electrode and through a 50 Ω resistor, to give a voltage signal of between 50 and 100 mV and 10 ns duration at the base connection of the tube. In this way a single ion entering the detector results in a measurable output signal, and it is this feature that makes the technique so sensitive.

The short duration of the pulse counting signal allows high count rates and rapid scanning of the mass range. The electron multiplier detector is able to count ion pulses at rates of up to 10^6 counts per second (Hz), which gives an effective linear dynamic range of about five to six orders of magnitude. However, at an ion count of above 10^6 Hz, which corresponds to a solution analyte concentration of above $1 \mu\text{g.ml}^{-1}$, counting fatigue occurs and the response is no longer linear. It therefore necessary to perform large dilutions on concentrated samples in order to reduce the analyte concentrations to below $1 \mu\text{g.ml}^{-1}$. This is time-consuming and introduces imprecision, and therefore it is desirable to have an extended capability. This can be achieved by altering the ion lens settings to reduce transmission, or by operating the detector in a low-gain analog mode.

In the analog mode of operation, a lower voltage (approximately -1500 V) is applied to the detector tube. At this voltage, the charge at the output end of the detector does not reach saturation and therefore varies considerably from pulse to

pulse. The signal is not obtained from the base of the detector, but rather from the collector electrode which is connected to a linear amplifier. The output of the amplifier is an analog signal which represents an average over time of the variable output pulses. The response time of the amplifier is set to give a representative average signal and yet still allow rapid scanning over the mass range.

The analog mode of operation extends the capability of the instrument to analyte concentrations of up to 1% m/v. However, at these high concentrations the degree of sample deposition on the interface cones becomes a problem, due to the blocking of the orifices and resultant loss of signal. Effectively the total dissolved solids content of sample solutions must be kept below 0.2% m/v. Despite this, the use of both analog and pulse counting modes of data acquisition gives a linear dynamic range of eight orders of magnitude, and therefore enables the determination of both traces and majors in samples. The analog data acquisition feature is not standard on ICP-MS instruments, but is available on the more advanced models. A diagram of a dual mode detector is shown in *Fig. 1.11*.

1.4.2.7 Data processing

In the normal mode of operation, data is acquired by scanning repeatedly across the required mass range and accumulating the counts. Because the scan rate is so high (the full mass range can be scanned in as little as 20 ms), it is necessary to store the acquired data as rapidly as possible. Different approaches to this problem

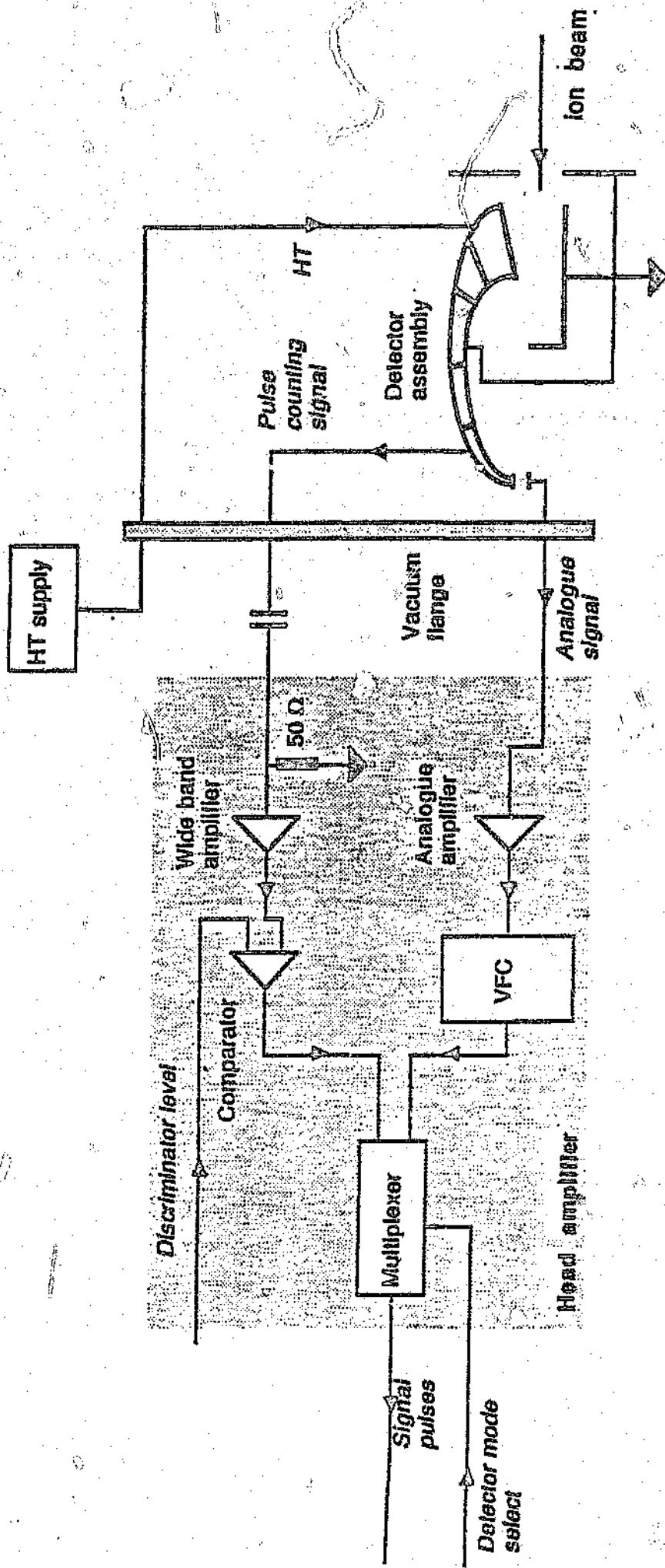


Fig. 1.11. The ion multiplier detector

(VG Plasmaguard System Manual 1985)

have been taken on the Sciex and VG instruments. On the Sciex instrument the acquired data is transferred to the computer at the end of each scan cycle and the counts are accumulated in memory, while on the VG instrument the data for each scan is accumulated by a multichannel analyzer and transferred to the computer at the end of the acquisition.

The software for the manipulation of acquired data is sophisticated, as is the case with most modern instruments. Options are available for qualitative analysis of scans, semi-quantitative and quantitative multielement analysis, isotope ratio measurement, and isotope dilution and standard addition analysis. In addition to these, there are also optional programs for time-resolved analysis, laser ablation, flow injection and electrothermal atomization. The software is also used to control many of the instrument functions such as plasma start-up and data acquisitions. The software is designed to run on IBM-compatible personal computers.

1.4.2.8 Vacuum and cooling systems

The vacuum systems of both the VG and Sciex instruments rely on a rotary pump, which is able to operate at high pressures, to achieve an intermediate pressure of approximately 5 mbar in the expansion chamber. However, the two instruments have different high vacuum systems. The VG instrument is divided into two chambers behind the expansion chamber, with a differential aperture between them. The two chambers, referred to as the intermediate and analyzer chambers,

each have their own diffusion pump. The intermediate chamber is maintained at a pressure of approximately 10^{-4} mbar, and the analyzer chamber at 10^{-5} to 10^{-6} mbar. A single rotary pump is used to provide backing for the diffusion pumps, as well as to perform initial evacuation of the chambers after vacuum shutdown. In the original Sciex system a single large helium cryopump was used to achieve the necessary vacuum for quadrupole operation, and there was no need for a differential aperture between chambers. This system has now been modified.

Cooling water is used for a number of purposes in the ICP-MS instrument. The ICP load coil is water cooled, and the plates to which the sample and skimmer cones are attached are water cooled to remove heat from the cones. Cooling water is also needed for the pumps. Water at room temperature is used for these purposes, but a chiller unit is required for the spray chamber cooling water, which is maintained at approximately 5°C to reduce solvent loading of the plasma.

1.4.3 Characteristics of ICP-MS analysis

1.4.3.1 Plasma composition and system response

A typical argon plasma into which a 0.01 mmol.l^{-1} analyte solution in 1% nitric acid is injected has an elemental composition (including both atoms and ions) of approximately $10^{18}\text{ atoms.cm}^{-3}$ argon, $10^{16}\text{ atoms.cm}^{-3}$ hydrogen and oxygen from the water, $10^{14}\text{ atoms.cm}^{-3}$ nitrogen from the matrix acid, and $10^{10}\text{ atoms.cm}^{-3}$

analyte. The analyte concentration is expressed in mmol.l^{-1} rather than the more usual mg.l^{-1} . This is done to remove the dependence of the atom concentration on the atomic mass of the analyte element. A molar concentration of 0.01 mmol.l^{-1} corresponds to 1 mg.l^{-1} of Rh, which is more or less central in the periodic table with an atomic mass of 103.

Since only ions are sampled from the plasma, the instrument response for a particular element is dependent on the degree to which the atoms of that element are ionised. The ratio of ions to atoms for a particular element in a plasma can be determined from the Saha equation:

$$\frac{M^+}{M} = \frac{1}{n_e} \left(\frac{2\pi m_e kT}{h^2} \right)^{\frac{3}{2}} \cdot \frac{Q^+}{Q} \cdot e^{-\left(\frac{IP}{kT}\right)}$$

where :

M^+ = ion concentration of the element

M = atom concentration of the element

n_e = electron density

m_e = mass of electron

k = Boltzmann's constant

T = temperature

h = Planck's constant

Q^+ = partition function of the ion

Q = partition function of the atom

IP = ionisation potential of the element

The Saha equation applies to systems at thermal equilibrium. Although the plasma is not at equilibrium, it is not far from it, and therefore the Saha equation can be used to calculate a reasonable approximation of the degree of ionisation of an element in the plasma. A periodic table showing calculated degrees of ionisation for the elements is shown in *Fig. 1.12*²². These figures are based on a plasma temperature $T = 7500$ K and an electron density $n_e = 1 \times 10^{15} \text{ cm}^{-3}$.

From this table it can be seen that more than 90 % ionisation occurs for most of the elements. Ionisation efficiencies are lowest for the elements with high first ionisation energies, i.e. the non-metallic elements, and therefore the degree of ionisation is relatively low for argon (approximately 0.04 %). However, the high argon atom concentration ensures that Ar^+ is the major positively charged species present in the plasma, with an ion population in the typical working plasma described above of 10^{14} to $10^{15} \text{ ions.cm}^{-3}$. H^+ and O^+ are present at approximately $10^{14} \text{ ions.cm}^{-3}$ and nitrogen from the matrix acid at about $10^{13} \text{ ions.cm}^{-3}$. These species are all present at considerably higher concentrations than the analyte ions which have a population of about $10^{10} \text{ ions.cm}^{-3}$. The predominance of background ions causes spectral interference problems due to background peak overlaps, which will be discussed in the following section.

0.1 H																	He				
100 Li	75 Be															58 B	5 C	0.1 N	0.1 O	F	Ne
100 Na	98 Mg															98 Al	85 Si	33 P	14 S	0.9 Cl	0.04 Ar
100 K	99 Ca	100 Sc	99 Ti	99 V	98 Cr	95 Mn	96 Fe	93 Co	91 Ni	90 Cu	75 Zn	98 Ga	90 Ge	52 As	33 Se	5 Br	0.6 Kr				
100 Rb	96 Sr	98 Y	99 Zr	98 Nb	98 Mo		96 Tc	94 Ru	93 Rh	93 Pd	85 Ag	99 Cd	99 In	96 Sn	78 Sb	66 Te	29 I	8.5 Xe			
100 Cs	91 Ba	90 La	98 Hf	95 Ta	94 W	93 Re	78 Os		Ir	62 Pt	51 Au		Hg	100 Tl	97 Pb	92 Bi	Po	At	Rn		
Fr	Ra	Ac																			
			98 Ce	99 Pr	99 Nd	Pm	97 Sm	100 Eu	93 Gd	99 Tb	100 Dy		Ho	99 Er	91 Tm	92 Yb	Lu				
			100 Th		100 Pa																

Fig. 1.12. Degree of ionisation over the periodic table (%)

(Data and Gray 1989)

Despite the high ionisation efficiency of most elements in the plasma, the various processes involved in getting the analyte to the detector are very inefficient. These processes include nebulisation, transport to the plasma, sampling of the plasma, ion beam focusing and mass analysis, and each process results in a substantial loss of potential signal. At a typical sample uptake rate of $1.2 \text{ mL} \cdot \text{min}^{-1}$, the $1 \text{ mg} \cdot \text{l}^{-1}$ Rh analyte solution discussed above is sampled at a rate of approximately 10^{14} atoms $\cdot \text{s}^{-1}$. The analyte ion current reaching the detector is approximately 10^6 ions $\cdot \text{s}^{-1}$, and therefore only 1 in 10^8 atoms sampled ever reaches the detector. However, the exceptionally high sensitivity of the detector and low background ion count rates enable detection below the $\text{ng} \cdot \text{mL}^{-1}$ level for most elements.

The response for the metallic elements tends to increase with the mass number, although the variation is not much more than an order of magnitude over the full mass range. Relatively high detection limits which are obtained for certain of the metallic elements are due to background ion interferences rather than variations in response. The responses of selected elements across the spectrum, corrected for degree of ionisation and isotopic abundance can be used to plot a curve from which responses of other elements can be predicted. This provides a means of semiquantitative analysis without standardisation, by relating the response of unknown elements to that of a single element of known concentration via the response curve.

1.4.3.2 Spectra and interferences

One of the most significant features of ICP-MS, particularly when compared to ICP-AES, is the simplicity of the spectra obtained. The major peaks for each element are from singly charged ions, with each isotope being represented by a single peak. The number of naturally occurring isotopes of each element ranges from one to ten, with an average of 3.6 isotopes per element. This is in sharp contrast to the thousands of lines observed for each element in ICP-AES. This simplicity is a great advantage, since the likelihood of peak overlap interferences is very much smaller in ICP-MS than in ICP-AES. However, the small number of analyte peaks for each element can be a disadvantage, since it can result in unavoidable interference problems. For example, if a monoisotopic element has a peak overlap interference of some sort on its only isotope, it is difficult to analyze that element by ICP-MS. By contrast, in ICP-AES it is usually possible to select at least one of the many analyte lines which is free of interference for a particular matrix. The sources of peak overlap interferences in ICP-MS are background monoatomic singly charged ions, polyatomic singly charged ions, doubly charged ions, and isobaric overlaps. These interferences can be reduced by optimisation of the operating conditions²³.

Fig. 1.13 shows the background spectrum obtained from a 2% (v/v) nitric acid solution. A log plot has been used to show all the peaks on the same scale. It can be seen that most of the major background peaks are below mass 45, with isolated

Fig. 1.13. Background peaks in the mass spectrum

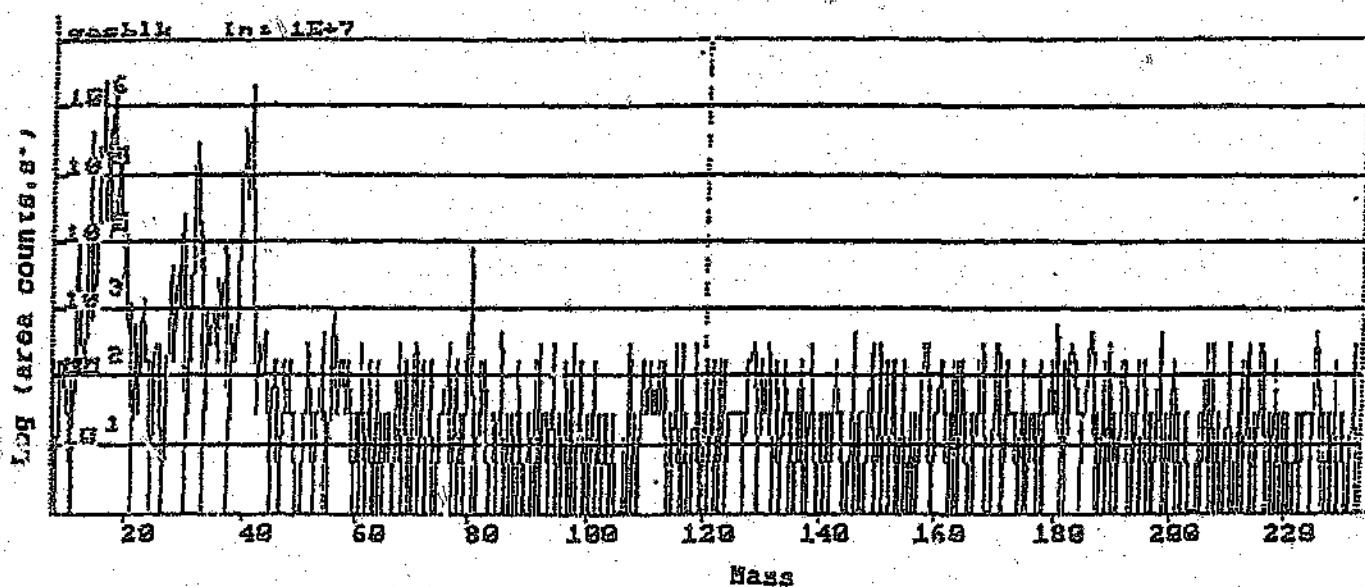


Fig. 1.13a. Full mass range

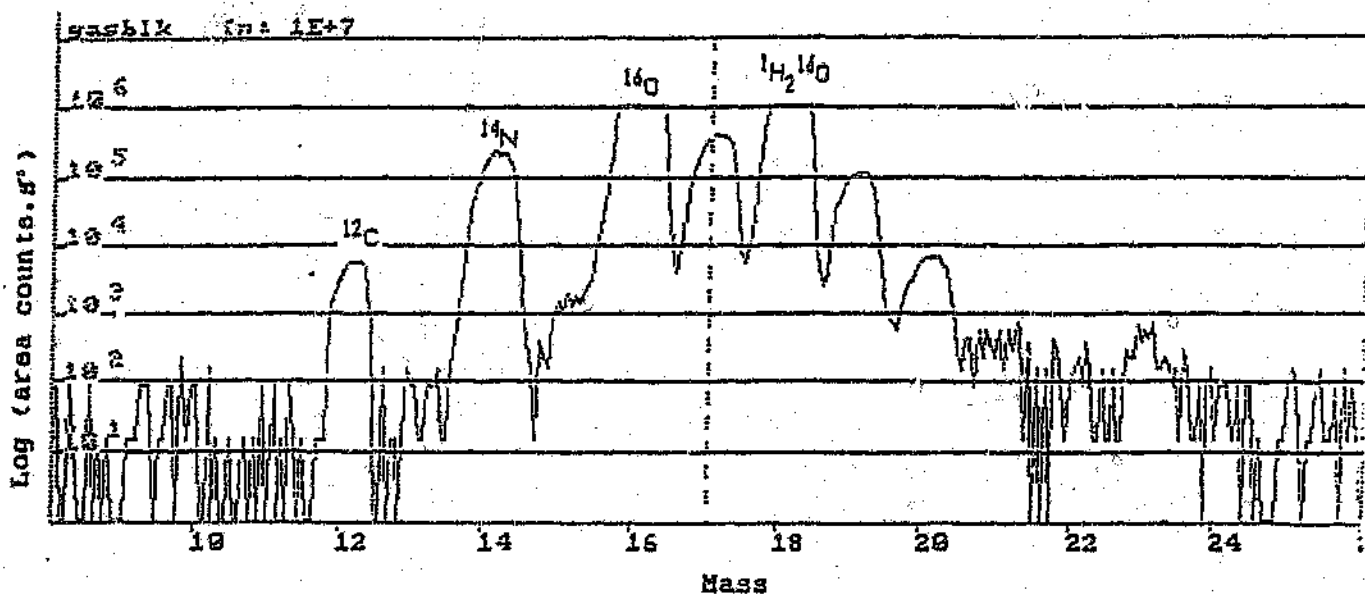


Fig. 1.13b. Masses 8 to 26

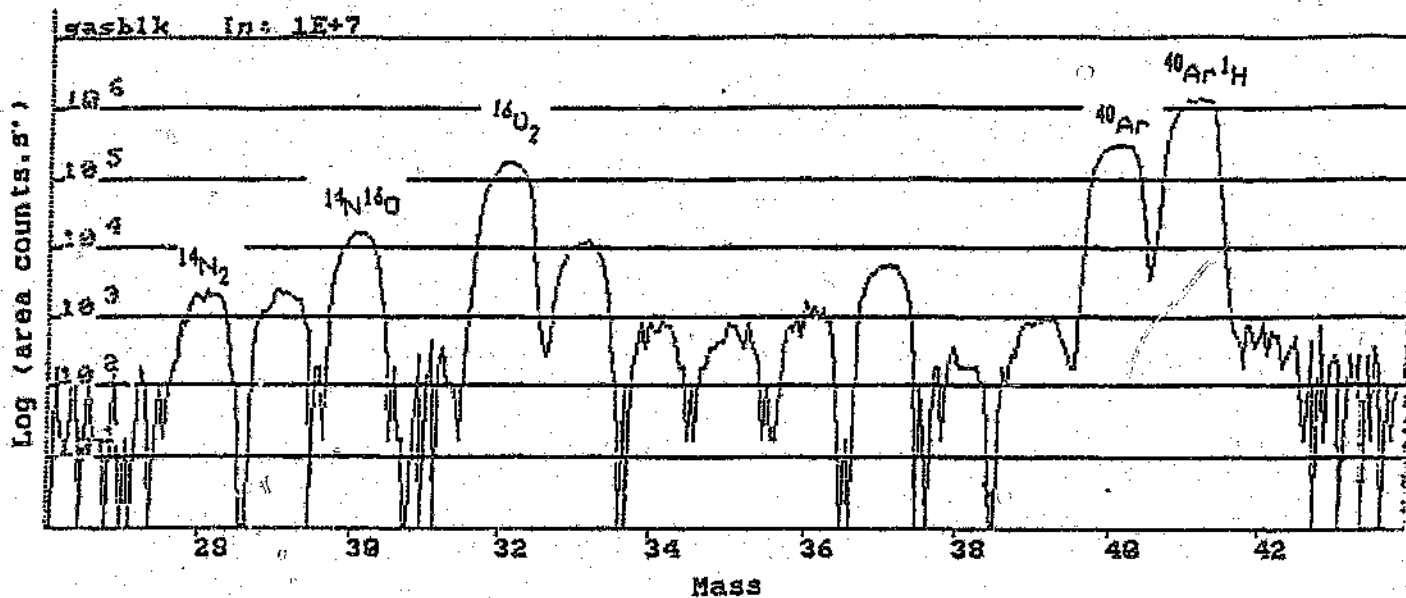


Fig. 1.13c. Masses 26 to 44

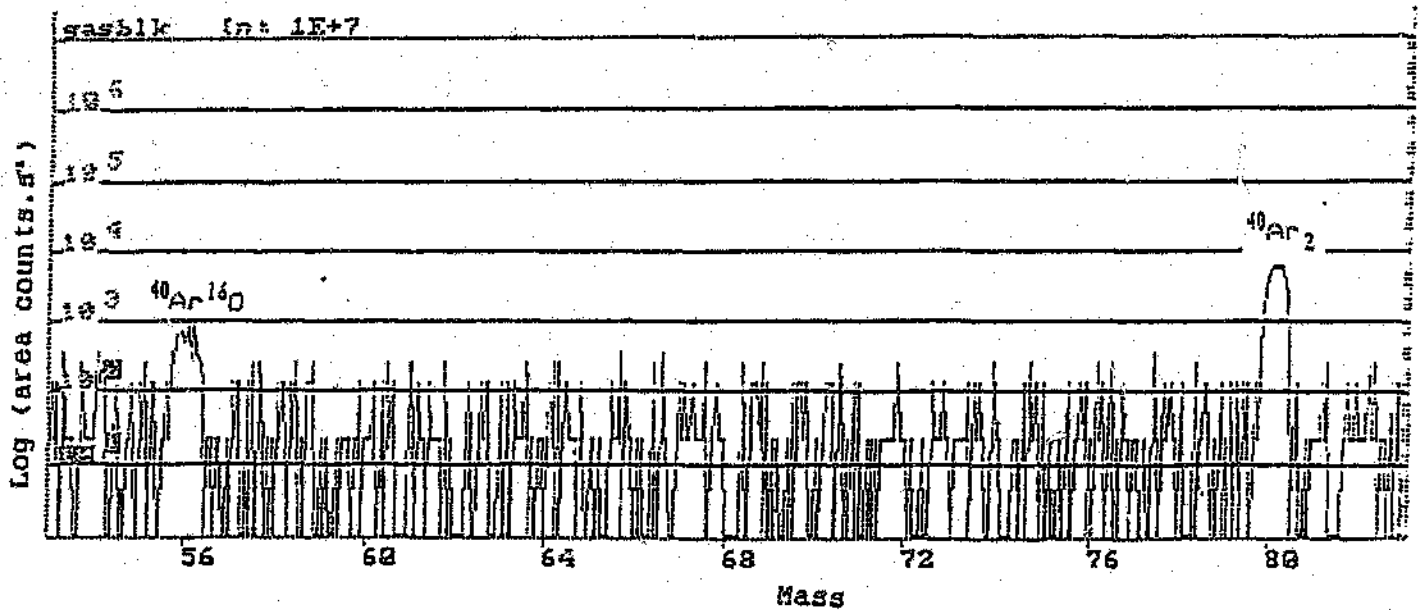


Fig. 1.13d. Masses 55 to 83

peaks being evident up to mass 80. These mass regions have been expanded to show the background peaks more clearly. The high background noise level over the rest of the spectrum is due to the use of the analog mode of detection for the scan. This, coupled with partial detuning of the ion lenses, was necessary to enable scanning over the intense background peaks without causing damage to the detector.

In addition to the various peak overlap interferences there are also non-spectral interferences. These include matrix and memory effects, and cone deposits.

Background monoatomic singly charged ions

These ions originate from plasma argon, water and acid from the analyte solution, and air, which is present as an impurity in the argon and may also be entrained in the plasma. Background contributions from the interface cones and other metallic components in the system are so small that they can be ignored. The major monoatomic background ions are therefore due to Ar, O, H, N and C. Since nitrogen is present in any case, nitric acid is commonly used as the matrix acid to avoid the introduction of additional background species. The concentrations of the background species in the plasma are considerably higher than typical analyte concentrations, and therefore these species cause significant interferences. The signals from certain of the background ions are sufficiently large to damage the detector, and as a result it is necessary to skip over these peaks when scanning the

mass spectrum. Since the background elements themselves are generally not of analytical interest, and since with the exception of argon they do not coincide with the peaks of other elements, these background ions do not cause serious problems. Argon, however, directly interferes with the major isotopes of Ca and K. The result is that the background counts, and therefore the limits of detection for these elements are particularly high.

Polyatomic singly charged ions

Dissociation of molecular species is essentially complete in the plasma. However, a certain amount of polyatomic ion formation occurs in the sampling process, when the gas is rapidly cooled but is still at a sufficiently high pressure for collisions between particles to occur at a significant rate. These polyatomic ions consist of combinations of background species, as well as background/matrix and background/analyte combinations. The peaks resulting from polyatomic species are very much smaller than the monoatomic peaks. However, the concentrations of background species are high relative to analyte species, and as a result polyatomic ions cause significant interferences. An example of an element which is particularly affected by polyatomic ion overlaps is silicon, which has $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}^{16}\text{O}$ overlapping on its three isotopes at masses 28, 29 and 30 respectively.

Certain analyte elements form oxide and hydroxide species. The signals from these species are small relative to the monoatomic ion signal, although in the case of

elements which form refractory oxides such as the rare earths the oxide signals may be as large as 1 % of the monoatomic signal. Oxide and hydroxide peaks can therefore cause significant interferences 16 and 17 mass units above the interfering element. An example of this type of interference is the overlap of $^{153}\text{Eu}^{16}\text{O}$ on ^{169}Tm . Thulium is monoisotopic and therefore can not be easily determined in the presence of significant quantities of europium.

Doubly charged ions

Any element with a second ionisation energy ($E_i^{(2)}$) which is lower than the first ionisation energy of argon (27.5 eV) may form doubly charged ions. Barium ($E_i^{(2)} = 10.0$ eV) and Ce ($E_i^{(2)} = 10.8$ eV) have the lowest second ionisation energies and have doubly charged ion signals of 2-4 % of the singly charged signals. Approximately thirty elements form doubly charged ions which, since the quadrupole discriminates on the basis of mass/charge ratio, appear at half the mass number of the element. However, these signals are generally small and interferences can usually be avoided by careful selection of analyte isotopes. In fact, doubly charged ions can be used as a means of avoiding other interference problems by using the doubly charged species of an element as the analyte, as demonstrated by Jarvis²⁴. Elements with isotopes with odd mass numbers are particularly suited to this type of analysis, since the doubly-charged analyte peak

appears at a half-integral mass number and the quadrupole resolution can be tuned to half a mass unit, thus removing any possible interference.

Isobaric overlaps

Isobaric overlap interference is the direct overlap of different species with the same nominal mass number. Isobaric interferences result from both background (gas) and analyte ions.

There are many isobaric interferences across the mass spectrum, ^{186}W on ^{186}Ta , and ^{150}Nd on ^{150}Sm being two examples. However, with the exception of indium, in every case of isobaric interference there is always at least one isotope which is free of interference. Therefore isobaric interference does not generally cause serious problems provided that care is taken in the selection of analyte isotopes.

Non-spectral interferences

There are three main types of non-spectral interferences in ICP-MS. Two of these are common to both ICP-MS and ICP-AES, namely matrix suppression and memory effects, which have been described in Section 1.3.4.2. The third type is unique to ICP-MS, namely cone deposits.

The temperature of the interface cones at the orifice is obviously very much lower than that of the plasma gas, and material from the plasma condenses on the rim of the orifices. This leads to gradual loss of signal and may result in memory effects due to the re-volatilisation of condensed material. This problem can be avoided by limiting the level of dissolved solids in samples and cleaning the cones on a daily basis.

1.4.3.3 Detection limits

Detection limits for ICP-MS can vary considerably depending on the width of the mass range examined and the integration period used for each peak, as well as the sample matrix. Instrumental detection limits for each element are generally based on single ion monitoring, but practical detection limits are in fact different for each analytical method. The instrumental detection limits for the elements which are not affected by background ion interferences or high first ionisation energies are generally between 0.1 and 10 ng.ml⁻¹. These limits are one to two orders of magnitude lower than those obtained by ICP-AES for most elements.

1.4.3.4 Precision and accuracy

Although quadrupole scan rates are very fast, ICP-MS measurement is still essentially sequential and therefore the precision of a particular measurement is dependent on the scan speed. Reported precisions for most applications are two

to three per cent, which is slightly worse than the typical precision of ICP-AES measurements, but is still quite acceptable for most purposes. Good accuracy is attainable by ICP-MS provided that care is taken to nullify interferences by matrix matching and careful analyte isotope selection.

1.4.3.5 Dynamic range

As was described in Section 1.4.2.6, ICP-MS has an exceptionally wide linear dynamic range, and linear calibration curves spanning five to six orders of magnitude are attainable. With the use of extended dynamic range detection, it is possible to increase the range to eight orders of magnitude. However, as is the case with ICP-AES, excessively long signal wash-out times limit the ranges that are used in practice.

1.5 Instruments used for experimental work

The ICP-MS instrument used in this work was a VG Plasmaquad II+ (VG Elemental, Winsford, Cheshire, U.K.) with the dual detection system. The ICP-AES instrument was a Spectroflame (Spectro Analytical Instruments GmbH, Kleve, Germany) simultaneous/sequential instrument with a vacuum polychromator for the sensitive detection of wavelengths below 200nm.

1.6 Summary

Both ICP-AES and ICP-MS are well-established techniques for elemental analysis. Both techniques are capable of rapid multielemental analysis with good accuracy and precision and low detection limits. Since the principles of mass and emission spectrometry are entirely different, the spectra produced by the two techniques are subject to different types of spectral interferences. As a result the techniques complement each other well.

For most analytical applications the two techniques employ the same method of sample introduction, namely pneumatic nebulisation of a liquid sample and transport of the resulting aerosol via a spray chamber to the plasma. Pneumatic nebulisation is the most commonly used sample introduction method because of its simplicity and ease of use. However, there are several problems associated with this method, including poor transport efficiency, viscosity and memory effects, and the requirement that samples be in solution form. The objective of this work is to broaden the applicability of ICP-AES and ICP-MS and to improve the quality of analysis by the employment of alternative sample manipulation and sample introduction techniques.

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Chapter 2. Application of Laser Ablation ICP-MS to the Determination of Trace Impurities in Tantalum Oxide and Niobium Oxide

2.1 Introduction and theory

2.1.1 Introduction

There is an ever-increasing demand in industry for a wide variety of high-purity materials, which are used in specialised applications where trace contaminants can have serious adverse effects on their performance. To certify the purity of these materials, it is necessary to perform quantitative determinations of a number of possible contaminant elements at the $\mu\text{g.g}^{-1}$ level and below. Consequently, a considerable amount of research has been and is being aimed at the development of analytical instrumentation and procedures which are capable of achieving these low limits of determination.

Mintek is involved in the development of methods for the production of high-purity (99.99% pure) tantalum oxide (Ta_2O_5) and niobium oxide (Nb_2O_5). These materials are not useful in themselves, but can be used to produce tantalum and niobium metals, carbides and ceramics which have a variety of applications in industry. It is necessary to determine the concentrations in these products of certain elements which are associated with the raw materials. These elements are : magnesium, aluminium, silicon, calcium, titanium, manganese, iron, silver, tin and tungsten in both materials, as well as tantalum in Nb_2O_5 and niobium in Ta_2O_5 . Since the requirement of 99.99% purity allows a maximum of $100 \mu g \cdot g^{-1}$ total impurities, a lower limit of determination of $1 \mu g \cdot g^{-1}$ is desirable for each analyte element. Besides the certification of final products, analyses of intermediate materials are required for the monitoring of plant processes, and therefore a short analysis time is required.

The determination of trace impurities in Ta_2O_5 and Nb_2O_5 is difficult for several reasons. The presence of the matrix causes complications for most spectroscopic techniques, and a trace-matrix separation is usually necessary before analysis. However, these refractory materials are difficult to dissolve quantitatively, and a slow dissolution step coupled with a lengthy trace-matrix separation is unsatisfactory when analysis results are required for plant monitoring. Dilution of the sample in the dissolution process is also a problem because of the low limits of determination which are required.

The existing method for determining impurities in Ta_2O_5 and Nb_2O_5 at Mintek is a d.c. arc atomic emission spectrographic procedure using carrier distillation¹. In this procedure the solid sample is mixed with a carrier compound. The sample is then weighed into a graphite cup electrode and an arc is struck between the cup electrode and a counter electrode. The carrier compound promotes selective volatilisation of the volatile impurity elements while suppressing the volatilisation of the refractory matrix. The sample is atomised in the arc, the emitted light is dispersed and the spectrum is recorded on photographic plates. The emission line densities of the analyte elements are then compared with those of calibration standards to obtain concentration values. Carrier distillation is essential to reduce the complexity of the matrix spectrum, and thus limit the number of line overlap interferences. However, the carrier also suppresses the refractory analyte elements, i.e. tantalum in Nb_2O_5 , niobium in Ta_2O_5 , and tungsten in both materials. Since the emission lines of these elements are relatively weak even without suppression, these elements can not be analyzed satisfactorily by this method.

Inductively coupled plasma-mass spectrometry (ICP-MS) using laser ablation as a means of solid sample introduction is in principle well suited to the analysis of Ta_2O_5 and Nb_2O_5 , since dissolution of the sample is not necessary, and the technique is relatively free of matrix interferences so trace-matrix separation can be avoided. This work describes the development of sample preparation techniques and analytical methods for the determination of trace impurities in Ta_2O_5 and Nb_2O_5 by laser ablation ICP-MS.

2.1.2 Aims of the investigation

The primary aim of this investigation is to establish quantitative methods for the determination of trace impurities in Ta_2O_5 and Nb_2O_5 by laser ablation ICP-MS. However, laser ablation ICP-MS is a relatively new technique and little has been published in this field. Consequently, the secondary aims of this investigation are to gain a better understanding of the processes which take place during laser ablation, and to establish instrumental parameters and methods of sample preparation which are applicable to other sample types.

2.1.3 Occurrence, properties and uses of tantalum and niobium

2.1.3.1 Occurrence

Tantalum and niobium (also referred to as columbium) almost invariably occur together in nature. The most important mineral is $(FeMn)(Ta,Nb)_2O_6$, which is called tantalite or columbite depending on which element predominates. Tantalum and niobium products are obtained from this mineral, but most of the world's production is obtained as a by-product of tin refining. The tin ore cassiterite contains significant amounts of tantalum and niobium, which report in the slag during the tin smelting process, and which can be beneficiated from this slag².

Brazil is the world's largest producer of tantalum and niobium products. South Africa has produced minor amounts of mineral concentrates from mines in the

Cape Province, but the major producer in South Africa is the Iscor tin smelter at Vanderbijlpark which processes concentrates from the Uis mine in Namibia and produces tantalum- and niobium-bearing slags as a by-product. The work in which Mintek is engaged is the production of Ta_2O_5 and Nb_2O_5 from these slags³.

2.1.3.2 Properties

Tantalum and niobium have similar properties. They are both ductile, refractory metals with high melting points (tantalum 2996°C, niobium 2468°C), high electrical and thermal conductivities, and extremely high corrosion resistance, niobium being slightly more reactive than tantalum⁴. The oxides are even more resistant to chemical attack, and in fact the corrosion resistance of the metals is due to the presence of a naturally occurring stable oxide layer which protects the metal from attack. This resistance to corrosion is a very useful property in certain applications, but it makes dissolution of the materials prior to analysis very difficult. Hydrofluoric acid, which prevents the formation of the oxide layer, rapidly dissolves the metals, and the oxides can also be quantitatively dissolved in hydrofluoric acid (with the addition of nitric acid to ensure dissolution of the other elements present). However, dissolution of the oxides is more difficult than the metals, requiring several hours of digestion at high temperature and pressure.

2.1.3.3 Uses

Most of the world's production of tantalum is used in capacitors. Tantalum is particularly suited to this application due to the stable dielectric surface oxide film, and is superior to any other type of material used in capacitors. The purity of the metal is critical in this application, the higher purity enabling higher working voltages. Tantalum metal is also used in high-temperature superalloys and tantalum sheet is used extensively in linings for chemical equipment due to its excellent corrosion resistance. Tantalum carbide is used in combination with tungsten and titanium carbides in the manufacture of steel-cutting tools, where it imparts improved wear resistance³.

The main use of niobium is as ferroniobium, which is used in carbon and high-strength, low-alloy steels to increase the strength of the steels. Niobium is also used in non-ferrous metallurgical applications: zirconium-niobium alloy is used as cladding for nuclear fuel rods, and another niobium alloy is used for rocket nozzles in spacecraft and missiles because of its strength and corrosion resistance at temperatures up to 1200°C. Like tantalum, niobium is used in chemical equipment for its corrosion resistance, and a combination of niobium carbide and hafnium carbide is used as a lower-cost substitute for tantalum carbide in cutting tools. Niobium metal and several niobium alloys are superconductors at low temperatures, and for these applications very high purity niobium is required⁴. Other uses of high-purity tantalum and niobium are in electro-optical and electroceramic devices and ceramic chips⁵.

2.1.4 Analytical techniques used for trace analysis in tantalum and niobium metals and compounds

Besides the d.c. arc emission spectrographic procedures described previously, a wide variety of instrumental techniques have been applied to trace analysis in tantalum and niobium metals and compounds, generally involving dissolution followed by separation of the analyte elements from the matrix. Impurities in tantalum metal have been determined by radiochemical neutron activation analysis involving impurity separations before and after irradiation⁶, and by separation followed by thin-film x-ray fluorescence spectrometry⁷, and secondary ion mass spectrometry has been used to determine Al and B in tantalum disilicide thin films⁸. Trace impurities in niobium metal have been determined by emission spectrometry⁹, by spectrochemical techniques¹⁰, by neutron activation analysis¹¹, and by ICP-AES¹², all of these techniques requiring pre-separation of the impurities from the niobium matrix. Solution ICP-MS has been used to determine trace impurities in niobium metal, both with and without trace-matrix separation¹³. A spectrophotometric method has been used to determine tantalum in niobium oxide¹⁴ and radiotracer techniques have been used to study the solvent extraction of impurities from niobium in hydrofluoric acid solution.

2.1.5 Laser ablation (Ready¹⁶ and Laserlab Manual¹⁷)

2.1.5.1 Theory of lasers

Laser is an acronym for Light Amplification by Stimulated Emission of Radiation.

A laser is a device which produces an intense, coherent beam of monochromatic light. Although there are many different types of lasers, they all consist of an optically transparent medium positioned between two highly reflecting mirrors (referred to as the resonator), and an excitation (or "pumping") source.

The optical medium is either a crystal or a tube of gas or liquid containing atoms, ions or molecules which are easily raised from the ground state to an excited state. Excitation energy is introduced by a flash tube or an electrical discharge and the active species is excited. On returning to the ground state, the active species emits a photon of energy:

$$h\nu = \frac{hc}{\lambda} = E_2 - E_1$$

where h = Planck's constant, ν = photon frequency, c = speed of light, λ = photon wavelength, and E_2 and E_1 are the energies of the excited and ground states of the active species. The emitted photon is able to initiate further emissions from excited species by the process of stimulated emission. The resulting photons are coherent with the initiating photon and have the same wavelength. However, the emitted

photon may also be absorbed by a ground state species. Therefore, for a net gain of photons to occur, more than half of the active species must be in the excited state. This condition, referred to as population inversion, is achieved by the excitation source.

The resonator consists of a pair of highly reflecting mirrors, one on each side of the optical medium, separated by a distance :

$$D = \frac{N\lambda}{2}$$

where λ = emitted photon wavelength, and N is an integral number. This causes the emitted photons to form a standing wave which stimulates further emissions. Any light of the wrong wavelength is rapidly lost from the system and the light contained in the resonance chamber is essentially monochromatic.

There are various means of obtaining an emission beam from the resonance chamber. In the simplest system, one of the chamber mirrors is only partially reflective, so that part of the light is transmitted. The transmission may be in the form of a series of pulses 100 to 500 μ s in duration, or a continuous beam, depending on the type of excitation used. This mode of operation is referred to as fixed quality resonance cavity or "fixed Q" mode. In systems where the active species has an excited state with a relatively long lifetime, it is possible to obstruct the resonance cavity in such a way that a large proportion of the active species is excited and photon emission is suppressed. When the obstruction is removed, the total excited species energy is released in a single pulse of much higher intensity

and shorter duration than the fixed Q pulse. This is referred to as "Q-switched" mode because the quality of the resonance cavity is switched. Q-switching is achieved by a variety of means, including bleachable dyes, rotating reflectors and electro-optical devices.

There are many different types of laser, with power outputs ranging from less than 1 mW up to 1 GW and frequencies ranging from the near ultra-violet to the infra-red. Gas type lasers include atomic (HeNe), ionic (Ar, Kr), molecular (CO_2) and excimer (KrF) devices. Solid-state lasers include crystalline and semiconductor devices. Crystalline devices are pumped by xenon flash lamps and include the ruby laser, in which Cr^{3+} is the active species and Al_2O_3 the optical medium, and the Nd:YAG laser, which consists of a crystal of yttrium aluminium garnet doped with the active species Nd^{3+} (Fig. 2.1). The most commonly used semiconductor in lasers is gallium arsenide, although other materials have also been used. The only liquid type lasers are the organic dye lasers, which have the useful characteristic of being tuneable to a specific wavelength. Dye lasers require a separate laser system (usually an argon laser) to pump the dye laser. Each type of dye gives a narrow wavelength range, but the use of a variety of dyes gives full coverage of the range from 400 to 1000 nm.

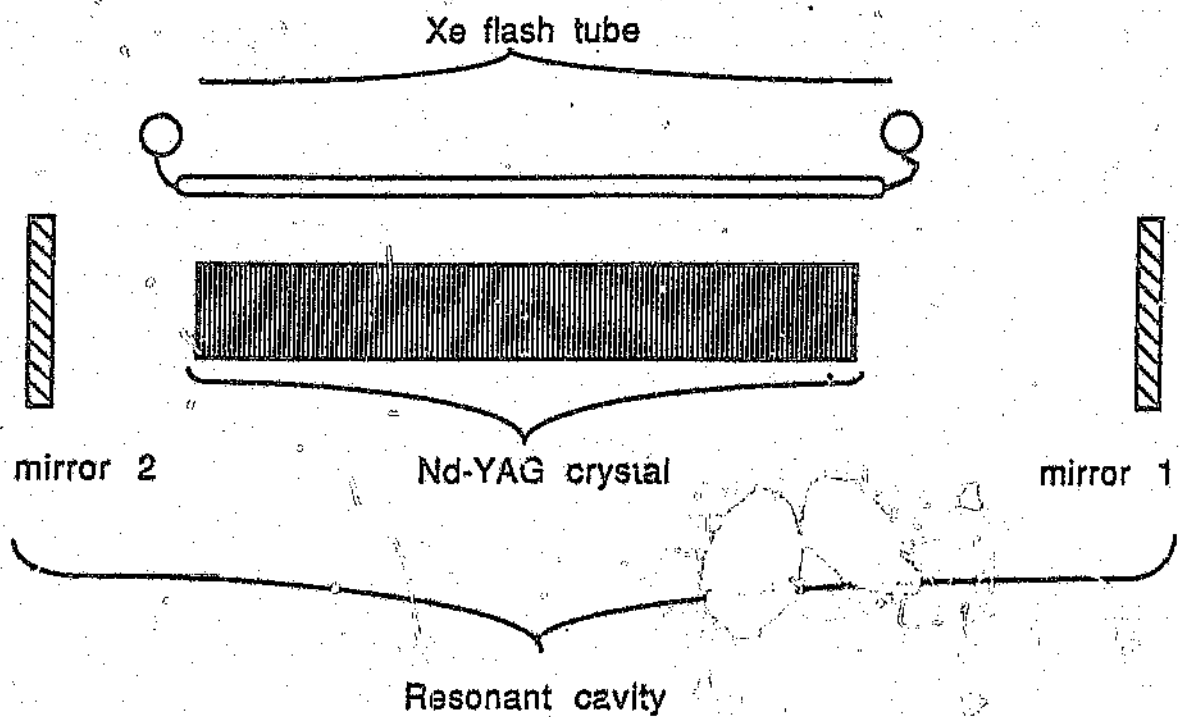


Fig. 2.1. Nd:YAG laser system

(VG LaserLab Manual 1988)

2.1.5.2 Lasers in spectroscopy

Lasers have proved to be extremely versatile tools with a very wide range of applications in different spheres, from the Strategic Defense Initiative to microsurgery, and from cutting and welding of metals to compact disc players and supermarket check-outs. Lasers have also found many uses in chemistry, particularly in the field of spectroscopy.

It is evident that a source of intense, coherent, monochromatic light, which in certain instances is tuneable to a required wavelength, is potentially a very useful spectroscopic tool. Lasers have been used to improve existing spectroscopic techniques, and new techniques have been developed based on the unique capabilities of lasers.

Examples of techniques which utilise the spectral characteristics of lasers are Raman spectroscopy¹⁸, laser-induced atomic fluorescence spectroscopy¹⁹, laser enhanced ionisation spectrometry²⁰, resonance ionisation spectroscopy²¹ and resonance ionisation mass spectrometry²². However, apart from their use as a light source, lasers are also used as a means of sampling solid materials. Certain types of lasers produce pulses which are sufficiently powerful, when focused on a small area of a solid material, to atomize a portion of the material. This characteristic has been utilised in a variety of ways. The microplasma which is induced by the laser pulse is sufficiently energetic to excite the atomised species, and has therefore been used as an analytical emission source. The usefulness of the laser

induced microplasma as an emission source is limited due to matrix effects, poor precision and poor sensitivity. This was largely due to the poor excitation characteristics of the microplasma^{21,24}. However, as a source of atoms, laser ablation (sometimes referred to as laser sampling) has been linked to several spectrometric techniques. These include atomic absorption^{25,26}, microwave induced plasma emission^{27,28}, direct current plasma emission^{29,30}, inductively coupled plasma emission^{31,32}, laser induced fluorescence³³, resonance ionisation spectroscopy³⁴, resonance ionisation mass spectrometry^{35,36} and inductively coupled plasma-mass spectrometry.

The first application of laser ablation as a means of solid sample introduction for ICP-MS was reported by Gray in 1985³⁷. In this work a ruby laser was used to obtain mass spectra of geological reference materials. The ruby laser has a maximum pulse repetition rate of 1 Hz, and it was suggested that the use of a laser with a higher pulse rate would give a more uniform signal. In 1987 Arrowsmith reported the application of a Nd:YAG laser to ICP-MS, using pulse rates of up to 20 Hz, for the analysis of standard steels³⁸. This work showed considerable promise, and commercial laser ablation units are now available as accessories for ICP-MS. There is a growing number of reports of laser ablation ICP-MS applications. Most of the work reported to date has been on the analysis of materials for which there are reference standards, i.e. geological materials³⁹⁻⁴³, steels and slags⁴⁷, because of the problems associated with the preparation of solid calibration standards. However, previously analyzed samples have been used as calibration standards for the determination of traces in plastics⁴⁸ and the

determination of rhenium in metal concentrates⁴⁹. The capability of ICP-MS to perform semi-quantitative analysis without calibration standards has also been used in combination with laser ablation^{50,46}. Another area which has been investigated is the modification of the laser to achieve better spatial resolution^{45,44}. Laser ablation ICP-MS has been reviewed by Denoyer *et al.*⁵¹

2.1.5.3 The laser ablation system for ICP-MS

The laser ablation system can be divided into a number of sub-systems. These systems are: the laser itself, the optical system, the sample stage and the carrier gas system (*Fig. 2.2*).

The laser is of the pulsed neodymium: yttrium aluminium garnet (Nd:YAG) type. It is pumped by a xenon flash tube and produces output at the fundamental wavelength of 1064 nm, which is characteristic of Nd:YAG systems. The pulse rate and input energy can be set manually, to a maximum of 20 Hz and 500 mJ. The laser can be operated in fixed Q or Q-switched mode.

The laser output beam is horizontal, and a mirror is set at 45° to the beam to direct it down into the sample cell. The beam passes through a lens which is used to focus the beam onto the surface of the sample. The lens also forms part of a binocular microscope through which the sample may be viewed and the laser beam focused. The eyepieces of the microscope are adjustable to enable focus of the

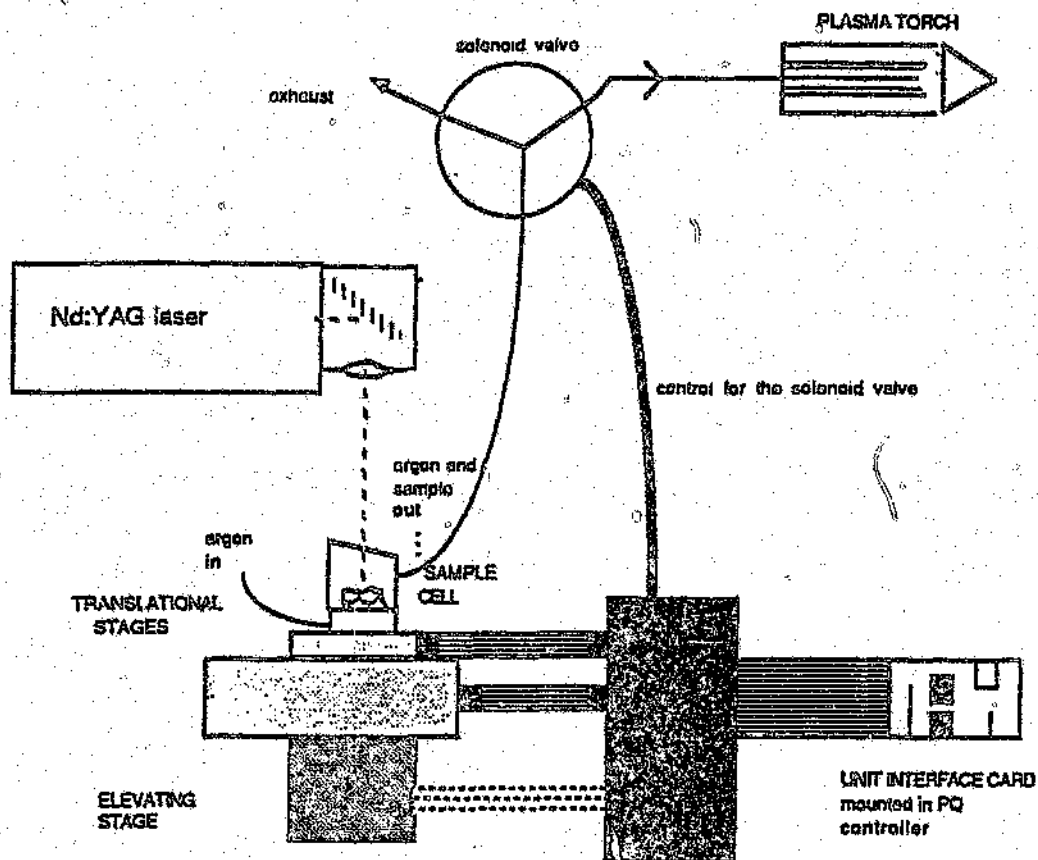


Fig. 2.2. Laser ablation system

(VG LaserLab Manual 1988)

laser beam at a point below the surface of the sample. This slows the loss of focus due to erosion of the sample surface by repeated laser shots.

The sample cell consists of a quartz cylinder, open at the lower end, with a sloping upper surface and a carrier gas outlet tube in the side. The reason for the sloping upper surface is to prevent the reflection of part of the laser beam back into the optical system. The cell is mounted on a teflon base through which the carrier gas enters, which is in turn mounted on a stage driven by a pair of stepper motors. This stage allows the remote positioning of the sample in between laser pulses by means of a joystick, or via the computer.

Plastic tubing is used to connect the sample cell outlet directly to the injector tube of the ICP torch, bypassing the nebuliser and spray chamber. Sample material which is ablated by a laser pulse is carried in the stream of argon into the plasma. A solenoid valve connected to a microswitch on the door of the laser ablation chamber directs the argon flow to waste while the door is open. This is to remove any air which may enter the cell when samples are changed, since the plasma may be extinguished by large amounts of air in the carrier gas.

2.1.5.4 Characteristics of laser ablation ICP-MS

The use of laser ablation as a sample introduction technique for ICP-MS has the obvious advantage of eliminating dissolution and dilution of the sample. In addition to this, there is the advantage of separating the volatilisation step from the

ionisation step⁵¹. This results in much greater freedom from matrix effects, which are a serious problem for techniques such as glow discharge and spark source mass spectrometry, where volatilisation and ionisation occur in the same process.

Another advantage of laser ablation is its versatility. The laser is able to ablate almost any type of solid material, both conducting and non-conducting. However, some materials such as glasses which are transparent at the wavelength of the laser beam will only couple with the laser in Q-switched mode. This is because in fixed Q mode the laser tends to interact directly with the sample material, while in Q-switched mode the laser interacts with the carrier gas above the surface of the sample, creating a plasma which vaporises the sample material⁵².

The background peaks in the laser ablation ICP-MS spectrum are relatively small compared to those of solution ICP-MS. This is due to the absence of solvent loading of the plasma. However, there are still background peaks from the plasma gas, the sample matrix and impurities in the plasma gas.

The greatest disadvantages of laser ablation ICP-MS for quantitative analysis are the difficulties experienced with matching calibration standards to samples and the relatively poor precision of measurement.

2.2 Experimental

2.2.1 Introduction

The determination of trace impurities in tantalum and niobium oxides was the first analytical method developed using laser ablation ICP-MS at Mintek. Very little information about the technique was available in the literature. Consequently, it was necessary to investigate various aspects of the technique in order to develop acceptable analytical methods. These investigations included the trial of sample preparation methods, optimisation of instrumental operating conditions, studies of time-resolved analyte signals, and studies of the composition of ablated material by scanning electron microscopy.

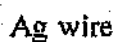
2.2.2 Apparatus

The laser ablation unit used was a VG Laserlab (VG Elemental, Winsford, Cheshire, UK), which was supplied with the instrument. Samples were ground in a McCrone micronising mill (McCrone Research Associates, London, UK), and particle size measurements were performed using a Malvern particle sizer (Malvern Instruments, Malvern, Worcestershire, UK). Pellets were pressed using a 30 ton ring press (Research and Industrial Instrument Company, London, UK). Electron microscope studies were performed on a JEOL 840A scanning electron microscope (JEOL, Tokyo, Japan) coupled with a Tracor Northern TN 5500

energy dispersive spectrometer (Noran Instruments Inc., Middleton, Wisconsin, USA).

2.2.3 Chemicals

Standards were prepared by spiking Grade 1 Ta_2O_5 and Nb_2O_5 with high-purity compounds of the required analyte elements. The compounds used were as follows:



All of the above materials were obtained from Johnson Matthey, Orchard Rd, Royston, Herts UK, with the exception of CaCO_3 which was obtained from Cerac Inc, Milwaukee, Wis. USA.

The binders which were used were:

CF 11 cellulose powder (Whatman International Ltd, Maidstone, Kent UK)

Boric acid (Johnson Matthey, Orchard Rd, Royston, Herts UK)

Mowiol (Aldrich Chemical Company Inc., Milwaukee, Wis. USA).

Internal standard solutions were prepared from high-purity materials. The materials used were:

Rhenium metal (Johnson Matthey)

Indium metal (Cerac)

Scandium oxide (Sc_2O_3) (ICN Pharmaceuticals Inc., Plainview, N.Y. USA).

Other reagents used were :

Acetone, A.R. grade

Nitric acid, 65% A.R. grade.

2.2.4 Preparation of calibration standards

To eliminate matrix effects, it was necessary to match the matrix of the calibration standards to that of the sample materials. There are no certified reference materials with similar matrices to the samples, and therefore synthetic calibration standards were prepared. Johnson Matthey Grade 1 Ta_2O_5 and Nb_2O_5 were used as starting materials, and these were spiked with high-purity compounds of the required analyte elements to produce 5 per cent stock mixtures. The compositions of the stock mixtures are shown in Table 2.1.

To avoid problems experienced with the blending of silver compounds into solid standards, the silver nitrate was freshly prepared by dissolving silver wire in nitric acid and drying. The above stock mixtures were thoroughly blended by repeated wet grinding with acetone. A zirconium pestle and mortar were used to grind the standards since zirconium was not one of the required analyte elements and therefore did not pose a contamination problem. Each stock mixture was diluted with the appropriate matrix material to produce a suite of standards ranging from 1 to 300 $\mu\text{g g}^{-1}$, and each standard was thoroughly blended.

2.2.5 Sample preparation

The method of sample preparation was developed for Ta_2O_5 , and the same method was used for Nb_2O_5 , since the materials are physically similar. The requirements of the sample preparation procedure were a small sample particle size, and a means of immobilising the sample for ablation.

Table 2.1 Compositions of stock mixtures for calibration standards

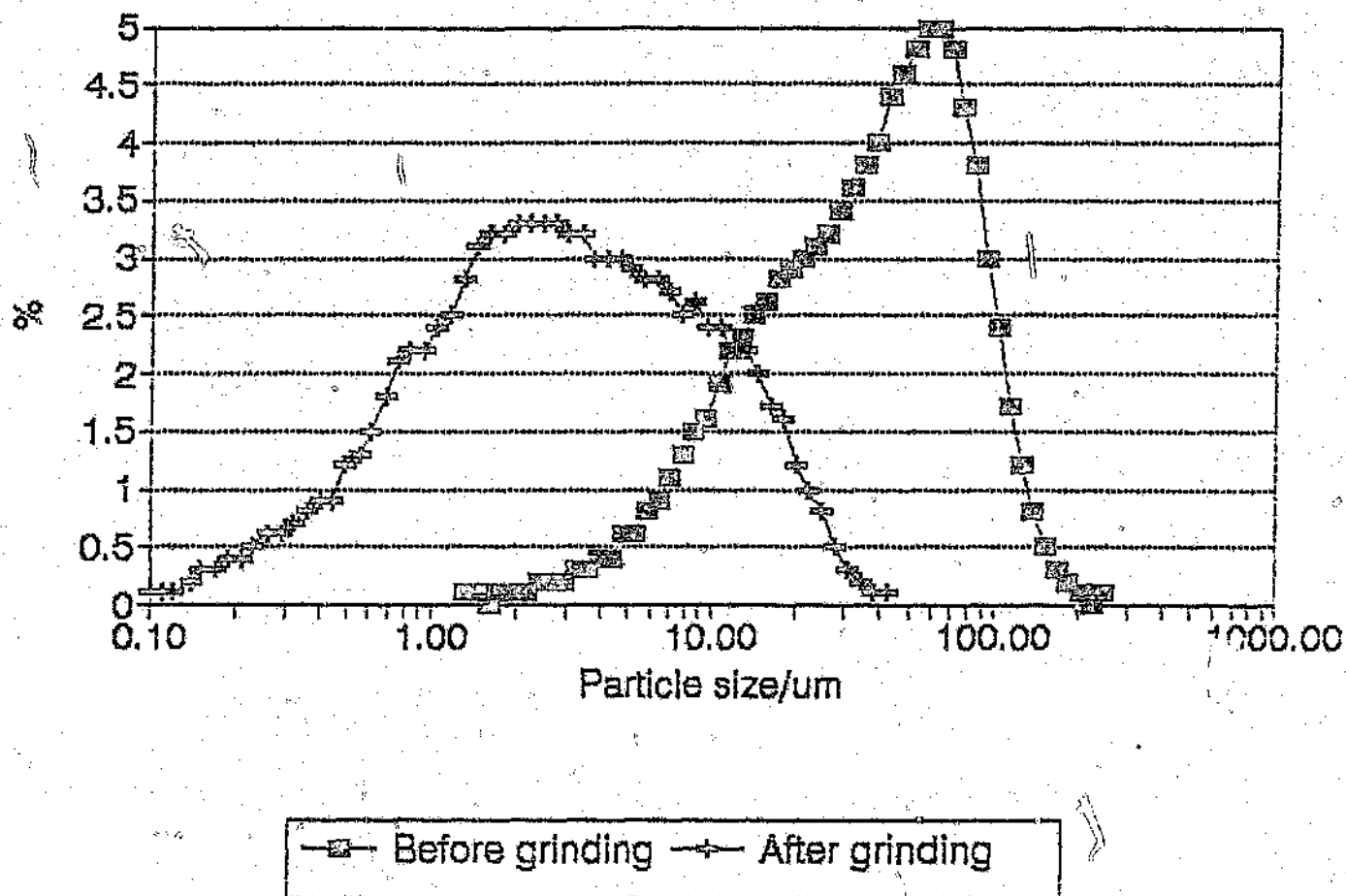
<u>Ta₂O₅</u>		<u>Nb₂O₅</u>	
Ta ₂ O ₅	79.8 mg	Nb ₂ O ₅	90.3 mg
MgO	82.9 mg	MgO	82.9 mg
Al ₂ O ₃	94.5 mg	Al ₂ O ₃	94.5 mg
SiO ₂	107.0 mg	SiO ₂	107.0 mg
CaCO ₃	125.0 mg	CaCO ₃	125.0 mg
TiO ₂	83.5 mg	TiO ₂	83.5 mg
MnO ₂	79.1 mg	MnO ₂	79.1 mg
Fe ₂ O ₃	71.5 mg	Fe ₂ O ₃	71.5 mg
Nb ₂ O ₅	71.5 mg	AgNO ₃	78.7 mg
AgNO ₃	78.7 mg	SnO ₂	63.5 mg
SnO ₂	63.5 mg	Ta ₂ O ₅	61.0 mg
WO ₃	63.0 mg	WO ₃	63.0 mg

2.2.5.1 Sample Grinding

A requirement of any solid sampling technique is that the samples must be homogeneous. This is particularly important in laser ablation, where very tiny amounts of material are sampled. A typical ablation crater is approximately 200 μ m in diameter and 50 μ m deep. In the case of powders such as Ta₂O₅ and Nb₂O₅, it is necessary to reduce the particle size as much as possible.

Various methods of grinding were attempted and the effectiveness of the methods was determined by particle size analysis of the ground samples. Ta₂O₅ before grinding was found to be 90 per cent below 85 μ m. Wet grinding with acetone in a zirconium mortar reduced the 90 per cent fraction below 27 μ m. Grinding with zirconia beads in a McCrone micronising mill produced the smallest particle size (90 per cent below 3 μ m). On analysis of the sample it was however found to have been contaminated by impurities in the zirconia beads. All other commonly used grinding materials were rejected because of contamination by one or more of the analyte elements, and eventually plexiglass beads were selected for use in the micronising mill. These gave a particle size of 90 per cent below 13 μ m and introduced no significant contamination. This method of grinding was used in all subsequent work. Graphs showing the particle size distribution in a Ta₂O₅ sample before and after grinding with plexiglass beads are shown in *Fig. 2.3*.

Fig. 2.3. Particle size analysis of a TaO_3 sample before and after grinding



2.2.5.2 Sample Immobilisation

Samples cannot be ablated in a powder state as the acoustic shock of the laser pulse scatters the material. It is therefore necessary to immobilise the sample, either by using a binder, or pressing a pellet, or both. An attempt was made to press pellets of Ta_2O_5 powder in a 10 mm diameter die using a 30 ton ring press. These pellets were found to be fairly robust but tended to crack when ablated, and therefore it was necessary to use a binder.

Boric acid is commonly used as a binder, and attempts were made to press pellets from Ta_2O_5 /boric acid mixtures. These mixtures produced robust pellets which could withstand the shock of ablation pulses. However, it was discovered that $^{11}\text{B}^{16}\text{O}$ was contributing to the background of the ^{27}Al isotope and raising the detection limit for aluminium, which was one of the required analyte elements. Since aluminium is monoisotopic, there was no alternative isotope to be used, and therefore boric acid could not be used as a binder. The use of cellulose powder was attempted, but on ablation of a blank cellulose pellet, it was found to contain unacceptably high levels of certain of the analyte elements, in particular iron.

The next binder which was investigated was Mowiol, a particular grade of polyvinylalcohol. An aqueous solution of Mowiol was used, following the procedure described by Darke et al.³⁹ This procedure involves mixing the sample with the binder solution, drying at 50°C and pressing into a pellet. However, when this method was duplicated, it was found that if the sample and binder mixture

was simply dried in a 15 mm diameter plastic Polytop lid, it set into a smooth resinous disc which was suitable for ablation without being compacted under pressure. The disc pressing step, which is time-consuming and can result in contamination of the sample by the die, was therefore omitted. The procedure used for immobilising samples prior to ablation was as follows : a 1 ml aliquot of 2.5 % (m/v) Mowiol solution was thoroughly mixed with 500 mg ground sample and the mixture was transferred to a 15 mm diameter polytop lid. The lid was placed in an oven and dried at 50°C for 3 hours, after which it was ready for ablation. These samples had a large enough surface area to allow up to 30 laser ablations without overlapping of the ablation craters.

2.2.5.3 Introduction of internal standards

Initial laser ablation studies performed on Ta_2O_5 samples indicated that the amount of material ablated varied considerably from one laser ablation pulse to the next, resulting in poor precision of analyte signals. It was therefore decided to use internal standardisation as a means of overcoming this problem.

The procedure of internal standardisation involves the normalising of analyte signals to the signal obtained for an element of known concentration, which is usually kept constant in both standards and samples throughout the analysis. Internal standards are extensively used in solution ICP-MS work, mainly to correct for matrix effects.

An internal standard for a particular analyte element should ideally meet several requirements: it should be present in the sample or standard at a constant concentration, the isotope used should be free of interference, the internal standard signal should be roughly similar in size to that obtained for the analyte, and the mass and ionisation potential of the internal standard should be similar to that of the analyte element. In solution ICP-MS internal standard solutions are simply added to the standard and sample solutions. However, in laser ablation work it is less easy to introduce internal standards. Where possible, it is most convenient to use a low abundance isotope of an element which is present in the standard and sample matrices as the internal standard.

Tantalum has two naturally occurring isotopes, the major isotope ^{181}Ta which is 99.988 % abundant, and the minor isotope ^{180}Ta which is 0.012 % abundant. The major isotope can not be used as an internal standard for the determination of impurities in Ta_2O_5 , as the count rates obtained from this isotope would be too high relative to the analyte counts. In fact, it is necessary to skip over the ^{181}Ta isotope when analysing Ta_2O_5 samples to prevent the excessively high ion current from damaging the detector. However, the minor isotope ^{180}Ta is of sufficiently low abundance to give a similar count rate to that of the analyte isotopes (^{180}Ta has a concentration of $98 \mu\text{g.g}^{-1}$ in pure Ta_2O_5). Since the samples are of high purity, the concentration of tantalum does not vary significantly from one sample to another. ^{180}Ta is subject to an isobaric interference from ^{180}W , and tungsten is one of the analyte elements. However, the ^{180}W isotope is only 0.126 % abundant. A concentration of $800 \mu\text{g.g}^{-1}$ tungsten in a Ta_2O_5 sample, which is considerably

higher than normal, would only raise the ^{180}Ta counts by 1 %. The ^{180}W interference is therefore not significant. Accordingly, ^{180}Ta was used as the internal standard isotope for all Ta_2O_5 analyses.

Niobium has only one naturally occurring isotope, which can not be used as an internal standard because of the problem of detector overload, as described above. Nb_2O_5 standard and samples must therefore be spiked with an internal standard before analysis. The most convenient way of doing this was to spike the aqueous binder solution with a choice of internal standards. Scandium, indium and rhenium are commonly used as internal standards in solution ICP-MS analysis, as they are rarely present in most sample types and give good coverage of the mass spectrum. It is usual to select the internal standard which is nearest in mass to the analyte elements. Since the analyte elements in Nb_2O_5 are spread over virtually the entire mass range, from magnesium (atomic mass = 24.3) to tungsten (atomic mass 183.8), all three internal standards were used. To test the feasibility of adding internal standards with the binder, a 2.5% Mowiol solution containing $10\text{ }\mu\text{g.ml}^{-1}$ scandium, indium and rhenium was prepared. This binder solution was used to prepare a set of Ta_2O_5 standards and samples which were analyzed. Results were calculated using ^{45}Sc , ^{115}In and ^{185}Re as internal standards and compared with results obtained using ^{180}Ta as internal standard. There was good agreement between the two sets of results, and the relative standard deviations were similar, an indication that spiking of the binder solution with internal standards is an acceptable method of introducing internal standard elements to standards and

samples. Accordingly, ^{45}Sc , ^{115}In and ^{185}Re were used as internal standard isotopes for the analysis of Nb_2O_5 samples.

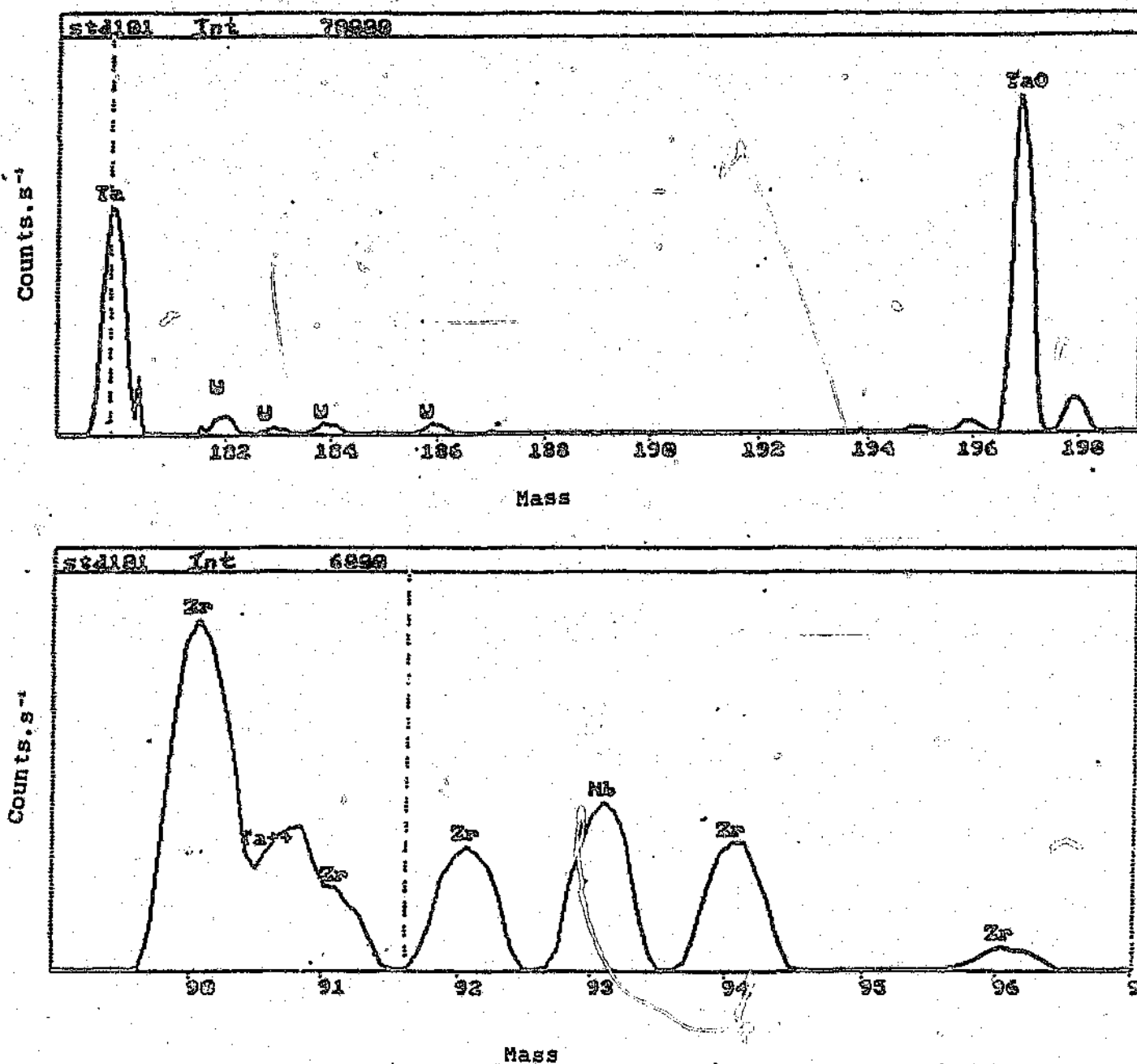
2.2.6 Laser ablation ICP-MS analysis

Preliminary survey scans were performed to see what sort of signal could be obtained from the ablation of Ta_2O_5 samples. Selected regions of a typical scan are shown in *Fig. 2.4*. These studies indicated that, as expected, the sensitivity of the instrument was more than adequate for the determination of the analyte elements over the required calibration range. Therefore it was not necessary to optimise sensitivity. However, the precision of laser ablation results was considerably worse than that typically obtained for solution ICP-MS work. Consequently a study was made of time resolved laser ablation signals of the analyte elements with the purpose of improving the reproducibility of the signal.

2.2.6.1 Time resolved signal studies

Using laser ablation and the single ion monitoring software option (which allows continuous signal measurement at a particular mass number), plots of count rates vs time were obtained for several analyte isotopes. These plots were compared with similar plots obtained by solution nebulisation. A comparison of laser ablation and solution nebulisation signals is shown in *Fig. 2.5*. It can be seen that the height of the spikes in the signal (or "noise") relative to the signal itself is considerably higher for the laser ablation signal than the solution nebulisation

Fig. 2.4. Selected regions of the laser ablation ICP-MS spectrum of a TaO_3 standard containing $10 \mu\text{g.g}^{-1}$ of each analyte element. Mass 181 is skipped to avoid saturating the detector with matrix ions. the zirconium peaks are due to contamination from the zirconium mortar and pestle.



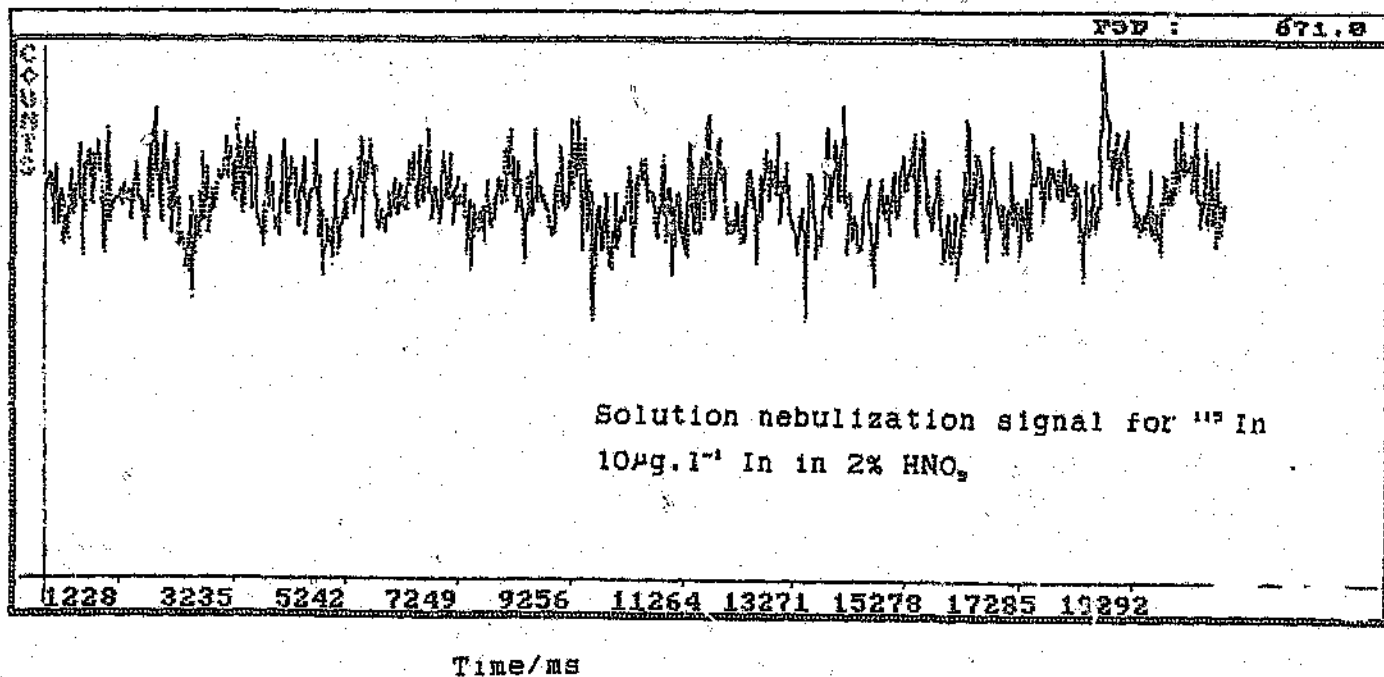
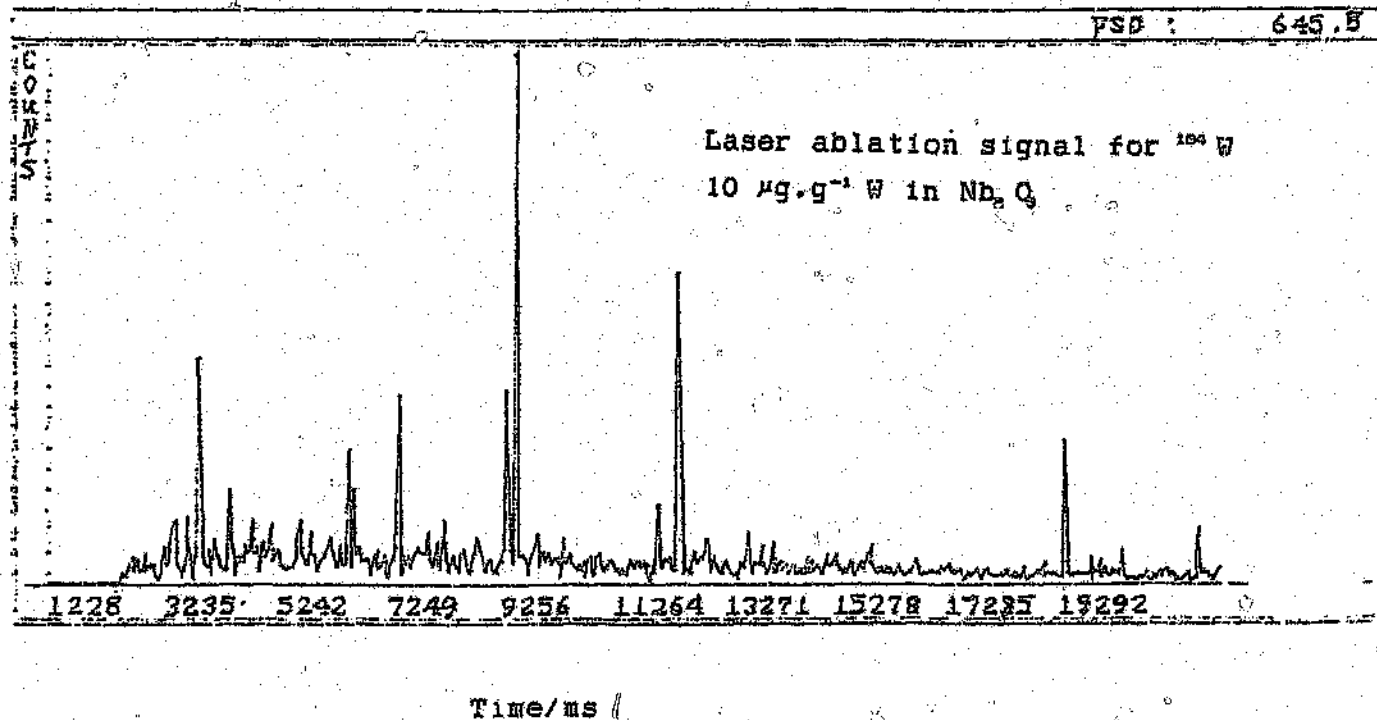


Fig. 2.5. Time-resolved signals resulting from laser ablation and solution nebulisation

signal. Therefore the signal-to-noise ratio is worse for laser ablation signals. This was suspected to be due to ablated particles of varying size passing into the plasma, which would result in a less stable plasma and therefore a noisier signal. To test this theory, a 0.3 μm Millipore filter paper was placed in the carrier gas line between the ablation cell and the plasma torch, a sample was ablated repeatedly, and the collected material was examined under the scanning electron microscope.

2.2.6.2 Scanning electron microscope studies

The electron micrographs of ablated material are shown in *Fig. 2.6*. These images exhibit several interesting features. Firstly, part of the material is in the form of a network of fine filaments $\approx 0.1 \mu\text{m}$ in diameter, which can be seen in *Fig. 2.6a* at 10 000 x magnification. These filaments were confirmed to be ablated material and not filter paper by qualitative energy dispersive spectrometry. A micrograph of a blank filter paper at the same magnification is shown in *Fig. 2.6b*. The origin of the filaments is not known, but may be condensation of vaporised material. Secondly, a portion of the material is in the form of spheres $\approx 1 \mu\text{m}$ in diameter (*Fig. 2.6a*) which are presumably condensed molten droplets. A third portion of the material is made up of irregular chunks $\approx 20 \mu\text{m}$ in size. These are visible in *Fig. 2.6c*, which is at 500 x magnification. Once again, these chunks and the spherical particles were confirmed to be sample material (and not contamination) by energy dispersive spectrometry. These particles appear to be sample material

Fig. 2.6. Scanning electron microscope images of ablated Nb_2O_5 sample material collected on 0.3 μm filter paper.

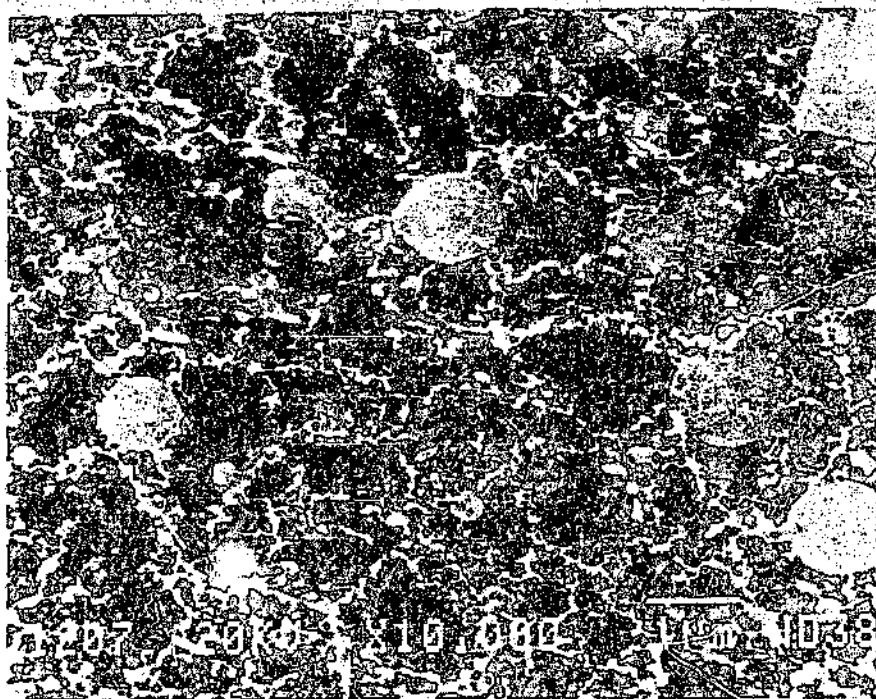


Fig. 2.6a. Ablated material.

Magnification : 10 000 x



Fig. 2.6b. Blank filter paper.
Magnification : 10 000 x

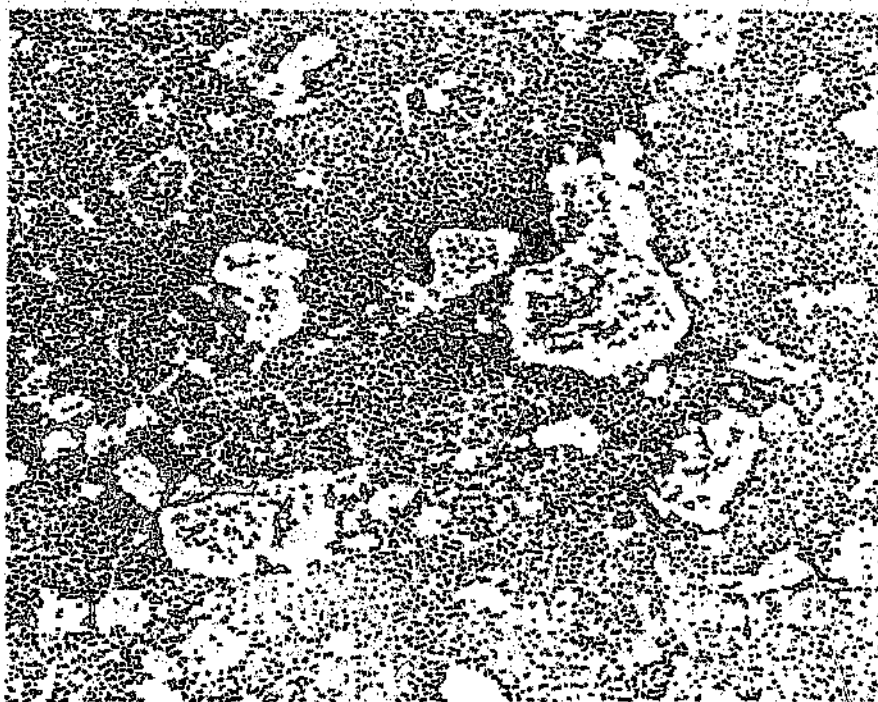


Fig. 2.6c. Ablated material.

Magnification : 500 x

which has not been vaporised or melted, but broken off by the shock of the laser pulse.

The scanning electron microscope studies confirm that particles of widely varying size are transported to the plasma, and provide an explanation of the noisy nature of the laser ablation signal. An attempt was made to filter off the larger particles using a coarse filter paper, and thus improve the precision of the signal. However, the paper rapidly became clogged and the signal was lost. It was therefore necessary to use the system without filtration and to select instrumental conditions which would give the best possible precision despite the instability of the laser signal.

2.2.6.3 Instrumental operating conditions

It was found that the transient signal obtained from a single laser pulse gave more reproducible results than the steady state signal from repeated pulses. A set of instrumental operating conditions were derived based on single pulse acquisitions. To obtain the maximum signal from a single laser pulse, the laser was set virtually at maximum power, and was focused at the maximum depth below the surface of the sample. The Q-switched mode of laser operation was used, which gives a pulse of shorter duration but greater intensity than the fixed-Q (or free-running) mode, and was found to give more reproducible ablation craters. A summary of the operating conditions is shown in *Table 2.2*.

2.2.6.4 Selection of analyte isotopes

The isotope selected for the analysis of a particular element should ideally be a major isotope (i.e. of fairly high abundance), to ensure reasonably high count rates, and should be free of interference. Interference-free isotopes could be found for most of the analyte elements. However, there were problems in selecting analyte isotopes for certain of the elements due to background ion interferences.

Background ion interferences are less severe in laser ablation ICP-MS analysis than they are in conventional solution nebulisation. This is due to the absence of water and matrix acid contributions to the background. However, there are still significant background peaks resulting from the sample matrix, the binder, traces of air and other impurities in the plasma argon, and the plasma argon itself.

Table 2.2 Instrumental operating conditions

Laser type	Nd:YAG
Wavelength/nm	1064
Pulse energy/mJ	250
Laser pulse	1
Mode	Q-switched
Outer gas flow/dm ³ min ⁻¹	16
Intermediate gas flow/dm ³ min ⁻¹	0.5
Carrier gas flow/dm ³ min ⁻¹	1.0
R.f. power/kW	1.4
Acquisition mode	Peak jump
Detector	Pulse counting
Peak Jump Dwell Time/ μ s	10240
Data points/peak	5
Mass Range Sweeps	50
Acquisition Time/s	35

Silicon and calcium

Silicon and calcium are particularly difficult to analyze by ICP-MS as every one of their naturally occurring isotopes is subject to severe interference problems. The isotopes of silicon are: ^{28}Si (abundance = 92.18 %), ^{29}Si (abundance = 4.79 %) and ^{30}Si (abundance = 3.12 %). ^{28}Si has an interference from the molecular background ion $^{14}\text{N}_2$, ^{29}Si has interferences from $^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}_2\text{H}$, and ^{30}Si has an interference from $^{14}\text{N}^{16}\text{O}$. The main calcium isotope ^{40}Ca (abundance = 96.92 %) has a direct isobaric overlap of ^{40}Ar , which is the main argon isotope. ^{44}Ca , the second most abundant calcium isotope (abundance = 2.13 %) has interferences from $^{40}\text{Ar}^4\text{He}$ and $^{12}\text{C}^{16}\text{O}_2$. There are four other naturally occurring calcium isotopes, but these all have very low abundances (0.003 to 0.64 %). Two of these (^{46}Ca and ^{48}Ca) have interferences from more abundant isotopes of titanium, which is also present in the standards and samples. The other two (^{42}Ca and ^{43}Ca) have interferences from background ions. The concentrations of these background ions are small by comparison to other background ions, but they are large relative to the low abundances of the calcium isotopes. Although the interferences on the silicon and calcium isotopes are less severe in the dry plasma, it was not possible to determine these elements at the required levels by laser ablation ICP-MS.

Iron and aluminium

Like calcium and silicon, iron and aluminium are also subject to background ion interferences. However, these interferences are less severe than those on calcium and silicon.

Aluminium has only one naturally occurring isotope, ^{27}Al . The cause of the interference on this isotope is not definite, but is probably $^{13}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{15}\text{N}$ overlap. However, the interference on ^{27}Al is relatively minor and the isotope can be used for analysis.

Iron has four naturally occurring isotopes, all of which are subject to interferences. The major isotope ^{56}Fe (abundance = 91.52 %) has an interference from $^{40}\text{Ar}^{16}\text{O}$. The second most abundant isotope, ^{54}Fe (abundance = 5.90 %) has an interference from background $^{40}\text{Ar}^{14}\text{N}$ as well as an isobaric overlap of ^{54}Cr . ^{57}Fe (abundance = 2.25 %) has interferences from $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ and $^{40}\text{Ar}^{17}\text{O}$. The other iron isotope ^{58}Fe is only 0.33 % abundant and has interferences from background $^{40}\text{Ar}^{16}\text{O}$ and ^{58}Ni isobaric overlap. The ^{56}Fe isotope has the largest background interference, but this interference is the least significant relative to the analyte signal, due to the high abundance of ^{56}Fe . The ^{56}Fe isotope was therefore selected as the analyte isotope for iron.

Other analyte elements

The other analyte elements were free of significant interferences. For each of the elements, the most abundant isotope was selected in order to obtain the highest sensitivity. The selected analyte isotopes are shown in *Table 2.3*.

Table 2.3 Selected isotopes for analyte elements

Element	Isotope	Abundance/%
Mg	24	78.60
Al	27	100.00
Ti	48	73.45
Mn	55	100.00
Fe	56	91.52
Nb	93	100.00
Ag	107	51.35
Sn	120	32.97
Ta	181	99.99
W	184	30.64

2.3 Evaluation of the Methods

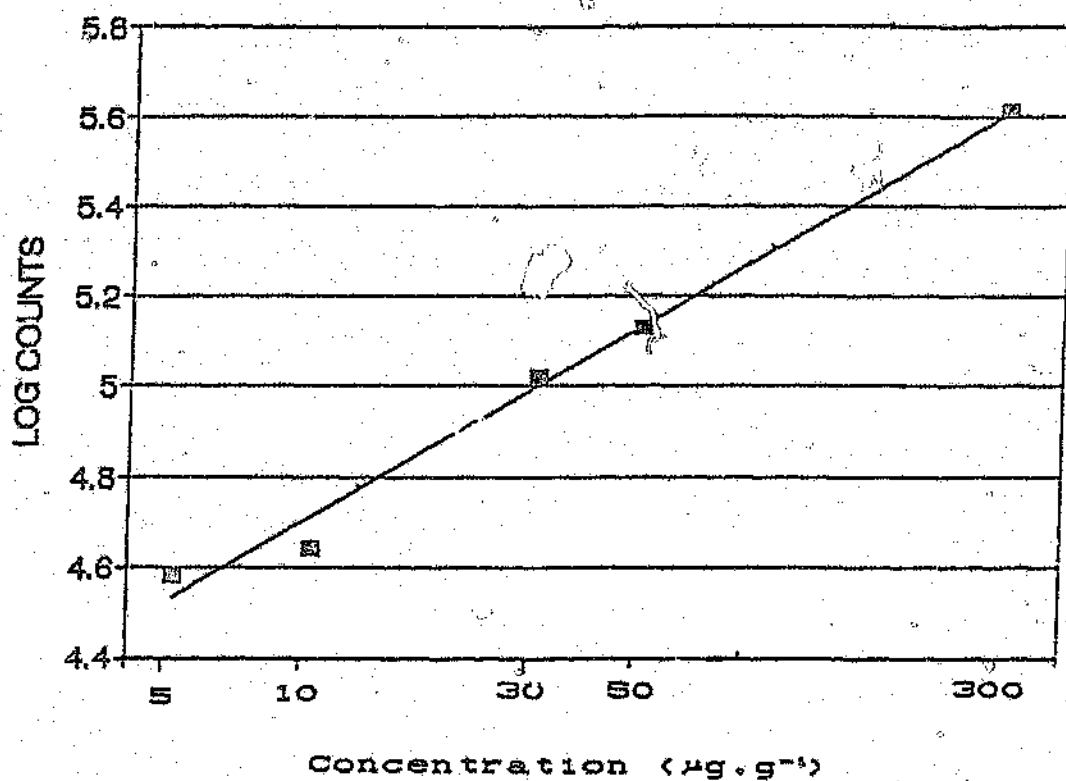
2.3.1 Determination of impurities in tantalum oxide

2.3.1.1 Calibration

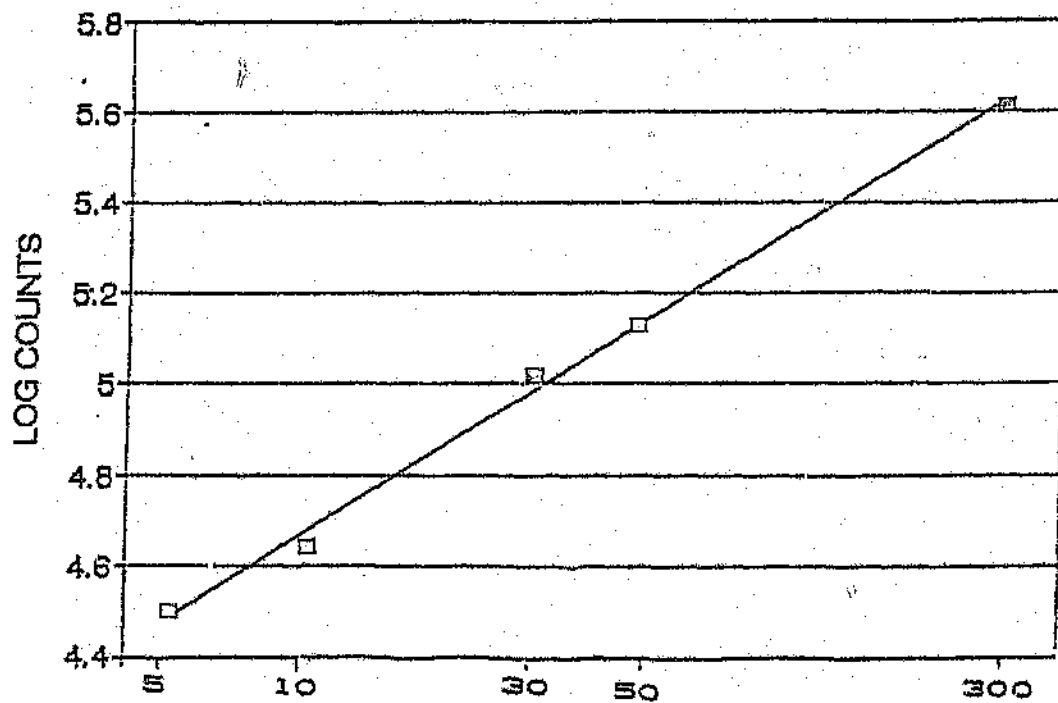
The measured area counts.s⁻¹ for a particular analyte element, normalised to the measured counts for the internal standard isotope (¹⁸⁰Ta), were plotted against the concentration of the element for each standard to obtain the calibration curve. The normalisation factor for each sample was defined as the internal standard counts for the current sample divided by the internal standard counts for the first sample measured. As has previously been discussed, the precision of laser ablation ICP-MS analysis is relatively poor in comparison to solution ICP-MS. As a result it is not advisable to use two- or three-point calibration curves for laser ablation analysis, although such curves are commonly used in solution analysis. To allow for the spread of data, a suite of five standards was used, and each was analyzed in duplicate. This gave sufficient data to enable identification and elimination of occasional spurious data points. The use of this calibration procedure resulted in good, linear calibration curves being obtained for all of the analyte elements. Typical examples of calibration curves are shown in *Fig. 2.7*. Plots of log(area counts.s⁻¹) vs log(concentration) are used to show the full concentration range of the standards, which spans three orders of magnitude.

Fig. 2.7. Typical calibration curves for impurities in Ta_2O_5 .

Iron in tantalum oxide



Magnesium in tantalum oxide



2.3.1.2 Lower limits of determination

The limits of detection for laser ablation ICP-MS have been variously quoted as being from 10 ng.g^{-1} ³⁷ up to $2 \mu\text{g.g}^{-1}$ ³⁸, depending on the sample type and the elements examined. In solution ICP-MS, detection limits can be based on measurements of a very high purity blank solution. In laser ablation ICP-MS it is necessary to base detection limits on the measurement of the blank material which has the highest purity available and which matches the sample type. Other blank measurements can be used, such as the "plasma blank" with no laser shots being fired, or ablation of a high-purity, non matrix-matched material. However, these measurements do not give a true reflection of detection limits because the presence of ablated material alters the ionisation characteristics of the plasma, and these will change with variations in the sample matrix. Therefore, when referring to quantitative methods of analysis, it is more appropriate to use the term "lower limits of determination", for a particular sample matrix type. These limits are governed by the purity of the blank material and the precision of measurement, rather than the sensitivity of the technique. Very much lower limits of detection can be obtained for qualitative analysis, based on the identification of spectral peaks. However, these limits are difficult to quantify.

When a sample of the Grade 1 Ta_2O_5 blank material was analyzed, the counts obtained were considerably higher than the plasma blank for all of the interference-free analyte isotopes. Examination of the spectral peaks confirmed that there were traces of most of the analyte elements in the blank material. The blank

sample was analyzed repeatedly against the calibration standards and lower limits of determination were calculated based on three times the standard deviation (3σ) of these results. The results are shown in *Table 2.4*. These limits are generally close to the desired level of $1 \mu\text{g.g}^{-1}$. The higher limit obtained for iron is due to the $^{40}\text{Ar}^{16}\text{O}$ background overlap on the iron analyte isotope ^{56}Fe .

Table 2.4 3σ Lower limits of determination for impurities in Ta_2O_5

Element	Isotope	Lower limit of determination $\mu\text{g g}^{-1}$
Mg	24	1.1
Al	27	1.9
Ti	48	0.42
Mn	55	0.12
Fe	56	10
Nb	93	0.66
Ag	107	2.3
Sn	120	0.22
W	184	0.75

2.3.1.3 Precision and accuracy

As has been mentioned previously, there are no certified reference materials available with which to test the accuracy of the method. However, real samples were available. To determine the accuracy and precision of the method when applied to real samples, a typical sample from the purification plant which had been repeatedly analyzed by d.c. arc emission spectrography was analyzed ten times by the laser ablation ICP-MS method. Relative standard deviations (S_r) were calculated and the results were compared to those obtained by emission spectrography, the results are shown in *Table 2.5*.

The relative standard deviations of the laser ablation ICP-MS results are similar to those obtained by d.c. arc emission, and are adequate for the purposes of this work. The agreement between the two sets of results is reasonably good for most elements, although the laser ablation ICP-MS results are somewhat lower for Fe and Al. Ca and Si were not determined by Laser ablation ICP-MS due to the background ion interferences discussed previously.

Table 2.5. Comparison of laser ablation ICP-MS with emission spectrographic results for a purification plant Ta₂O₅ sample.

Element	Emission spectrography		Laser ablation ICP-MS	
	Conc./ $\mu\text{g g}^{-1}$	S _r	Conc./ $\mu\text{g g}^{-1}$	S _r
Mg	42	0.21	47	0.07
Al	260	0.25	170	0.15
Si	>300	—	N.D.	—
Ca	130	0.21	N.D.	—
Ti	24	0.23	23	0.07
Mn	3	0.07	2	0.25
Fe	160	0.18	100	0.12
Nb	<10	—	7	0.16
Ag	8	0.09	6	0.16
Sn	<3	—	3	0.24
W	N.D.	—	2	0.42

N.D. : Not determined.

S_r : Relative standard deviation

2.3.2 Determination of impurities in niobium oxide

2.3.2.1 Calibration

Calibration standards were analyzed as for Ta_2O_5 . However, for Nb_2O_5 , three internal standards were used and therefore a different normalisation algorithm was used. For analyte masses less than the lowest internal standard mass (^{45}Sc), only ^{45}Sc was used as the internal standard. For masses greater than the highest internal standard mass (^{185}Re), only ^{185}Re was used. For masses between two internal standard masses (e.g. ^{55}Mn , which is between ^{45}Sc and ^{115}In), a linear interpolation was made between the two normalisation factors.

2.3.2.2 Lower limits of determination

The Grade 1 Nb_2O_5 blank was analyzed as was done for Ta_2O_5 , and lower limits of determination were determined in the same way. The results are shown in *Table 2.6*. The high detection limit for Ta was due to a persistent memory effect resulting from the prior analysis of Ta_2O_5 . This Ta memory effect was only observed when laser shots were fired, and therefore the origin appears to be residual Ta_2O_5 particles which are dislodged from the walls of the ablation cell and tubing by the acoustic shock of the laser pulse. The memory was reduced but not eliminated by replacing the tubing and thorough cleaning of all components. This problem is likely to be experienced frequently when changing from one sample type to another. It may be solved by the manufacture of a number of exchangeable

ablation cells which would each be used for only one sample type. Detection limits for the other analyte elements were similar to those obtained for the Ta_2O_5 method. Once again, the detection limit for Fe was relatively high due to $^{40}\text{Ar}^{16}\text{O}$ overlap.

Table 2.6 Lower limits of determination (3σ) for impurities in Nb_2O_5

Element	Isotope	Lower limit of determination $\mu\text{g g}^{-1}$
Mg	24	0.84
Al	27	0.32
Ti	48	0.83
Mn	55	0.63
Fe	56	11
Ag	107	0.07
Sn	120	0.47
Ta	181	29
W	184	0.37

2.3.2.3 Precision and accuracy

A typical plant sample was analyzed repeatedly to determine relative standard deviations (S_r), as was done for Ta_2O_5 . The results are shown in Table 2.7. S_r s are similar to those of the Ta_2O_5 method. No spectrographic results were available for comparison.

Table 2.7. Analysis results for a purification plant Nb_2O_5 sample

Element	Concentration/ $\mu g.g^{-1}$	S_r
Mg	1	0.14
Al	4	0.06
Ti	16	0.19
Mn	1	0.06
Fe	<11	—
Ag	<0.07	—
Sn	3	0.16
W	1000	0.14
W	47	0.18

2.4 Discussion and conclusions

Methods have been developed for the determination of trace impurities in Ta_2O_5 and Nb_2O_5 by laser ablation ICP-MS. No dissolution of the refractory sample materials is necessary, and the sample preparation procedure is rapid and simple.

2.4.1 Interferences

Of the elements for which analysis is required, four are affected by overlap interference problems, namely silicon, calcium, iron and aluminium. The interferences on calcium and silicon are so severe that they can not be determined at the required concentration levels. Iron can be determined, though with a relatively high lower limit of determination. The determination of aluminium is not significantly affected by the presence of the interfering peak. The other analyte elements, namely magnesium, titanium, manganese, silver, tin, tungsten, niobium in Ta_2O_5 and tantalum in Nb_2O_5 are all essentially free of interference.

2.4.2 Memory effects

A severe tantalum memory effect was encountered when Nb_2O_5 samples were analyzed after many Ta_2O_5 analyses had been performed. This memory effect persisted despite measures such as replacing the sample transfer tubing and thoroughly cleaning the cell. Memory effects are likely to be a problem whenever changing from one sample type to another, and are likely to affect the

determination of niobium in Ta_2O_5 , now that the system is also contaminated with niobium. It is anticipated that this problem will be alleviated by the manufacture of exchangeable ablation cells, each of which would be dedicated to a single sample type.

2.4.3 Precision and accuracy

The precision of measurement for the methods which have been developed is considerably worse than that obtained for solution methods, due to the relatively poor signal to noise ratio of laser ablation analyte signals. This appears from electron microscope studies to be due to large particles of the sample material entering the plasma. Methods of alleviating this problem, for example electrostatic precipitation of large ablated particles, are to be investigated in the future. However, the precision of measurement for the laser ablation methods is similar to that obtained by the existing spectrographic methods.

2.4.4 Lower limits of determination

The lower limits of determination are below the required level of $1\mu g\ g^{-1}$ for most of the analyte elements. The elements which have elevated limits of determination due to interferences, i.e. silicon, calcium, aluminium and iron, can all be determined by spectrographic methods. Conversely, the elements which can not be determined satisfactorily by the spectrographic methods i.e. tantalum, niobium and tungsten can all be determined by laser ablation ICP-MS. However, memory

effects, which affect the determination of tantalum in Nb_2O_5 and niobium in Ta_2O_5 , remain a problem.

2.4.5 Conclusions

Apart from the development of necessary analytical methods, this research has also served to increase expertise in the use of laser ablation ICP-MS. Several rules of thumb have been established with regard to sample preparation and instrumental operating conditions, which will be applicable to other methods in future. A good understanding has been obtained of the capabilities and limitations of the technique.

The use of laser ablation as a sample introduction method for ICP-MS enables rapid analysis of solid materials without dissolution. The technique can be used for quantitative analysis despite relatively poor precision.

2.5 Publication details

The work in this chapter has formed the basis of a paper presented at the IUPAC Third International Symposium on Analytical Chemistry in the Exploration, Mining and Processing of Materials, held in Sandton on 2-7 August 1992⁵³. The work has also been published in the Journal of Analytical Atomic Spectrometry⁵⁴.

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CHAPTER THREE. SAMPLE MANIPULATION AND SAMPLE INTRODUCTION BY MEANS OF FLOW INJECTION ANALYSIS (FIA)

3.1 Introduction and Theory^{1,2}

3.1.1 Introduction

Both ICP-AES and ICP-MS are rapid and efficient multielemental techniques, and the time required for actual measurement of the elemental composition of a sample is generally under one minute. If one includes the time required for the analyte signal to reach steady-state prior to measurement, and the time required for the signal to return to the baseline after measurement, the total analysis time per sample is still under five minutes. The use of a sample changer enables automation of the measurement process, which further increases the efficiency of the techniques. However, the preparation of the sample prior to measurement is still to a large extent a manual process which requires a much greater portion of the analyst's time than the measurement process. The reason for this is that the batch

operations that make up the sample preparation process do not lend themselves to automation.

Many of the batch operations involved in conventional sample preparation, including dilution, preconcentration, separation and addition of reagents can be replaced by flow operations. Flow operations consist of sequential movements of liquids in tubes. The technique of flow injection analysis is based on the reproducible injection of a well-defined volume of sample into a carrier stream, which carries the sample to a detector. FIA can therefore be used in combination with any fluid analysis technique, including ICP-AES and ICP-MS. There are several potential advantages to the linking of FIA with ICP-AES and ICP-MS. The most important advantage is the automation of sample preparation steps, which can be easily implemented in an FIA system. A second advantage is the reduction of sample volumes, which can be used to shorten wash times between samples and to enable the analysis of solutions with higher dissolved solid content than is possible in conventional steady-state analysis.

3.1.2 Origins of Flow Injection Analysis

There are many precedents to the technique of FIA, and the origins of the technique can be traced as far back as 1957, when the concept of sample injection into a flowing stream was introduced in gas chromatography⁴. As a result, some controversy exists concerning the historical origin of FIA. However, establishment

of FIA as distinct from other flow methods of analysis was largely due to the work of two groups, one led by Růžicka in Denmark and the other by Stewart in the USA. Růžicka introduced the term 'flow injection analysis' in 1975³, and described the distinguishing features of the technique.

3.1.3 Principles of Flow Injection Analysis

FIA is characterised by the reproducible, direct insertion of a sample into a continuous, unsegmented flow which transports the sample to a detector monitoring the flow. Physical or chemical processes may occur during the transport process. The degree of dispersion of the sample can be varied according to the requirements of the analysis. Continuous measurement by the detector results in a transient signal. Since measurement is not made at steady state, careful control of the timing of operations is important.

A flow injection system in its simplest form consists of a pump which drives a stream of carrier solution through a narrow tube, an injection port by which a highly reproducible volume of sample is introduced into the carrier stream, an optional reactor to prepare the sample for detection, and a detector. In early FIA systems the sample was literally injected into the carrier stream by means of a syringe. However, injection valves have replaced syringes in most applications. *Fig. 3.1* is a diagram of a simple flow injection system utilising an eight-port injection valve. The sample and carrier streams are fed into the flow injection

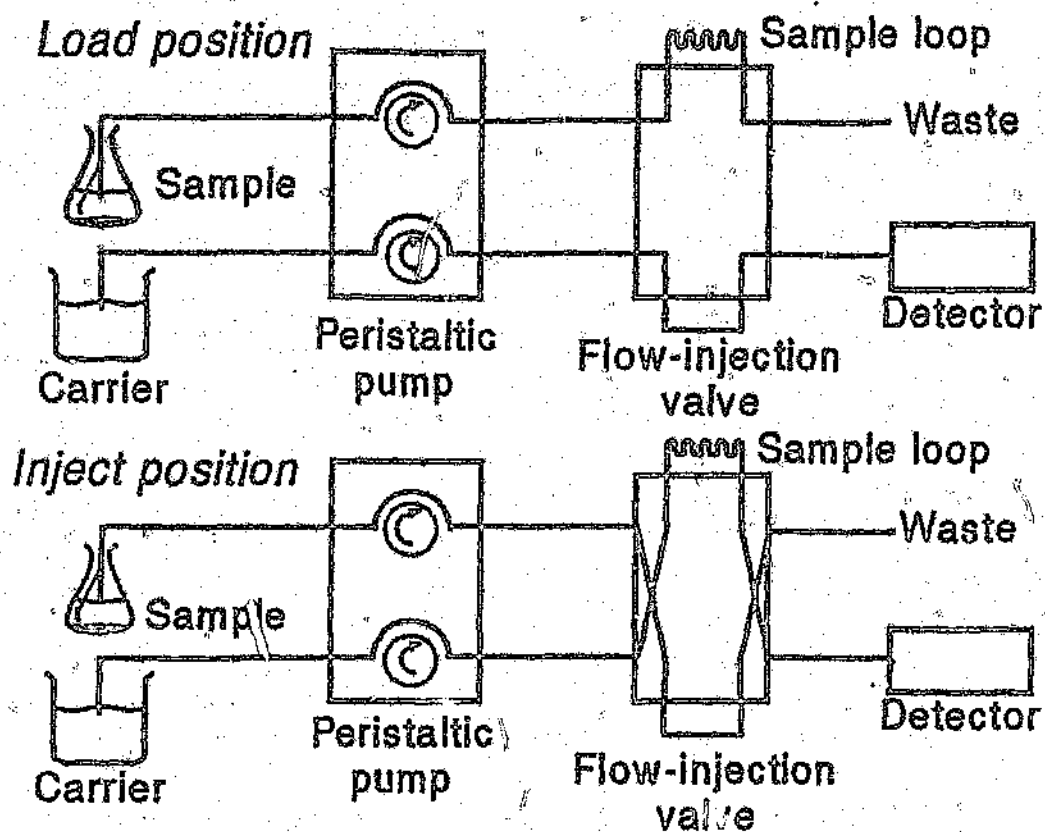


Fig. 3.1. A simple FIA system

(Růžicka and Hansen 1988)

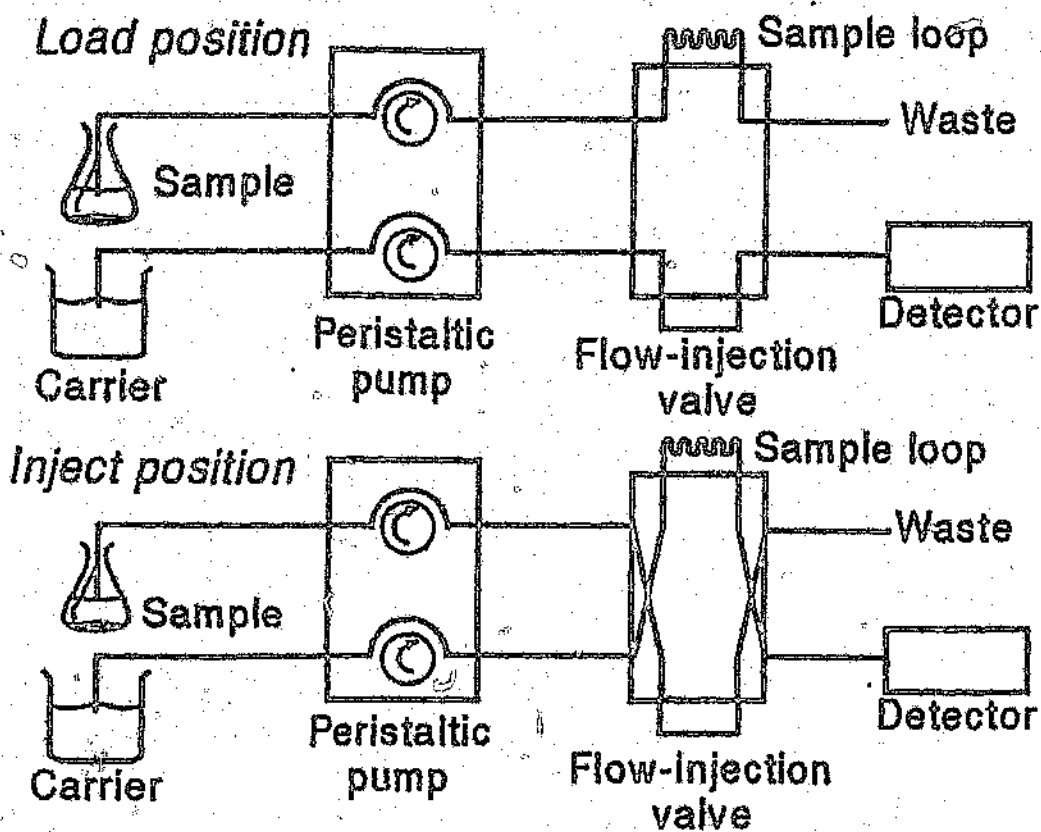


Fig. 3.1. A simple FIA system

(Růžicka and Hansen 1988)

valve by a peristaltic pump. The valve can be switched between two positions, 'load' and 'inject'. In the 'load' position, the sample passes through the sample loop and runs to waste, while the carrier solution passes through to the detector. In the 'inject' position, the two streams are switched so that the carrier stream pushes the contents of the sample loop to the detector.

The signal resulting from continuous detection of an analyte species in an FIA system is a peak which is approximately Gaussian in shape. *Fig. 3.2* shows a comparison between FIA and steady-state signals detected by ICP-MS. The size and shape of an FIA peak is dependent on the concentration of the analyte species, the volume of injected sample and the degree of dispersion of the sample in the carrier stream. The most important requirement of an FIA system is a high degree of reproducibility of the sample volume and of dispersion of the sample, which enables accurate correlation of peak magnitude to analyte concentration. The various methods of quantifying an FIA peak are shown in *Fig. 3.3*. These methods are:

- 1) Measurement of peak height. The peak height is proportional to the concentration of the analyte species. Peak height measurement is the most commonly used method in simple FIA systems since peak height is the easiest parameter to measure. However, in measurement systems where signal noise is a significant feature, a smoothing algorithm is necessary to ensure accurate measurement of the peak height.

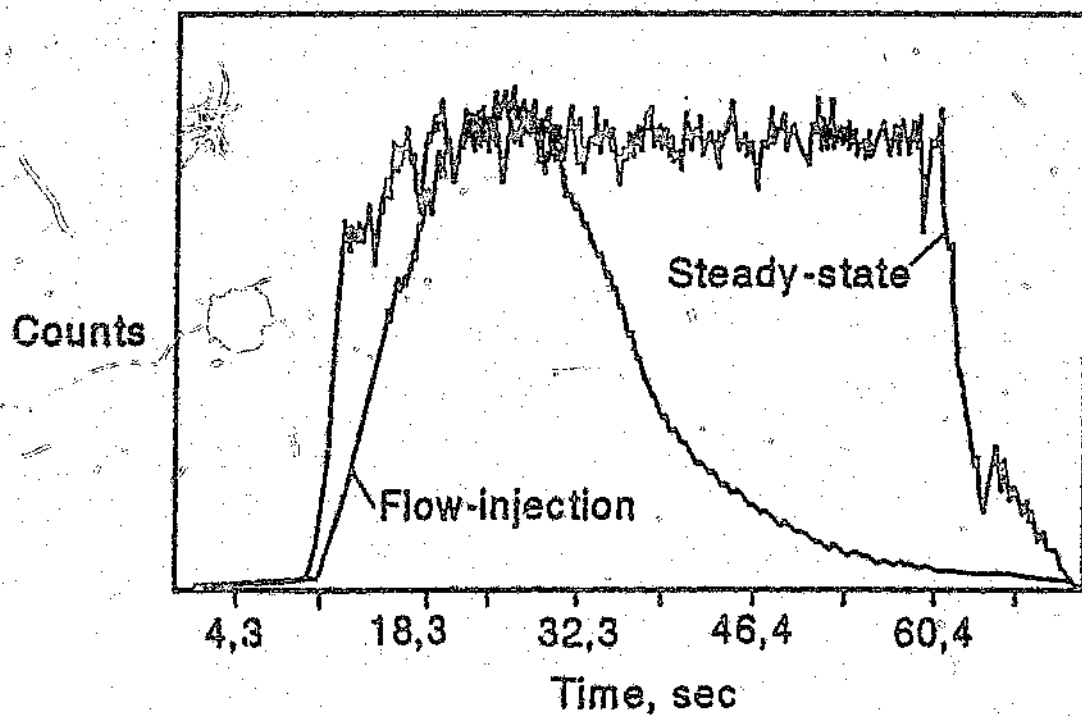


Fig. 3.2. Comparison of FIA and steady-state signals

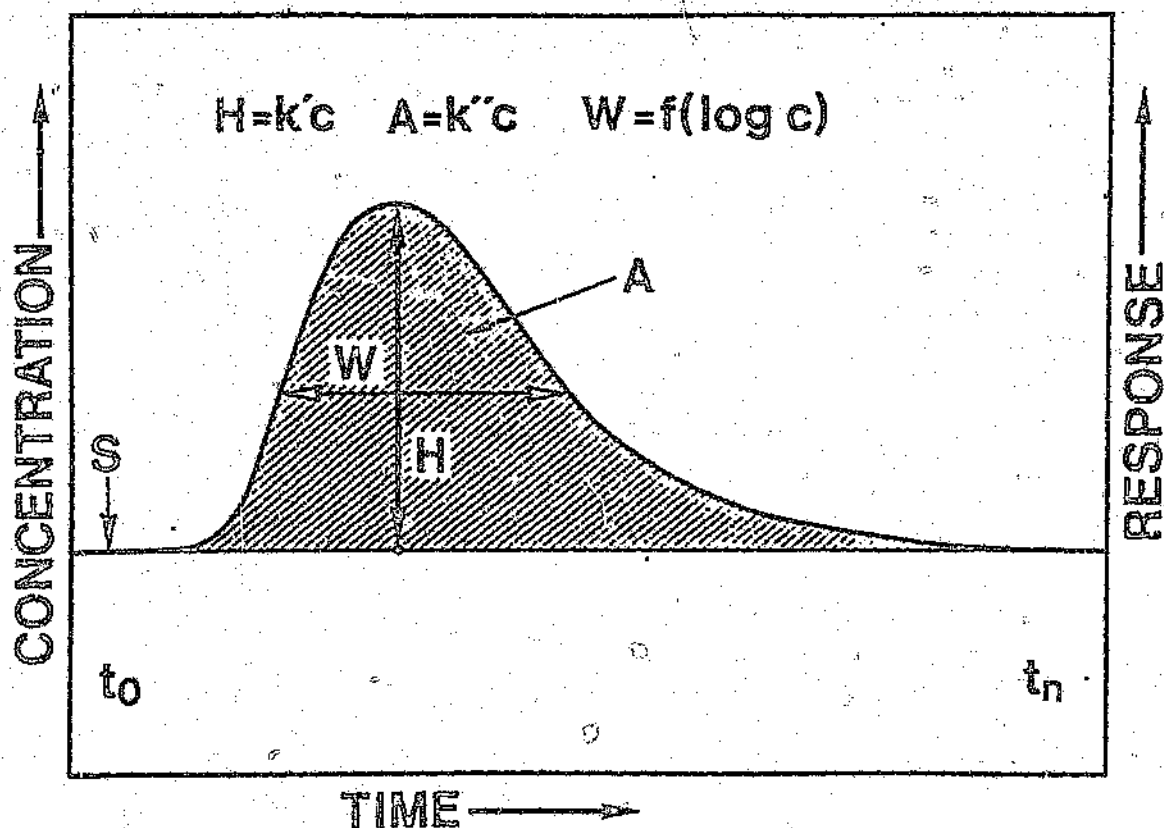


Fig. 3.3. Peak measurement strategies. H = height, A = area, W = width.

(Růžička and Hansen 1988)

2) Measurement of peak area. The peak area is also proportional to analyte concentration, and this measurement is used in systems where signal integration over time is appropriate. A drawback of peak area measurement is that the signal to noise ratio decreases on either side of the apex of the peak, and therefore selection of the integration period is critical to the precision and sensitivity of measurement.

3) Measurement of peak width. The peak width at a particular response level is proportional to the log of the analyte concentration. Measurement of peak width can therefore be useful in applications where the analyte concentrations can vary by several orders of magnitude. Due to the logarithmic relationship, concentrations calculated from peak width measurements tend to be relatively imprecise when compared to those calculated from peak height or peak area measurements. Peak width measurement is therefore more appropriate for semi-quantitative measurement over wide concentration ranges.

3.1.4 Compatibility of Flow Injection Analysis with ICP-AES and ICP-MS

Signal Detection

As has been mentioned previously, FIA is compatible with any technique where the sample is in the form of a fluid, and is therefore applicable to both ICP-AES and ICP-MS. However, another requirement of FIA is continuous detection of the analyte signal.

In the case of ICP-AES, sequential measurement of the analyte elements by a monochromator-based instrument is feasible provided that the signal remains at steady-state. However, in the case of FIA, due to the transient nature of the signal, simultaneous detection of all analyte elements is essential for efficient multielemental analysis. FIA is only really applicable to polychromator-based, simultaneous detection ICP-AES instruments.

In the case of quadrupole ICP-MS, detection is strictly speaking sequential, since the quadrupole scans across the relevant mass range during analysis. However, the time taken per scan is so short relative to the FIA peak width that the signal detection is to all intents and purposes simultaneous.

Quadrupole-based ICP-MS instruments and polychromator-based ICP-AES instruments are therefore suited to the application of FIA.

Data Processing

A factor which limits the effectiveness of FIA in combination with both ICP-MS and ICP-AES is the data processing software component of the instruments. The large quantity of raw data produced by multielemental measurement requires a dedicated personal computer with sophisticated software for processing of the data. Unfortunately, the software supplied by the instrument manufacturers is geared towards signal integration over a period of time at steady-state, i.e. area measurement. The VG Plasmaquad ICP-MS software has a multielemental time-resolved measurement feature, which allows height measurement of FIA peaks, but this feature is incompatible with the quantitative analysis software option. The Spectroflame ICP-AES has no time-resolved measurement option. As a result of this, peak area measurement is the only feasible method of peak quantitation on both the ICP-MS and ICP-AES systems. Sample volumes must therefore be sufficiently large to ensure that there is sufficient integration time to achieve adequate sensitivity and precision of measurement.

3.1.5 Applications of Flow Injection Analysis in ICP-MS and ICP-AES

There have been numerous reports in the literature of applications of FIA to ICP-AES. More recently several applications to ICP-MS have been published. The wide variety of situations in which FIA has been used is an indication of the versatility of the technique.

In combination with ICP-AES, FIA has been used to preconcentrate elements of interest by means of chelating resins⁵⁻⁹, alumina¹⁰ and ion-exchange resins¹¹. The technique has also been used for matrix matching standards and samples¹² and matrix separation¹³, automation of sample handling^{14,15}, solvent extraction¹⁶, hydride generation¹⁷⁻¹⁹, slurry nebulisation²⁰ and the analysis of organic solvents²¹.

In the field of ICP-MS, FIA has been employed to reduce matrix effects^{22,23} and to remove interfering matrix components²⁴. FIA has also been applied to analysis of organic solvents^{21,25}, hydride generation^{26,27}, direct injection nebulisation²⁸, direct sample insertion²⁹, and to elemental speciation using reversed-phase liquid chromatography³⁰.

3.1.6 Aim of the Investigation

The first objective of this investigation was to interface a flow injection system with both ICP-AES and ICP-MS systems, and to establish suitable operating conditions for the two techniques. The second objective was to evaluate the usefulness of the flow injection system by applying FIA to specific analytical problems.

3.2 Apparatus

The FIA system was designed and built by Taylor and Williams of the Process Analytical Group, which has constructed several FIA systems for use in a variety of applications in process environments. The system was designed to be compatible with both VG Plasmaquad II+ ICP-MS and Spectroflame ICP-AES instruments, which was relatively simple since the sample introduction systems of the instruments are similar and both systems employ Gilson automatic sample changers.

The FIA system consists of a Gilson four-channel peristaltic pump, Technico colour-coded pump tubing of various sizes, a Dionex eight-port pneumatic flow-injection valve, and an electronic control circuit. The valve is driven by compressed gas. The valve can be switched automatically in combination with a Gilson automatic sample changer, or it can be switched manually. Automatic switching is achieved by means of a microswitch fixed to the sample changer arm, which is triggered each time the arm moves from one sample to the next. The microswitch in turn triggers a solenoid valve that switches the gas flow to the pneumatic flow-injection valve and sets the valve to the 'load' position. An adjustable timer switch allows sufficient time for the sample to fill the sample loop and then switches the valve to the 'inject' position. If manual switching is required, the solenoid valve is replaced by a manual switching valve. The uptake delay period is a user-selected parameter in the data acquisition software, and this

period is used to synchronize the detection of the flow-injection signal with the acquisition of data by the instrument.

3.3 Applications of FIA-ICP-MS

3.3.1 Reduction of Analysis Time

When an instrument is required to perform a great deal of routine analysis, anything that enables a greater sample throughput is very advantageous. This is particularly true of ICP-MS, where the high cost of the instrumentation prevents the purchase of several instruments. Reducing the time required for routine analysis also frees the instrument for research applications.

Shorter analysis times are mainly achieved by reducing the sample loading of the instrument and thereby reducing the wash time between samples. In steady state analysis, several millilitres of sample are aspirated into the instrument per analysis and considerably more time is required for the sample to reach steady state in the plasma and to wash out of the system than is required for the acquisition of analytical data. By contrast, in FIA, sample volumes are typically of the order of a few hundred microlitres, and the wash time is much shorter. However, as was mentioned in Section 3.1.4, integration across the FIA peak results in a loss of sensitivity relative to measurement at steady-state. It is therefore necessary to select a compromise sample loop size that gives a short wash time while

maintaining adequate sensitivity. A number of different loop sizes were tested, and it was found that with a 350 μ l sample loop it was possible to achieve 70% of normal sensitivity while shortening the analysis time per sample by 40%.

A factor which degrades sensitivity and lengthens wash times in FIA analysis is dispersion of the sample plug in the tubing by the carrier stream. *Fig. 3.4* shows the behaviour of a sample plug from the moment of injection. Initially the plug is cylindrical, and if it were possible to measure the sample at the point of injection the signal would rise sharply to steady-state and return to the baseline as rapidly. However, due to the fact that the flowrate of a liquid in a tube is highest at the centre of the tube and tends towards zero at the walls, the plug is dispersed by the carrier stream as it flows through the tube. Therefore, the longer the tube between the injection valve and the nebuliser, the broader and flatter the time-resolved signal. To achieve the two objectives of good sensitivity and short wash time, the analyte signal should be as close to steady-state as possible during the integration period and should return to the baseline rapidly. Therefore, dispersion must be kept to a minimum. In an attempt to minimise dispersion, the injection valve was positioned as close as possible to the nebuliser. It was found that by placing the valve inside the torch box with only a few centimetres of tubing connecting the valve and the nebuliser, it is possible to obtain further improvement in sensitivity and reduction in wash times.

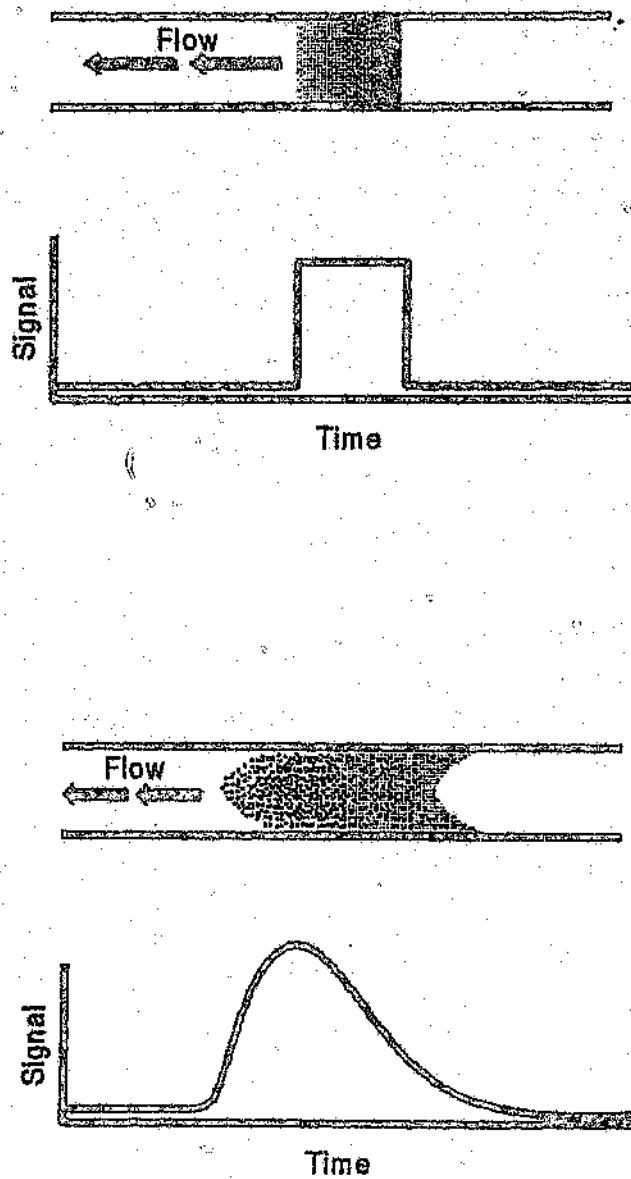


Fig. 3.4. Dispersion in a tube

(Režička and Hansen 1988)

3.3.2 High Dissolved-Solids Analysis: Application to the Determination of Trace Impurities in Tantalum Oxide

3.3.2.1 Introduction

In steady-state ICP-MS analysis, the generally accepted upper limit for dissolved solids in a sample solution is 0.2%. Higher levels result in blockages of the cone interface. Acid concentrations are usually restricted to 2%, since higher levels cause rapid deterioration of the cones. The result of this is that the analysis of solid materials inevitably involves large dilution factors, and therefore raised detection limits. This is particularly serious for samples that require dissolution by alkaline fusion. These samples are typically diluted 10 000 times before analysis, so that a detection limit of $1 \mu\text{g.l}^{-1}$ in solution equates to $10 \mu\text{g.g}^{-1}$ in the original material. In flow injection analysis, the volume of sample aspirated per analysis is typically an order of magnitude lower than the volume per steady state analysis, and therefore the sample matrix and acid concentration can be an order of magnitude higher without increasing the rate of cone blockage or wear. In this way lower detection limits can be achieved.

The use of laser ablation as a sample introduction method for tantalum oxide was described in Chapter 2. A solid sampling technique was used because quantitative dissolution of tantalum oxide is extremely difficult. However, due to the problems experienced with the laser ablation method, (i.e. memory effects and poor

precision) dissolution of the samples was investigated as an alternative. Dissolution of tantalum oxide can be achieved by fusion with a large excess of potassium pyrosulphate in a platinum crucible and dissolving the melt in a dilute hydrofluoric acid/hydrochloric acid mixture. Using steady-state analysis, a large dilution would be necessary because of the high flux-to-sample ratio and the presence of hydrofluoric acid. However, dilution must be kept to a minimum because of the required lower limits of determination. FIA was therefore utilised as a means of analysing more concentrated tantalum oxide samples.

3.3.2.2 Experimental

Using flow injection with 350 μ l sample volumes, it was found that it is possible to analyze solutions with 1.1% dissolved solid content, which is over five times the upper limit for steady-state analysis, without any blockage of the interface cones. Fig. 3.5 shows the FIA manifold that was used. Two sample loops were used, each 350 μ l in volume. The advantage of this is that injection of the one loop and loading of the other loop with the next sample occur simultaneously, which reduces the time required per injection.

A 0.1000g portion of tantalum oxide sample was fused with 1.00g potassium pyrosulphate (PAL Chemicals, A.R. Grade) in a platinum/gold crucible. The melt was leached in 50 ml of an aqueous mixture containing 7ml hydrochloric acid (Merck, Suprapur, 30% v/v) and 3ml hydrofluoric acid (Merck, Suprapur, 40%

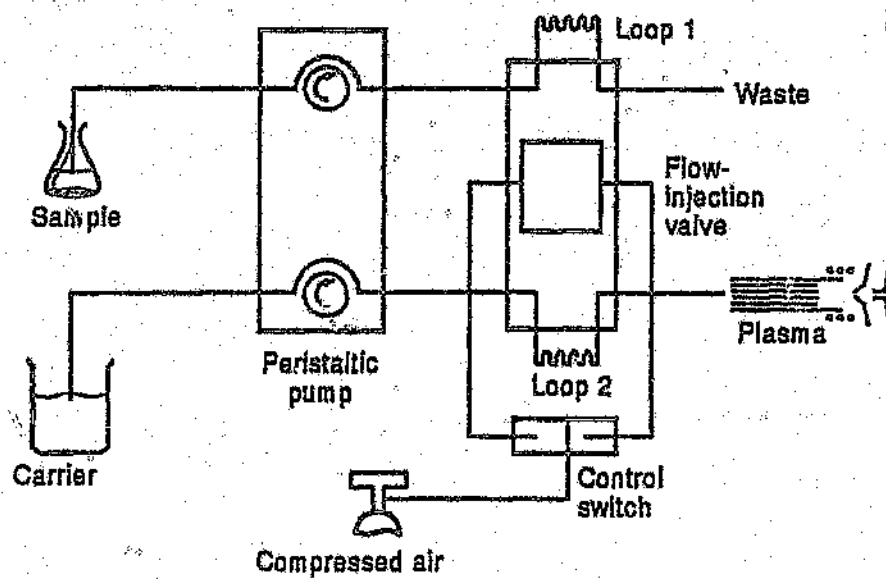


Fig. 3.5. FIA system for high solids analysis

v/v). Indium and rhenium were added as internal standards and the solution was made up to 100ml.

The samples were measured against matrix-matched standards with a calibration range of 0.5 to 50 $\mu\text{g.l}^{-1}$, corresponding to a range of 1.25 ppm to 125 ppm in the samples. The instrumental conditions that were used are shown in *Table 3.1*. The peak-jumping mode of data acquisition was used, because the analyte isotopes were spread over a wide mass range. The acquisition time was selected to give maximum sensitivity and precision for the selected loop size.

TABLE 3.1 Operating conditions for the determination of trace
impurities in tantalum oxide by FIA-ICP-MS

Loop size	350 μ l
Carrier-solution flowrate	0.7 ml/min
RF power	1.35 kW
Analysis mode	Peak jump
Detector	Pulse count
Mass-range sweeps	25
Injection delay	15 s
Acquisition time	20 s

3.3.2.3 Results and Discussion

The results of repeated analysis of a tantalum oxide sample are shown in *Table 3.2*. The concentrations are in $\mu\text{g.g}^{-1}$ in the solid sample. The limits of detection are based on three times the relative standard deviation of a reagent blank, taking the dilution factor into account. Detection limits were not established for conventional nebulisation were not determined due to the hydrofluoric acid content of the samples; however, the small dilution factor which is achievable with FIA

ensures superior detection limits in the solid sample. The relative standard deviations are all in the region of 5%. This level of precision is considerably better than that achieved for other techniques that have been used at Mintek to analyze tantalum oxide samples, including laser ablation ICP-MS and c.c. arc-emission spectrography. The accuracy of the method could not be verified due to the lack of reference materials. After a lengthy analysis procedure involving about 50 injections, the cones showed no sign of excessive build-up or wear. Therefore, it can be concluded that FIA is a useful tool for the analysis of solutions with a high dissolved-solids content by ICP-MS.

TABLE 3.2 Results obtained for impurities in tantalum oxide by FIA-ICP-MS

Element	Isotope	Concentration ($\mu\text{g}\cdot\text{g}^{-1}$)	RSD (%)	Limit of detection ($\mu\text{g}\cdot\text{g}^{-1}$)
Mg	24	1900	5.7	10
Mn	55	72	5.0	6
Nb	93	1600	3.3	0.7
Ag	107	31	2.2	2.8
Sn	120	21	2.6	6.8
W	184	17	4.1	1.4

3.3.3 On-Line Sample Manipulation

3.3.3.1 Introduction

As has already been described, flow injection can be used simply as a means of sample introduction for ICP-MS. As such, flow injection is able to increase sample throughput and increase the maximum allowable matrix levels in samples.

However, possibly the greatest capability of the technique is in the area of automation of sample preparation by on-line methods.

Sample preparation for ICP-MS analysis consists of a number of different operations. Solid samples must be dissolved, solutions must be diluted to suitable levels of matrix or analyte elements, internal standards are usually added to correct for instrument drift and matrix effects, and in some cases it is necessary to separate analyte elements from interfering elements or to preconcentrate analyte elements prior to analysis. Of these various aspects, sample dissolution is the most difficult to automate by incorporation into an on-line system. However, there is potential for the automation of all other aspects of sample preparation by using flow injection. Automation of sample preparation has two main advantages: it reduces manpower costs and improves the reliability of results by minimizing the possibility of analyst error.

3.3.3.2 On-Line Dilution and Internal Standard Addition

The simplest tasks to automate are dilution and internal standard addition. Automation can be achieved using the system shown in *Fig. 3.6*. The system uses a mixing tee which merges the sample with a stream containing diluent and internal standard. Mixing tees (Upchurch Scientific, Inc.) are designed to create turbulent flow in a very small dead volume at the point of merging, so that efficient mixing of the two streams is achieved. A limitation of this on-line

dilution system is that the dilution factor cannot be altered without changing the pump tubing.

An alternative system is shown in *Fig. 3.7*. In this manifold the sample and diluent streams are merged. The merged stream is then split and a part of the stream is pumped to the injection valve while the excess runs to waste. The diluted stream is merged with the internal standard stream before loading the sample loop. This system is able to achieve larger dilution factors (up to approximately 250 fold) without exceeding the flowrate specifications of the mixing tees. Another advantage of this system is that it is possible to select one of two different dilution factors without changing the pump tubing. Using this system, many samples which are received in solution form can be analyzed as received, with no sample preparation at all.

Platinum-group metal Analysis

The on-line dilution system was tested on a set of platinum-group metal (PGM) samples that had been analyzed in the conventional way. Samples included a solution prepared from a number of nickel sulphide collections on the certified reference material SARM 7 (Platinum Ore), which is used as a quality-control sample for routine steady-state analysis. The results obtained for SARM 7 are shown in *Table 3.3*. The agreement with the accepted values was good for all

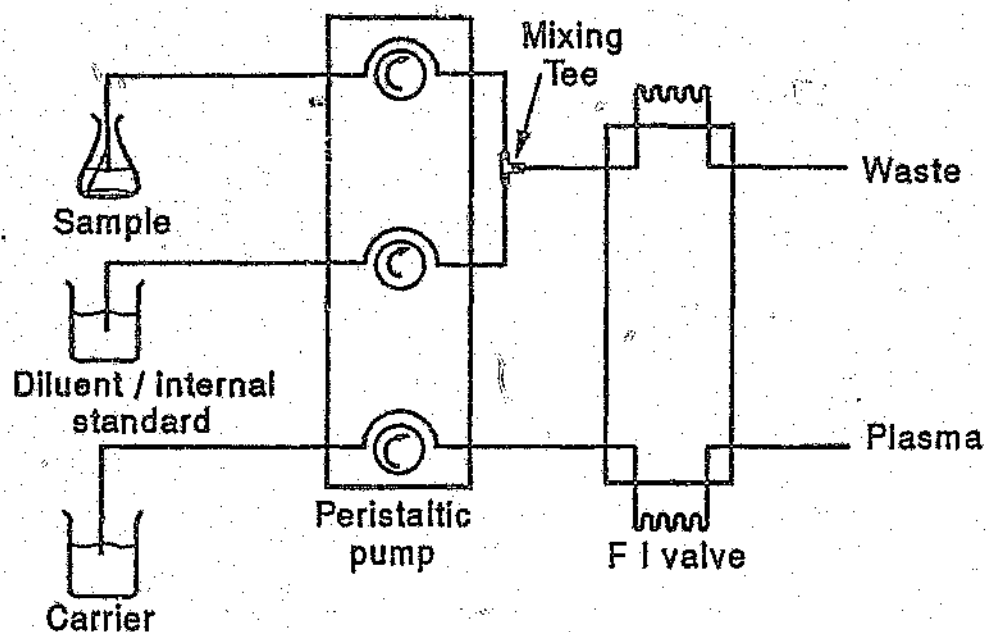


Fig. 3.6. On-line dilution manifold (1)

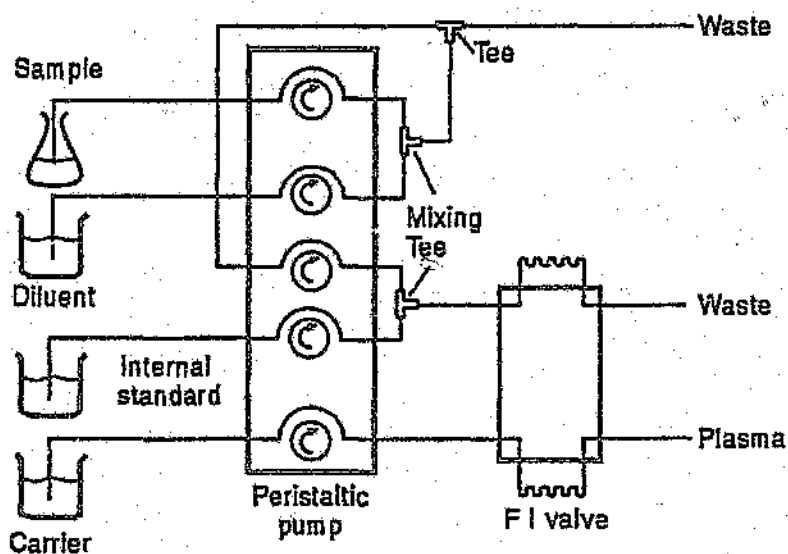


Fig. 3.7. On-line dilution manifold (2)

elements except palladium. The high value for palladium was due to a high blank resulting from an unrelated prior analysis, using conventional steady-state measurement, of solutions containing high levels of palladium. The precision of measurement was good, and good agreement with the results of the conventional analysis was obtained for the other samples.

Rare-earth element analysis

The system has also been used for rare-earth analysis. The results obtained for the analysis of an in-house quality-control sample containing the rare earths are shown in *Table 3.4*. The results are in good agreement with the accepted values, and good precision was achieved.

TABLE 3.3 Results of analysis of SARM 7 by FIA-ICP-MS using on-line dilution and internal standard addition

Element	Isotope	Concentration ($\mu\text{g.g}^{-1}$)	RSD (%)	Accepted value ($\mu\text{g.g}^{-1}$)
Pt	195	3.77	1.8	3.74
Pd	105	1.81	8.8	1.53
Ru	99	0.44	5.5	0.43
Rh	103	0.24	4.2	0.24
Ir	193	0.089	11.7	0.074
Au	197	0.33	4.6	0.31

TABLE 3.4 Results of analysis of rare-earth elements by FIA-ICP-MS using on-line dilution and internal standard addition

Element	Isotope	Concentration ($\mu\text{g}\cdot\text{g}^{-1}$)	RSD (%)	Accepted value ($\mu\text{g}\cdot\text{g}^{-1}$)
La	139	0.56	1.2	0.54
Ce	140	1.34	0.8	1.32
Sm	152	0.14	3.0	0.14
Pr	141	0.19	1.6	0.19
Y	89	0.11	1.8	0.11
Gd	157	0.10	3.4	0.10

3.4 Applications of FIA-ICP-AES

3.4.1 Introduction

The application of FIA to ICP-MS had shown that significant improvements in analysis time could be achieved due to the reduced volume of introduced sample. In ICP-MS, analyte concentrations may vary from 0.1 $\mu\text{g/l}$ to 1000 $\mu\text{g/l}$ in a single batch, which necessitates very long sample wash-out times, while in ICP-AES the range of concentrations is narrower and wash times are shorter. Consequently, the application of flow injection to ICP-AES was not found to reduce the analysis time per sample significantly. However, it was felt that in the area of on-line sample manipulation the use of the flow injection system would be advantageous.

Three sample types which are routinely analyzed using conventional steady-state measurement were selected for the investigation of on-line sample manipulation: ferro-chrome slags, acid-soluble copper/nickels, and base metal solutions containing low levels of precious metals. These methods were selected because they are all submitted for analysis on a regular basis, and each has scope for on-line sample manipulation prior to analysis. In all the following applications standard instrumental operating conditions were used, and measurements were made using the appropriate polychromator lines for the analyte elements².

3.4.2 Analysis of Ferro-Chromium Slags Using On-Line Internal Standard Addition

Ferro-chromium slags as well as other materials containing similar levels of iron, chromium and minor constituents are submitted for analysis on a regular basis.

The established sample preparation procedure for these materials is as follows:

0.200g sample is fused with 1.5g sodium peroxide and 0.7g sodium carbonate in a zirconium crucible. The melt is leached in 80 ml 1:1 nitric acid, 10ml of a 0.2 g/l scandium solution is added as an internal standard, and the solution is made up to a volume of 200ml. Only two or three millilitre of the sample solution is used in the analysis and the rest is discarded. This represents a considerable wastage of scandium, which is an expensive material. The large volume of the sample solution is due to three factors : the mass of solid sample needed to ensure representative sampling, the large flux:sample ratio required for quantitative dissolution, and the restriction on dissolved solid content which is imposed by the nebuliser system. Therefore, the volume of sample cannot be reduced. However, on-line addition of scandium solution would consume very much less scandium per analysis.

On-line internal standard addition was implemented by using the manifold as shown in *Fig. 3.6* (Section 3.3). To test the system, samples of the certified reference materials SARM 8 and SARM 9 (Chromium Ores) were prepared and analyzed repeatedly. Scandium is normally used as the internal standard for these

samples. However, to avoid the necessity of preparing standards without scandium, a molybdenum solution was used as the internal standard for the trial of the on-line system. The results are shown in *Table 3.5*. The precision of measurement was comparable to that of steady state measurement. However, the values obtained for the reference materials were two to six percent higher than the accepted values. This appears to indicate that molybdenum is not a suitable internal standard for this sample type.

and SARM 9 as references. However, for this trial new calibration standards and samples were prepared without the addition of scandium so that the scandium solution could be added on-line. The values obtained for the reference materials are shown in *Table 3.6*. The agreement with the certified values is good. To ascertain the precision of measurement using on-line scandium addition, a sample prepared from SARM 9 was measured twelve times. The relative standard deviation was 0.2% for both Fe and Cr. Therefore, good precision and accuracy can be achieved with the use of on-line internal standard addition.

TABLE 3.6 Analysis of SARM 8 and SARM 9 using steady-state measurement
with on-line internal standard addition

Sample	Element	Certified Value (%)	Measured Value (%)
SARM 8	Fe (as Fe_2O_3)	20.20	19.8
	Cr (as Cr_2O_3)	48.97	48.6
SARM9	Fe (as Fe_2O_3)	27.75	27.3
	Cr (as Cr_2O_3)	46.45	46.3

3.4.3 Analysis of Acid Soluble Copper-Nickels using On-Line Dilution

Flotation efficiencies in a sulphide flotation plant are monitored by measurement of the "acid-soluble" copper and nickel content of the floated concentrate and the residues. The samples are prepared by leaching with brominated hydrochloric acid.

which drives off the sulphur and dissolves the acid-soluble metal component of the sample. The copper and nickel content of the leachate are then measured. Since both concentrates and tailings are submitted for analysis, the concentrations of the analyte elements vary widely, and it is generally necessary to make serial dilutions to bring the analyte elements into the calibration range. This is time-consuming for the analyst and also wastes instrument time because the analyst has to leave the instrument to make the dilutions. It would therefore be useful to be able to dilute samples using an on-line system.

The dilution manifold which was used was the same as that shown in *Fig. 3.7* (Section 3.3). The degree of dilution of the sample can be altered by varying the sizes of the sample and diluent pump tubes (for example, a yellow/orange sample tube combined with a purple/orange diluent tube gives an effective 15x dilution factor). The accuracy of the dilution system was tested by analysing the in-house copper/nickel reference materials 1/91, 2/91 and 3/91 by flow injection, with and without dilution, and comparing the results with those of steady state analysis. The results are shown in *Table 3.7*. As can be seen, the agreement between the sets of results is good. However, the system has the disadvantage that the flow rates of the pump tubes must be calibrated regularly to eliminate errors which may result from changing flow rates due to tube wear. To overcome this problem it is necessary to monitor the flow rates continuously, and monitoring methods are to be investigated in the future.

TABLE 3.7 Acid soluble copper-nickel analysis using on-line dilution

Reference	Element	Accepted val. (%)	Flow Inj. (%)	On-Line Dil (%)
1/91	Cu	0.105 ± 0.06	0.103	0.103
	Ni	0.184 ± 0.08	0.171	0.172
2/91	Cu	2.37 ± 0.12	*	2.29
	Ni	2.56 ± 0.06	*	2.39
3/91	Cu	0.0149 ± 0.007	0.0150	0.0146
	Ni	0.0372 ± 0.028	0.0348	0.0350

* Samples were too concentrated to be measured undiluted

3.4.4 Analysis of Platinum-Group Metals in Base Metal Solutions Using On-Line Ion Chromatographic Separation

3.4.4.1 Introduction

The determination of low levels of the platinum-group metals (PGMs) in solutions containing high levels of base metals presents several interference problems in ICP-AES. The PGM analyte signals are altered, either due to background shift or to direct spectral overlap. It is therefore necessary to separate the PGMs from the base metals prior to analysis.

There is an existing off line separation method³² which involves passing the sample solution, made up in 0.1M HCl, through an ion exchange column containing a cation exchange resin (Dowex 50W-X8). The base metals which are present as cations load onto the column while the anionic chloro-complexes of the PGMs are eluted. The method is applicable to the determination of the non-volatile PGMs, i.e. platinum, palladium, iridium, rhodium and ruthenium. The separation is not suitable for gold and silver because gold recoveries are poor in the presence of high levels of base metals³³ and silver precipitates from the 0.1M HCl separation solution. The separation process is followed by repeated washing of the column to ensure quantitative elution of the PGMs, and then the collected eluent is boiled to reduce the volume prior to analysis. The procedure is time-consuming, and this investigation was undertaken to establish a more efficient on-line separation.

3.4.4.2 Apparatus

For an on-line ion exchange separation to be feasible, the separation column must be small, so that the flow rate through the column can be fast without excessive back-pressure. The column capacity will therefore also be small and sample volumes must be small to prevent saturation of the column. Flow injection is ideal for this purpose since small, reproducible slugs of sample can be injected through the column. A Dionex Ion Pac ASC-1 column was used. The column was packed with approximately 0.5g 200-400 mesh resin and positioned between the flow injection valve and the nebuliser.

3.4.4.3 Procedure

Reagents and materials

A pilot plant leach solution containing 50.7g/l Cu, 89.6g/l Ni and 1.1g/l Fe was obtained from the Hydrometallurgy Division at Mintek and used as a starting material. This solution was spiked with PGMs to test the efficiency of the base metal separation and PGM recovery. Measurements were made against pure PGM standards.

Sample preparation

The sample preparation procedure for the off-line separation was followed up to the separation step: to ensure that the PGMs were in the optimum oxidation state for separation, it was necessary to take an aliquot of the sample solution to dryness repeatedly with concentrated HCl. The residue was then redissolved in HCl and made up to ten times the original aliquot volume in 0.1M HCl prior to injection.

Measurement time

Time-resolved measurements were made to determine the optimum sample uptake and integration times. Fig. 3.8 shows a time-resolved signal for platinum when injected through the column. On the basis of this an uptake time of 25s and an integration time of 12s were selected.

Separation efficiency

The efficiency of the base metal removal from the sample stream was tested by injecting the concentrated leach solution through the column and measuring the base metal signals reaching the instrument. Fig. 3.9 shows the measured signals for Fe, Cu and Ni. It can be seen that only negligible amounts of the base metals are not retained on the column. To determine the number of injections possible

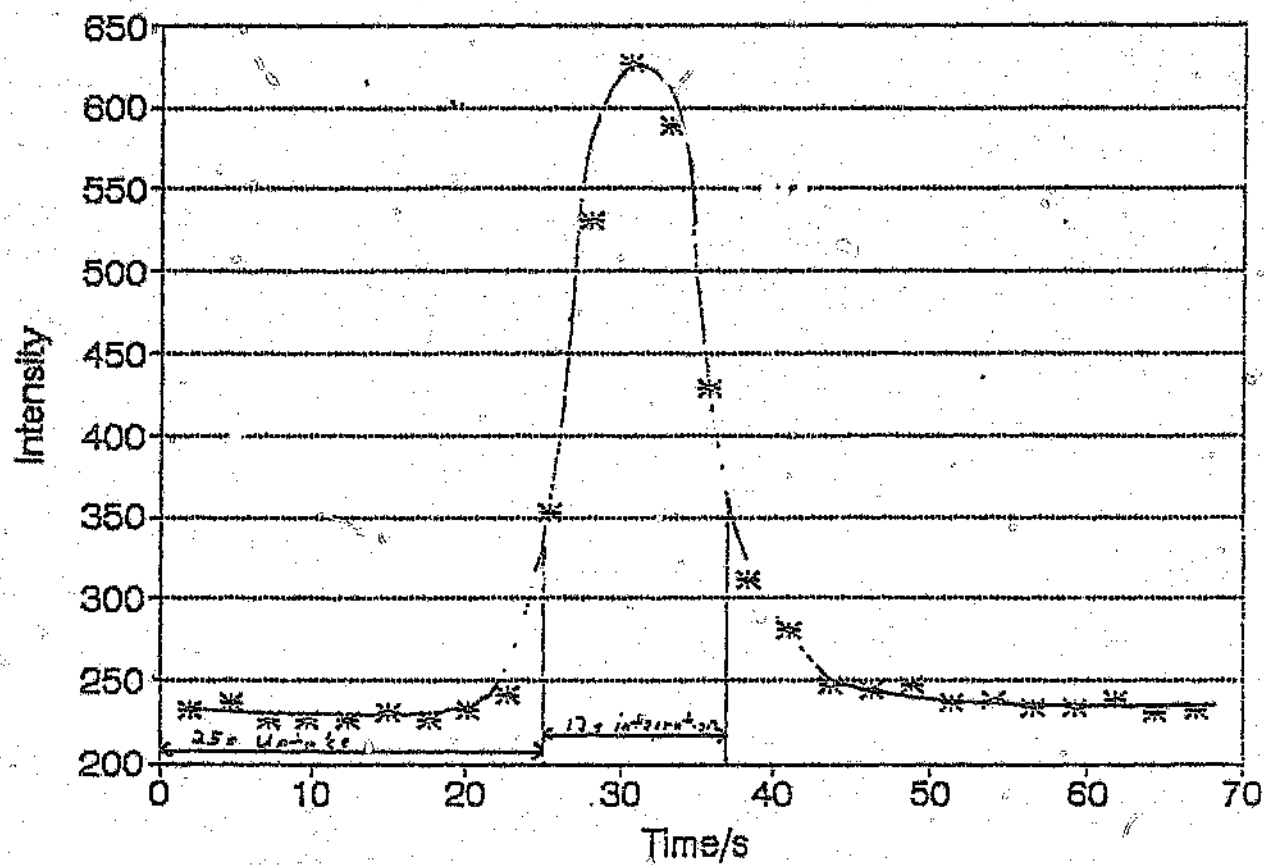


Fig. 3.8. Time-resolved signal for platinum

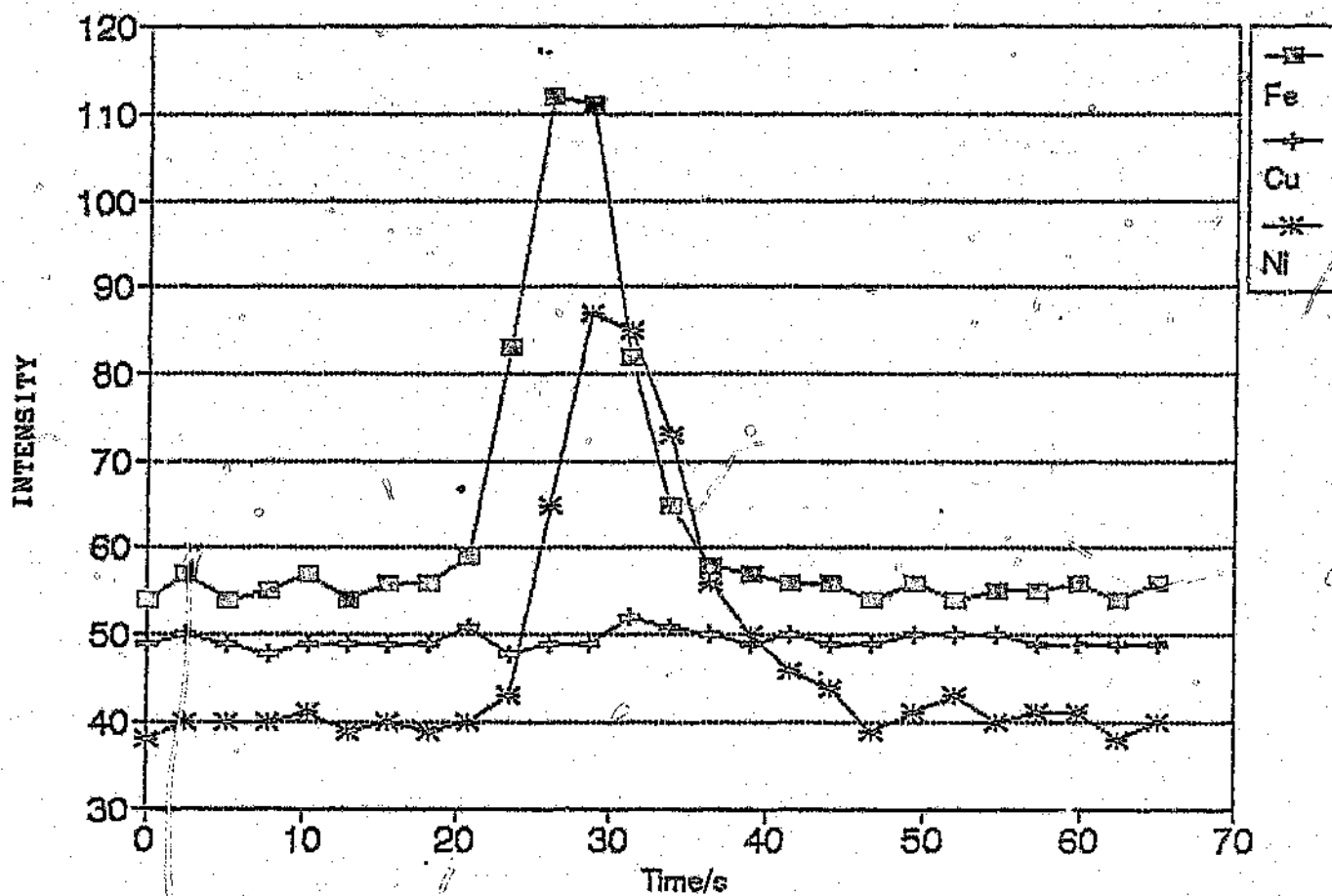


Fig. 3.9. Base metals passing through column

before the column becomes saturated, and also to investigate the effect of the base metals on the PGM background intensities, repeated injections of the leach solution were made while monitoring the apparent PGM signal intensities. The results are shown in *Fig. 3.10*. It can be seen that the column reached saturation on the tenth injection, and in future work the column was regenerated after a maximum of eight injections of base metal solution. Upon column saturation the background signals were lowered for all the PGM lines except iridium. The elevation of the iridium signal was due to the direct spectral overlap of the nickel line at 212.680nm on the iridium polychromator line at 212.681nm.

Internal standard

Selection of an internal standard was difficult, since it was necessary that the internal standard should not be retained on the column but should pass through with the analyte elements. A number of possible internal standard elements were tested, including scandium, indium, niobium and rhenium. Of these, only rhenium was found to pass quantitatively through the column, and rhenium was therefore selected as the internal standard. Since there was no polychromator line for rhenium on the instrument, the rhenium line at 221.427nm was located on the monochromator and used as the internal standard line.

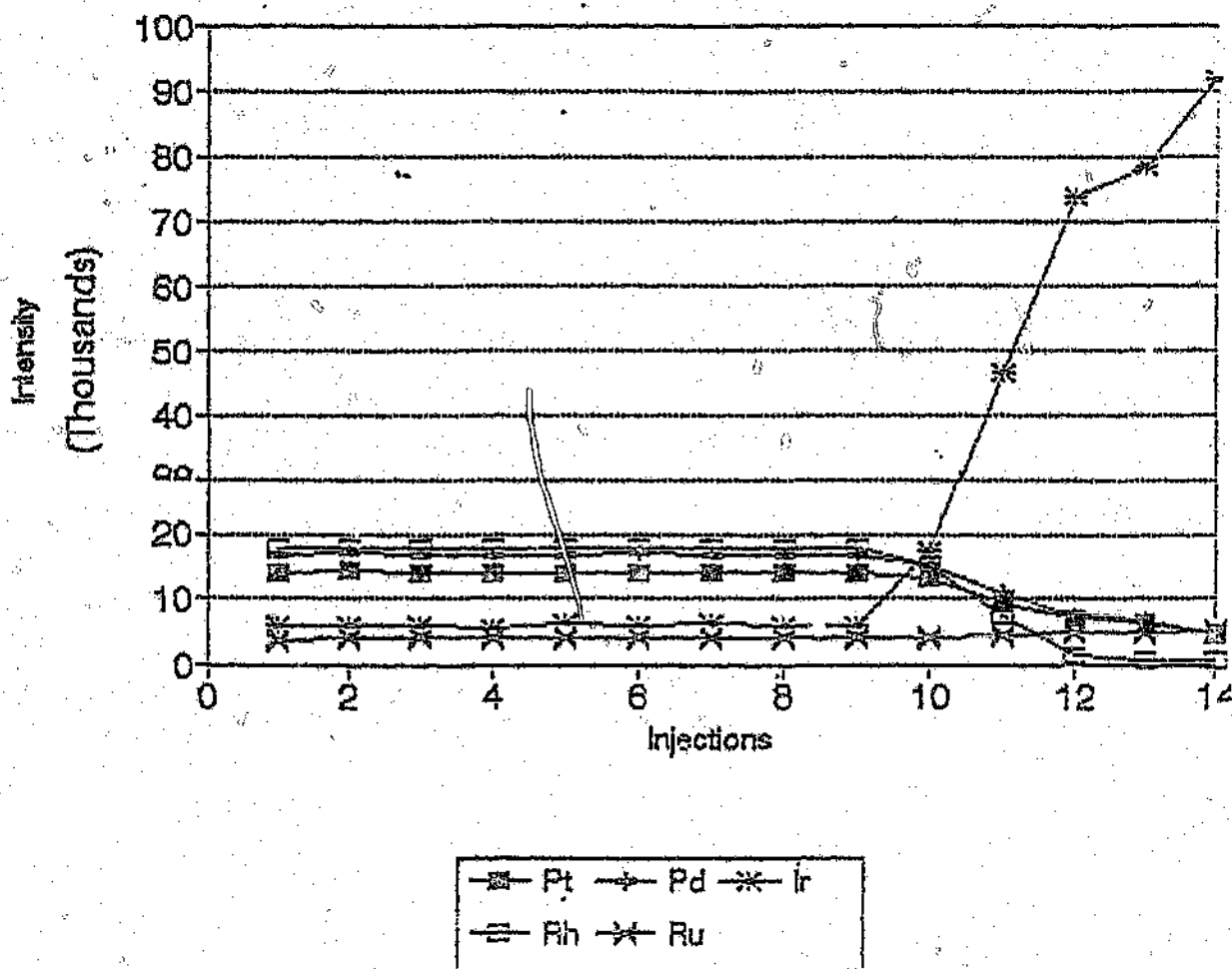


Fig. 3.10. Maximum injections to column saturation

Analyte recovery

To test whether the PGMs are recovered quantitatively from a solution containing high levels of base metals, the leach solution was spiked with a PGM solution. This sample was prepared and analyzed along with an unspiked sample and a sample containing only the PGMs. Per cent recoveries were calculated for each of the PGMs. The results are shown in *Table 3.8*. Recoveries were close to 100% for platinum, palladium, rhodium and ruthenium. The iridium recovery was slightly high, probably due to the relatively low signal intensity for iridium.

TABLE 3.8 Spike recoveries from leach solution

SAMPLE	Pt	Pd	Ir	Rh	Ru
Leach soln (mg/l)	2.9	4.4	0.8	2.6	3.7
Spike addn (mg/l)	44.5	22.3	19.8	22.2	27.4
Spike recovery (mg/l)	49.6	25.7	23.3	24.6	30.7
Per cent recovery	105	95.3	113	99.3	98.1

3.5 Discussion and conclusions

The flow injection system has been applied to ICP-AES and ICP-MS, and has been modified to perform a variety of on-line sample manipulation functions. An on-line dilution system has been tested and found to give good results, although the need for regular calibration of the pump tubing poses a problem for routine use. On-line internal standard addition has also been successfully implemented for flow injection and steady-state analysis.

The main advantages conferred by the FIA system when used in combination with ICP-MS are increased sample through-put and increased matrix tolerance. In combination with ICP-AES, the sample through-put was not greatly improved, due to the fact that sample wash-out times tend to be shorter. Increased matrix tolerance is potentially useful for ICP-AES, but no specific need for this feature was identified during the course of this work. The implementation of on-line internal standard addition enables a significant reduction in the use of expensive internal standard for ICP-AES. On-line column separation of the PGMs from base metals has been tested with good results, and this system can now be used for PGM analysis.

FIA is a versatile technique, as is apparent from the wide variety of the applications described in this work. The simplicity of the system is a useful feature, since it can easily be reconfigured as new applications arise. The

electronic control unit in the current system is rather primitive, and a more sophisticated microprocessor control unit would increase the usefulness of the system. A microprocessor unit is to be built in the future.

3.6 Publication details

The application of FIA to ICP-MS has formed the basis of a paper presented at the Third International Conference on Plasma Source Inductively Coupled Plasma Spectrometry held at Durham, U.K. on 13-18 September 1992³⁴. The paper was published in a book of conference proceedings³⁵. The application of FIA to ICP-AES was published as a Mintek Technical Memorandum³⁶.

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CHAPTER 4. APPLICATION OF HYDRIDE GENERATION TO THE DETERMINATION OF ARSENIC AND SELENIUM IN SOIL SAMPLES

4.1 Introduction and Theory^{1,2}

4.1.1 Introduction

Hydride generation is a term given to the formation of volatile covalent hydrides of a number of metals and metalloids found on the right hand side of the periodic table. The production of species of analyte elements which are gases at room temperature is advantageous in any atomic spectrometric technique which conventionally relies on solution nebulisation for sample introduction. The main advantage of gaseous sample introduction is that the sample introduction efficiency is excellent, unlike that of nebuliser-based systems. The limitations of conventional nebulisation were discussed in Chapter 1. This work describes the analysis of arsenic and selenium, both of which are amenable to hydride formation, by means of hydride generation. The technique was applied to the analysis of soils by both ICP-AES and ICP-MS.

4.1.2 Hydride generation chemistry

The hydride-forming elements which are of importance to atomic spectrometry are: germanium, arsenic, selenium, tin, antimony, tellurium, lead and bismuth. The hydrides of these elements are volatile at room temperature. The boiling points of the various hydrides are shown in *Table 4.1*.

Table 4.1 Boiling points of hydrides

Element	Hydride Name	Formula	B.P. (°C)
Ge	Germane	GeH ₄	-88.5
As	Arsine	AsH ₃	-62.5
Se		H ₂ Se	-41.3
Sn	Stannane	SnH ₄	-51.8
Sb	Stibine	SbH ₃	-18.4
Te		H ₂ Te	-2.3
Pb	Plumbane	PbH ₄	-13
Bi	Bismuthine	BiH ₃	-22

The formation of hydrides requires the generation of hydrogen radicals, which then reduce the cations of the hydride-forming element to form the hydride. An excess

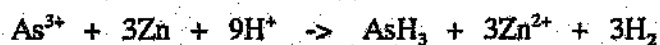
of hydrogen radicals is required, since diatomic hydrogen is a by-product of the hydride-forming reaction and there is a competing reaction in which hydrogen radicals combine with each other. A number of different reagent schemes have been used for hydride generation, including metal-acid combinations and sodium borohydride-acid.

Metal-acid reduction

The reaction of a metal with an acid was used in early work. The usual combination was zinc and hydrochloric acid, although other metals and acids have been used. In metal-acid systems the metal is added as a powder, a slurry or as grains to an acidic analyte solution, resulting in the evolution of the analyte hydrides as well as excess hydrogen. The generalised equation for the zinc-acid system is as follows:



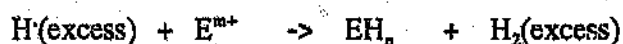
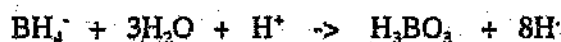
where E is the analyte element and m is not necessarily equal to n. The complete equations for the generation of arsine and the competing hydrogen-forming reaction are as follows:



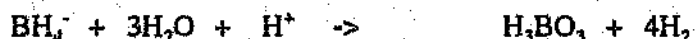
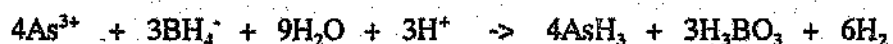
A disadvantage of metal-acid reactions is that the system is heterogeneous, and the rate of hydride formation is dependent on the metal surface area available for acid attack. Therefore, reaction times can be slow.

Sodium borohydride reduction

An alternative method for hydride generation is the sodium borohydride-acid reaction. Hydrochloric acid is most commonly used, but other acids can also be used. The generalised equation is as follows:



where E is the analyte element and m is not necessarily equal to n. The complete equations for the generation of arsine and the competing hydrogen-forming reaction are as follows:



Initially, sodium borohydride was used in a manner analogous to the metal-acid method, i.e. the borohydride was added in solid form. However, the addition of borohydride in solution form was found to give greatly increased efficiency of hydride generation, and this method is now in general use.

Sample pre-treatment

The efficiency of hydride generation is dependent on the oxidation state of the analyte element prior to reduction. Inefficient generation of the analyte hydrides results in lower sensitivity, and can also be a source of inaccuracy if samples and calibration standards contain different oxidation states of the analyte elements. It is therefore usually necessary to adjust the oxidation state of the analyte elements before the hydride generation step. Arsenic and selenium each have two common oxidation states. Arsenic occurs as As(III) and As(V), and selenium occurs as Se(IV) and Se(VI). For both elements the lower oxidation state is the optimum for hydride generation, and therefore pre-reduction is indicated. Potassium iodide is an established pre-reductant for As(V), but it has the disadvantage that it reduces Se(VI) to the elemental state, which prevents formation of the hydride. It is therefore not suited to simultaneous determination of arsenic and selenium. An

alternative is potassium bromide, which is a milder reductant. Addition of potassium bromide to an analyte solution, followed by gentle heating at 60°C for 20 minutes achieves reduction of both As(V) to As(III) and Se(VI) to Se(IV).

4.1.3 Hydride generation strategies

The hydrides may be generated by means of a batch process or a continuous process. In a batch process the reductant is added to the sample in a reaction vessel and the hydrides are allowed to form. The evolved hydrides are then purged from the vessel. In a continuous process, the sample, reductant and carrier gas flow continuously, so that the system reaches a steady-state condition. In each process the hydrides are to a large extent separated from the reagent solution. There are two main strategies for the treatment of the generated hydrides, i.e. collection and direct transfer.

In a collection system, the hydrides are collected in a trap, either by bubbling the carrier gas through a suitable reagent solution, or by passing the carrier through a U-tube immersed in liquid nitrogen, thus condensing the hydrides. If a solution trap method is used, the solution must be removed after collection and introduced to the detector by a solution technique. However, in a cold trap system, the hydrides can be transported directly to the detector by simply removing the U-tube from the liquid nitrogen. The hydrides are then liberated as the tube warms up. Collection systems require considerably more time per analysis than direct transfer

systems, but they have the advantage of preconcentrating the analytes, which results in low detection limits.

Direct-transfer systems rely on direct transport of the hydrides to the detector, without any collection step. Continuous-flow systems have the advantage of speed of analysis, but have higher limits of detection than collection systems as there is no preconcentration of the analytes. Batch systems can achieve a degree of preconcentration, since the hydrides are allowed to build up in the reaction vessel, but at a cost of increased time per analysis.

4.1.4 Advantages and disadvantages of hydride generation

The main advantage of hydride generation is the highly efficient introduction of the analyte elements to the detector, which enables low detection limits. The possibility of preconcentration allows even greater powers of detection. A further advantage is that the analytes are separated from potential interferents in the solution matrix.

There are two major disadvantages to hydride generation. Firstly, the acid and reductant concentration, as well as the oxidation state of the analyte are critical, and optimum conditions vary from element to element, which makes simultaneous multielemental analysis difficult. Secondly, species present in the matrix solution may interfere with the rate of hydride generation, and therefore it is sometimes

necessary to separate the analyte elements from the matrix prior to generation of the hydrides.

4.1.5 Applications of hydride generation in atomic spectrometry

Hydride generation was first applied to atomic absorption spectrometry by Holak in 1969, to determine arsenic using the zinc-hydrochloric acid method³. The technique has been very widely used in the field of atomic absorption spectrometry, and since the development of atomic fluorescence and plasma source atomic emission spectrometry, hydride generation has found applications to these techniques as well. These applications have been reviewed by Nakahara¹. Although ICP-MS is a relative newcomer to the field of atomic spectrometry, there have been several reports of applications of hydride generation to this technique. ICP-AES and ICP-MS have two main advantages over atomic absorption spectrometry for hydride generation: they have simultaneous multielemental analysis capability, and the high temperature of the plasma source eliminates interelement interferences which occur between analyte species during the atomisation step in atomic absorption analysis.

Applications to ICP-AES

The application of hydride generation to ICP-AES was first reported by Thompson *et al.*⁴ in 1978. This paper described a simple gas-liquid separator,

variations of which have since been widely used. This type of gas-liquid separator is used in many commercially available hydride generation systems. A second paper by Thompson *et al.* reported the suppression effect of metal ions on the hydride generation process, and described a separation method to remove the interfering species⁵. The large number of subsequent publications concerning the application of hydride generation to ICP-AES has been reviewed by Nakahara². The determination of arsenic and selenium in geological materials has been reported by several workers. Pahlavanpour *et al.* measured selenium in soils and sediments, using acid digestion and lanthanum hydroxide precipitation of interfering metals⁶. Liversage *et al.* determined arsenic in sediments using acid attack⁷. The simultaneous determination of arsenic and selenium has been reported in a variety of geological sample types, including soils,^{8,9} sediments⁹⁻¹¹ and rocks.^{10,12}

A variety of digestion methods were used, including various acid attack methods and alkaline fusion.

Applications to ICP-MS

The use of hydride generation as a sample introduction technique for ICP-MS was first reported in 1986 by Powell *et al.*, who used a commercially available hydride generation system. An alternative system has been described by Neitkemper and Caruso, in which the reaction mixture is nebulised without phase separation, which allows simultaneous determination of both hydride forming and non-hydride

forming elements¹⁴. Another system, described by Vijayalakshmi *et al.* employs a modified nebuliser to convert a conventional spray chamber into a gas-liquid separator¹⁵. Völlkopf *et al.* used a flow injection-hydride generation system for ICP-MS¹⁶. Hydride generation has been combined with ICP-MS to determine arsenic,¹⁷⁻²⁰ selenium,^{20,21} antimony,^{19,20} germanium,²² bismuth,²³ and lead.⁷

4.2 Aim of the investigation

The Geological Sciences Department at the University of Cape Town is currently undertaking a study of the distribution of biologically important elements in soils of the Western Cape region of South Africa. The main objective of the study is to obtain a better understanding of the distribution of these elements and interactions between the soil, rock and ground water. Further objectives are the establishment of natural background values for identification of pollution, and the production of a data base for use in other fields of study²⁵.

The study required determination of both total and leachable concentrations of the biologically important elements in soil samples, to establish the degree to which these elements are accessible to ground water and hence to plants and animals. The selected leaching method was agitation of the sample with a 1M ammonium nitrate solution. This method has been published and distributed as the preliminary norm DIN V 19730 in Germany²⁶. It is likely to be established by legislation in

Germany and has been proposed for international recognition. Maximum permissible levels of certain elements have been published²⁷.

Analysis of forty elements was required. Many of the elements were determined by X-ray fluorescence spectrometry, but for certain elements lower detection limits were required and Mintek was requested to determine these elements by ICP-MS. Two of the elements for which ICP-MS analysis was required were arsenic and selenium.

Direct determination of arsenic and selenium by ICP-MS is subject to severe interferences by background ions which degrade detection limits. The single ⁷⁵As isotope has an interference from ⁴⁰Ar³⁵Cl, and each of the various Se isotopes has interferences arising from atmospheric and plasma gases and from the sample matrix. The ⁷⁷Se isotope is relatively free of background gas interferences, the only possibility being ³⁶Ar⁴⁰Ar¹H, but if chloride is present in the sample matrix there is an interference from ⁴⁰Ar³⁷Cl.

The problem of chloride interference can be reduced by elimination of chloride from the sample preparation procedure, but varying levels of chloride in the samples themselves remains a problem. The introduction of a small amount of nitrogen into the plasma has been shown by Branch *et al* to reduce ArCl formation²⁸, and this technique has been successfully used at Mintek. However,

nitrogen addition was found to reduce analyte sensitivity which made the technique unsuitable for analysis at the required levels.

The aim of this investigation was to determine arsenic and selenium in soil samples by ICP-MS, using hydride generation to eliminate chloride interferences while maintaining sufficient analyte sensitivity. A secondary objective was to apply the hydride generation system ICP-AES so that the analytical performance and results of the two techniques could be compared.

4.3 Application to ICP-MS

4.3.1 Apparatus

A continuous hydride generation system was used, since this type of system is easily implemented and enables rapid analysis. In initial studies, a reaction and separation chamber of the type described by Thompson *et al.*⁴ was used. A diagram of the system is shown in *Fig. 4.1*. However, visible sodium emission from the plasma indicated that the gas-liquid separation with this system was inefficient, and that solution droplets were being entrained in the gas stream and transported to the plasma. The implication of this was that chloride interferences would not be totally removed, and that suppression of analyte signals could occur due to the presence of the sodium. To overcome this problem, a novel reaction and separation system was designed. A diagram of the system is shown in *Fig. 4.2*.

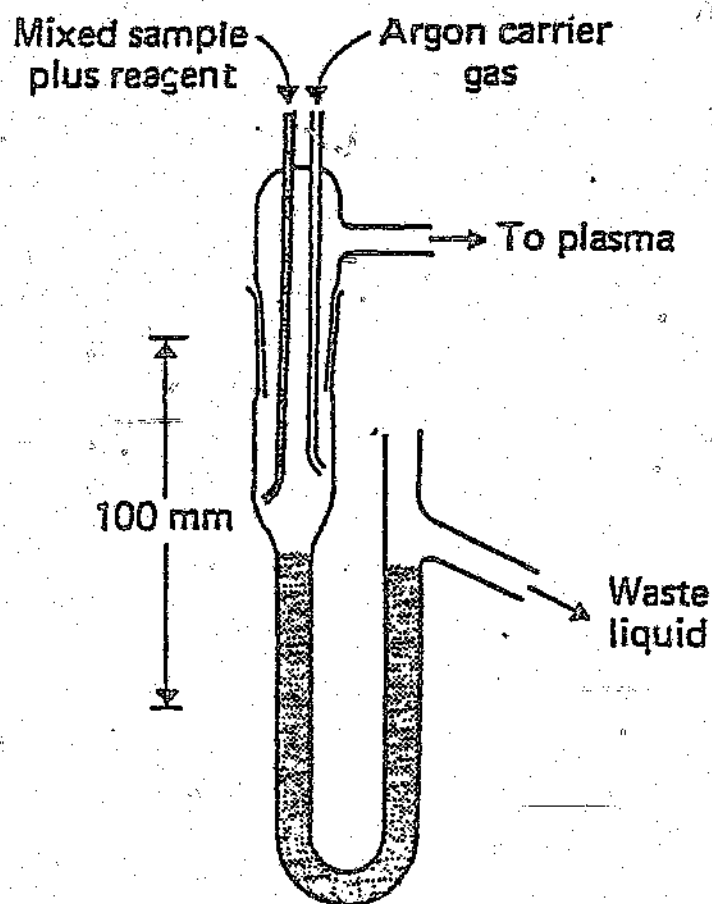


Fig. 4.1. The Thompson-type hydride generation system¹

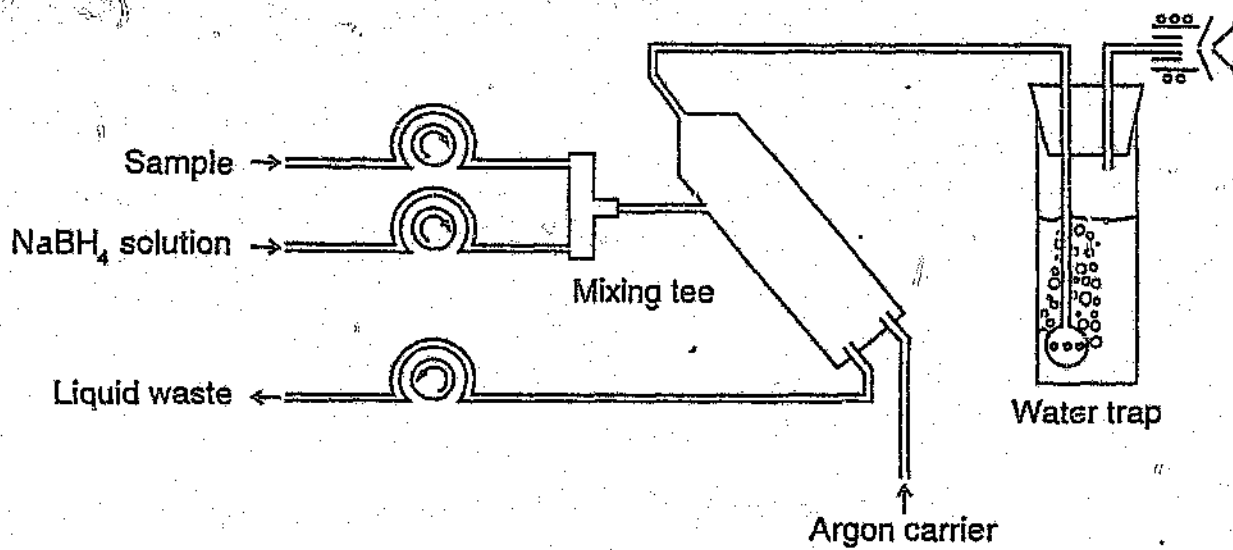


Fig. 4.2. The hydride generation system used in this work

The system consists of three components. The first is a four channel peristaltic pump (Gilson Minipuls 3) which delivers the sample and reagent streams to a mixing tee (Upchurch U 466), where the streams are efficiently mixed. The second is a reaction chamber which was constructed from a 50ml plastic syringe. The chamber is positioned at an angle to allow the reaction to take place while the mixture of sample and reagent runs down the side of the chamber before being pumped to waste by the peristaltic pump. A stream of argon carries the evolved hydrides to the third component, which is a water trap through which the argon stream is bubbled. The water trap removes entrained droplets from the argon stream, thus eliminating sodium chloride. The trap also removes hydrogen chloride vapour from the argon stream while allowing the covalent hydrides to pass through to the plasma. The effectiveness of the trap was tested by comparing the ICP-MS ArCl^+ background signals obtained from a sample matrix of 4M hydrochloric acid with that of 4M nitric acid. No difference in the background signals was observed, which indicated that the chloride interference was effectively removed. There was also no visible sodium emission from the plasma when the trap was used. The use of a water trap therefore ensures very efficient separation of the analyte hydrides from the interfering species.

4.3.2 Reagents

Sodium tetrahydroborate solution. A 10g.l^{-1} solution was prepared by dissolving 1.00 g sodium hydroxide (Associated Chemical Enterprises, A.R. Grade) in 100 ml deionised water, adding 2.50g sodium tetrahydroborate (Merck, A.R. Grade) and dissolving. The solution was filtered through Whatman No. 542 paper and the filtrate was diluted to 250 ml. This was freshly prepared on the day of use.

Potassium bromide solution 1M. (Saarchem, A.R. Grade)

Ammonium nitrate solution 1M. (Merck, A.R. Grade)

Hydrochloric acid 30% (Merck, Suprapur Grade).

Sodium peroxide granular (Chemworld, A.R. Grade).

Arsenic stock solution 5 g.l^{-1} prepared by dissolving 0.660g arsenic trioxide (As_2O_3 , Merck, A.R. Grade) in 3 ml 20% sodium hydroxide solution, acidifying with nitric acid and diluting to 100 ml.

Selenium stock solution 1 g.l^{-1} . Prepared by dissolving 0.100g selenium metal (Poly Metals, 99.999% pure) in 10 ml aqua regia and diluting to 100 ml.

4.3.3 Sample preparation

Two methods of sample preparation were used. For the determination of total concentrations the samples were dissolved by alkaline fusion and the arsenic and selenium were separated using the method described by Rob  rt²⁹. For the

determination of leachable elements the samples were prepared by the standard leaching method²⁶.

Total dissolution

A 0.200 g portion of sample was fused with 2.00 g sodium peroxide in a zirconium crucible and leached in 50 ml deionised water. The leachate was filtered through Whatman No. 542 filter paper to separate the analyte elements from the insoluble transition metal hydroxides²⁹ which could otherwise interfere with the hydride generation process⁵. The filtrate was acidified with 40 ml hydrochloric acid. Two ml of 1M potassium bromide solution was added and the solution was heated on a steam bath for 20 mins. The purpose of this step was to reduce any As(V) to As(III) and Se(VI) to Se(IV).

Leachable elements

A 20.00 g portion of the sample was weighed into a 100 ml polyethylene bottle. A 50 ml aliquot of 1 M ammonium nitrate solution was added and the sample was agitated for two hours and then centrifuged at 2500 r.p.m. for 15 minutes. The supernatant was filtered through Whatman No. 542 filter paper. It was not necessary to separate the analyte elements from the transition metals as the concentrations of the transition metals were too low to pose an interference.

problem. A 25 ml aliquot was transferred to a polyethylene bottle and acidified with 20 ml hydrochloric acid. One ml of 1M potassium bromide solution was added and the solution was heated on a steam bath for 20 minutes, as was done for the fusion samples. The sample was cooled and diluted to 50 ml.

Calibration standards

A suite of standards was prepared by diluting the stock solutions to the required concentrations, reducing with potassium bromide as was done for the samples, and diluting in 4M HCl.

4.3.4 System optimisation

The operating conditions are shown in *Table 4.2*. Standard instrumental operating conditions were used with the exception of the carrier gas flow rate which was optimised to give maximum sensitivity. A plot of signal strength vs carrier gas flow rate is shown in *Fig. 4.3*. On the basis of this plot the carrier flow rate was set at 1.0 l.min^{-1} . The ion lenses were tuned using a $10 \mu\text{g.l}^{-1}$ antimony solution, since antimony is also a hydride-forming element, and unlike arsenic or selenium is free of background interferences. The ^{121}Sb isotope was used for tuning.

The delivery rates of sample and reductant were optimised by varying the pump tube sizes. A limitation is placed on the reductant flow rate by the generation of

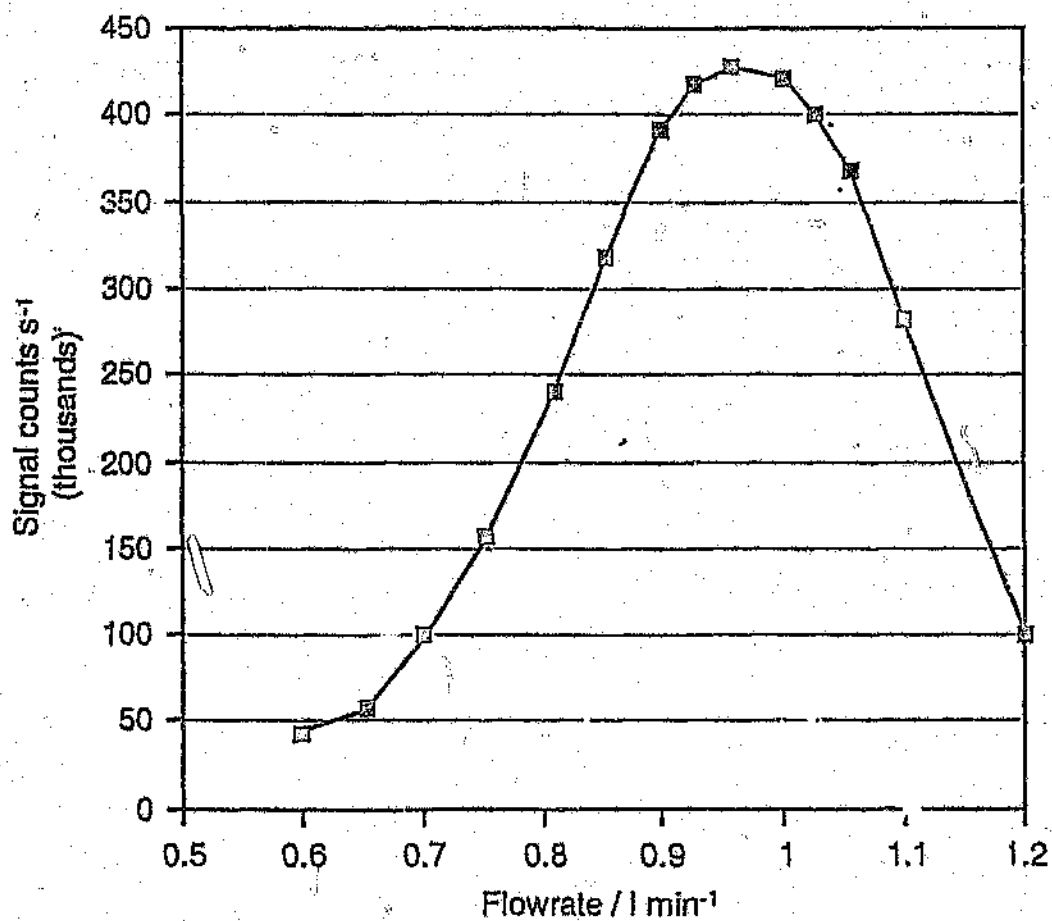


Fig. 4.3. Signal strength vs carrier gas flowrate for ICP-MS

excess hydrogen, which causes the plasma to become unstable and eventually extinguishes it. The reductant flow rate was therefore set at 1.18 ml.min^{-1} and signal to background ratios were measured at different sample flow rates. A plot of the results is shown in *Fig.4.4*. On the basis of these measurements a sample flow rate of 4.39 ml.min^{-1} was selected, which gave good sensitivity for both As and Se. However, it was discovered that at analyte concentrations above $100 \mu\text{g.l}^{-1}$ the analyte signals took several minutes to reach steady state, presumably due to insufficient reductant being present. The sample flow rate was therefore reduced to 2.38 ml.min^{-1} , at which rate the analyte signals were found to reach steady state within 40 seconds of aspiration.

Table 4.2. Operating conditions

Forward power	1.35 kW
Reflected power	14 W
Carrier gas flow rate	1.00 l.min ⁻¹
Auxiliary gas flow rate	0.70 l.min ⁻¹
Coolant gas flow rate	16.0 l.min ⁻¹
Sample flow rate	2.38 ml.min ⁻¹
Reductant flow rate	1.18 ml.min ⁻¹
Data acquisition mode	Scanning
Detector mode	Pulse counting
Mass range	73.92 to 78.59 u
No. of channels	1024
No. of scan sweeps	100
Dwell time	320 μ s
Sample uptake time	40 s
Data acquisition time	33 s

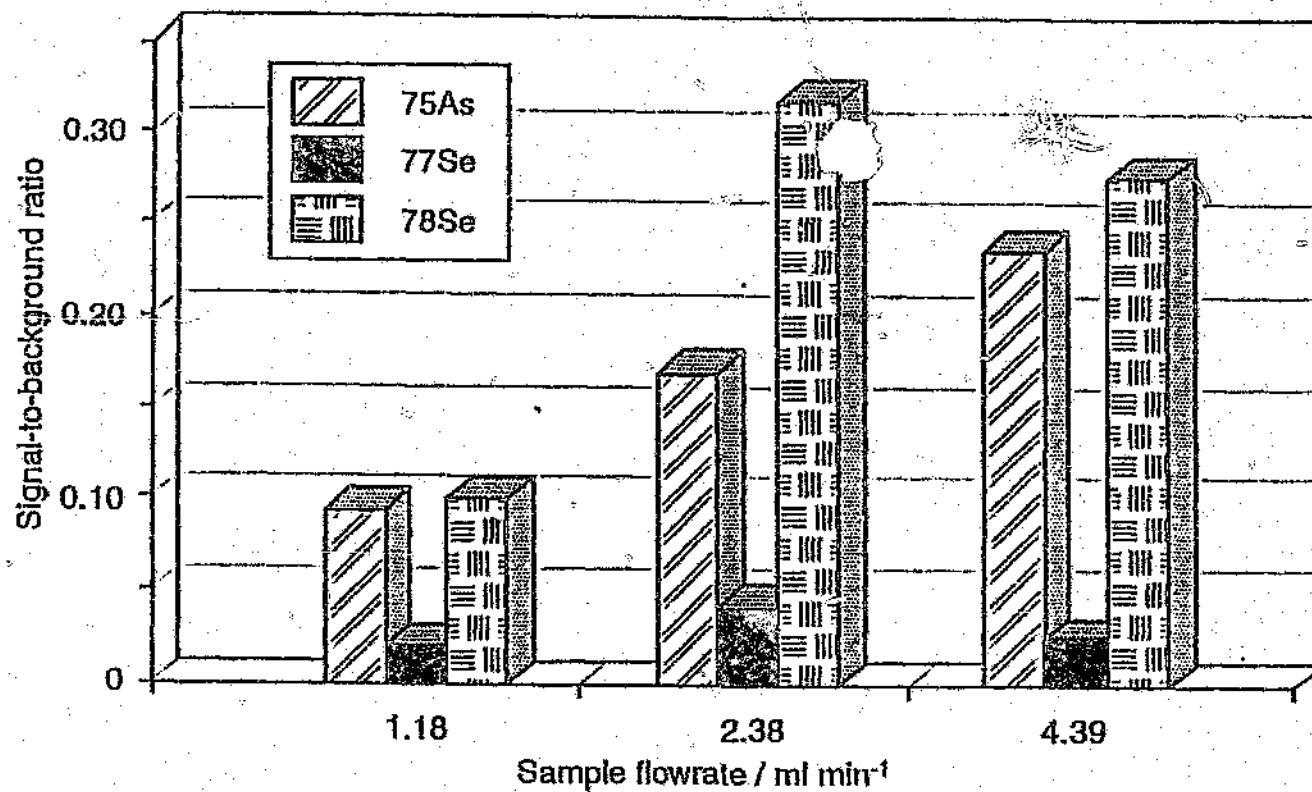


Fig. 4.4. Signal-to-background ratios vs sample flowrate

4.3.5 Results and discussion

Signal-to-background ratio (SBR), sensitivity and detection limits

To determine the most suitable isotope for selenium analysis, SBRs were measured for all the selenium isotopes (with the exception of ^{80}Se , which is the most abundant but has an exceptionally severe interference from $^{40}\text{Ar}_2$). It was expected that ^{77}Se (abundance = 7.5 %) would have the highest SBR due to the removal of the $^{40}\text{Ar}^{37}\text{Cl}$ interference. However, in practice it was found that the more abundant ^{78}Se isotope (abundance = 23.61 %) gave the best SBR despite an interference from $^{38}\text{Ar}^{40}\text{Ar}$. The inferior SBR of ^{77}Se was attributed to an interference from $^{36}\text{Ar}^{40}\text{Ar}^1\text{H}$, made more severe by the introduction of hydrogen into the plasma. Consequently, the ^{78}Se isotope was selected as the isotope for analysis.

The hydride generation system was found to give a forty fold improvement in sensitivity over conventional nebulisation for arsenic (46 000 vs 1100 counts.s⁻¹.(μg.l⁻¹)⁻¹). However, the sensitivity of the system did not produce correspondingly low detection limits, due to reagent blanks which were high despite the use of the highest purity available reagents. The background equivalent concentrations (BECs) of arsenic and selenium in the acid and reductant mixture were approximately 1 μg.l⁻¹, and the BECs of the fusion and leachate blanks were between 1.5 and 2 μg.l⁻¹. There were contributions to the blank from all of the

reagents used as well as the zirconium crucibles used for the fusions. The limitation imposed on detection limits by reagent blanks has been experienced by other workers.^{23,14,17,15} There is a great need for higher-purity reagents for sample preparation and for the hydride generation process, since the exceptional sensitivity of the technique is nullified to an extent by the reagent blank levels. Limits of detection (3s) were measured for a 4M hydrochloric acid blank solution, a blank prepared following the fusion procedure and a blank prepared following the ammonium nitrate leach procedure. These values were multiplied by the relevant dilution factors to give detection limits in the original sample (for the fusion procedure) and in the leachate solution. The results are listed in Table 4.3. It can be seen that the detection limits were generally in the range of 0.2 to 1.0 $\mu\text{g.l}^{-1}$ in the solutions analyzed. The detection limit of 1.0 $\mu\text{g.l}^{-1}$ for arsenic in the leach solutions was well below the recommended maximum arsenic concentration of 20 $\mu\text{g.l}^{-1}$, quoted in the leaching method². No recommended maximum concentration is given for selenium. Arsenic and selenium were present at measurable levels in the soil samples which were prepared by total dissolution, but in the leachates the levels were generally below the detection limits. An exception was a sample particularly high in arsenic (570 $\mu\text{g.g}^{-1}$) which gave a level of 22 $\mu\text{g.l}^{-1}$ in the leachate, slightly above the recommended maximum level. The leachable arsenic component was therefore only 0.01% of the total arsenic content of the sample.

Table 4.3. Limits of detection

	HCl blank	Fusion		NH ₄ NO ₃ Leach	
	$\mu\text{g.l}^{-1}$	Fusion blank	In sample	Leach	In
		$\mu\text{g.l}^{-1}$	$\mu\text{g.g}^{-1}$	blank	leachate
				$\mu\text{g.l}^{-1}$	$\mu\text{g.l}^{-1}$
⁷⁵ As	0.16	0.22	0.11	0.50	1.0
⁷⁸ Se	0.18	0.81	0.40	1.0	2.0

Calibration curves and precision of measurement

Good calibration curves were obtained for arsenic and selenium. The curves were linear between 2 and 200 $\mu\text{g.l}^{-1}$, although when the most sensitive interface cones were used, loss of linearity was observed above 100 $\mu\text{g.l}^{-1}$ due to excessively high count rates. Detuning the ion lenses would enable a greater dynamic range but excessive wash-out time becomes a limiting factor for measurement at higher concentration levels. The precision of measurement at the 10 $\mu\text{g.l}^{-1}$ level was 2.7% for arsenic and 3.7% for selenium.

Reference materials

Three certified reference materials with suitable values for arsenic and/or selenium were prepared by the fusion procedure and analyzed using the selected operating conditions. The selected reference materials were a soil (United States Geological Survey GXR-5), a marine sediment (National Research Council Canada MESS-1) and a coal fly ash (United States National Bureau of Standards 1633a). The coal fly ash was selected because it has a higher certified value for selenium ($10.3 \mu\text{g.g}^{-1}$) than any of the available geological reference materials. The results of the analyses are shown in Table 4.4. It can be seen that good agreement with the certified values was obtained.

Table 4.4. Analysis of reference materials by ICP-MS. Concentrations are in $\mu\text{g.g}^{-1}$

Reference	Arsenic		Selenium	
	Certified	Found	Certified	Found
GXR-5	11.2 ± 1.7	9.9 ± 0.3	1.12 ± 0.05	1.2 ± 0.1
MESS-1	10.6 ± 1.2	10.9 ± 0.1	0.4*	< 0.4
NBS 1633a	145 ± 15	132 ± 12	10.3 ± 0.6	10.6 ± 0.3

* Tentative value

4.4 Application to ICP-AES

4.4.1 Introduction

The hydride generation system which was used for the ICP-MS work was transferred without modification to the ICP-AES instrument, with the exception of the pump tubing sizes, which were optimised for ICP-AES. The same reagents and sample preparation procedures were used for both applications.

4.4.2 Instrumental parameters

To simplify the changeover between hydride generation and normal nebulisation, standard instrumental operating conditions were used,³⁰ with the exception of the carrier gas flow rate which was adjusted to obtain maximum sensitivity. The forward power was 1.2 kW. The analyte lines used were: arsenic - 197.20nm and selenium - 196.03nm. These lines were preset on the vacuum polychromator.

4.4.3 System optimisation

It had been found in the ICP-MS study that sensitivity was proportional to the sample and reagent flowrates, with the limiting factor being the ability of the plasma to tolerate the volume of excess hydrogen. When the hydride generation system was tested on the ICP-AES instrument, it was found that the plasma was

less sensitive to changes in the carrier gas composition than the ICP-MS plasma, possibly due to the absence of the cone interface. As a result, it was possible to use higher reactant flowrates than were possible in ICP-MS. A reductant flowrate of $2.96 \text{ ml} \cdot \text{min}^{-1}$ and a sample flowrate of $3.64 \text{ ml} \cdot \text{min}^{-1}$ was found to give the best sensitivity while still maintaining a reasonably stable plasma. The carrier gas flowrate was adjusted to give optimum sensitivity at the selected reagent and sample flowrates. A graph of signal vs flowrate is shown in *Fig. 4.5*. On the basis of this graph, the carrier gas flowrate was set at $0.75 \text{ l} \cdot \text{min}^{-1}$.

4.4.4 Results and discussion

Signal-to-background ratio (SBR) and detection limits

As expected, the hydride generation system conferred greatly increased sensitivity relative to conventional nebulisation. The SBRs and detection limits obtained by conventional nebulisation and hydride generation are compared in *Table 4.5*. The SBRs and detection limits obtained using the hydride generation system are approximately sixty times better than those of solution nebulisation, and compare favourably with those quoted by Thompson *et al.*⁴

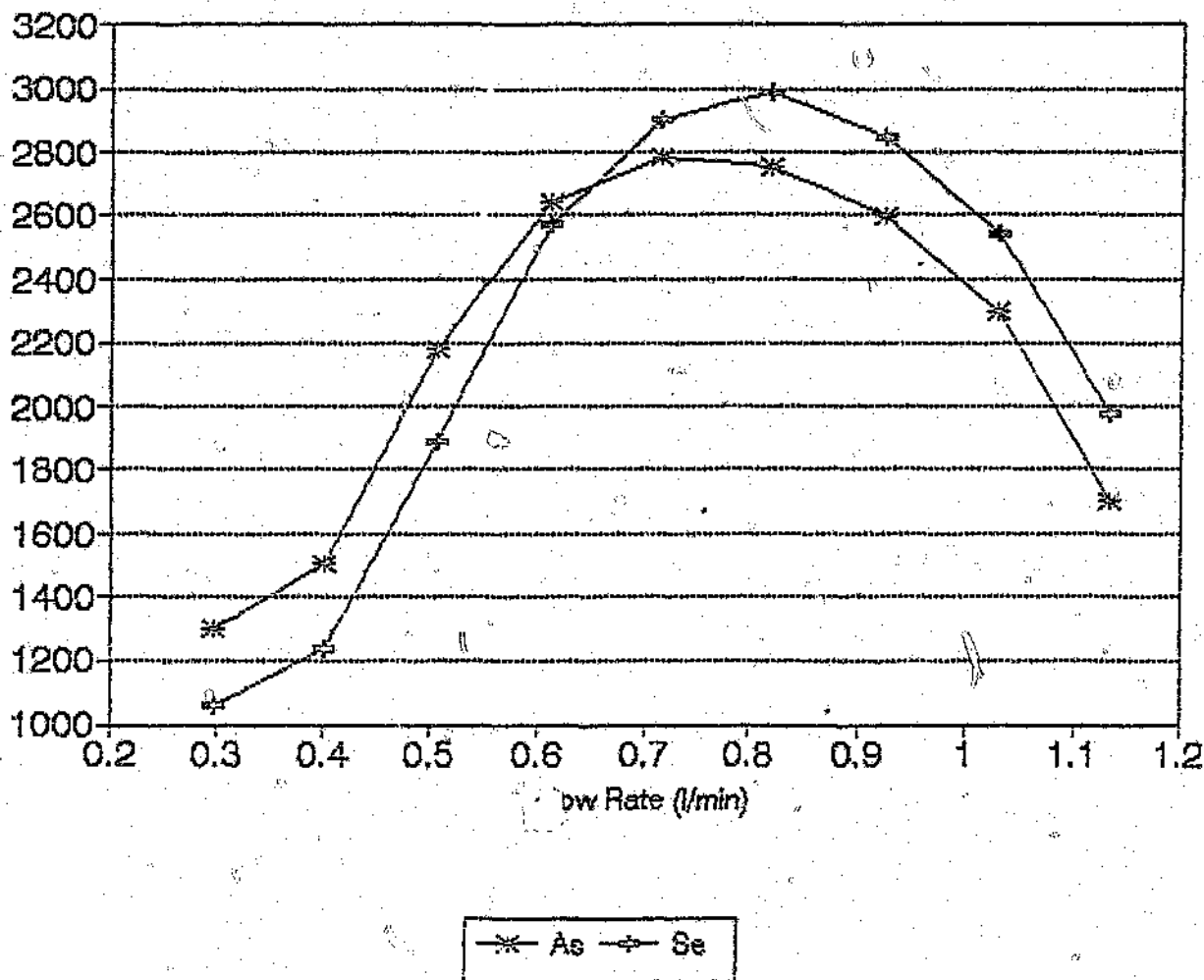


Fig. 4.5. Signal strength vs carrier gas flowrate for ICP-AES

Table 4.5. Comparison of SBRs and detection limits for hydride generation- and conventional nebulisation-ICP-AES

	Hydride generation		Nebulisation	
	Arsenic	Selenium	Arsenic	Selenium
SBR	81	87	1.4	1.3
Detection limit($\mu\text{g/l}$)	0.35	0.33	21.5	16.3
Quoted detection limits($\mu\text{g/l}$) ^a	0.8	0.8		

Calibration curves and precision of measurement

The linearity of the calibration curves was established up to $1000\mu\text{g.l}^{-1}$. The limiting factor at higher concentrations was the excessive time required for the analyte signal to return to the baseline. The precision of measurement at analyte concentrations of $40\mu\text{g.l}^{-1}$ was 1.0% for arsenic and 2.9% for selenium.

Reference materials

The same three certified reference materials that were analyzed in the ICP-MS studies were prepared by the fusion procedure and measured repeatedly by hydride generation-ICP-AES. The results of the analyses are shown in *Table 4.6*. As^a was the case with ICP-MS, good agreement with the certified values was obtained.

Table 4.6. Analysis of reference materials by ICP-AES. Concentrations are in $\mu\text{g.g}^{-1}$

Reference	Arsenic		Selenium	
	Certified	Found	Certified	Found
GXR-5	11.2 ± 1.7	11.9 ± 0.3	1.12 ± 0.05	1.08 ± 0.1
MESS-1	10.6 ± 1.2	10.9 ± 0.1	0.4 ^a	0.7 ± 0.1
NBS 1633a	145 ± 15	153 ± 2	10.3 ± 0.6	10.1 ± 0.1

^a Tentative value

4.5 Conclusions

A continuous hydride generation system has been assembled and has been employed as a sample introduction system for both ICP-MS and ICP-AES. The system has been successfully applied to the determination of total and leachable arsenic and selenium in soils. The system enables accurate and precise measurement of the analyte element at the $\mu\text{g.l}^{-1}$ level, which was confirmed by the good agreement with certified values that was obtained for the reference materials. The use of a water trap eliminates argon chloride interferences which pose a problem for ICP-MS, and removes sodium which suppresses analyte signals in both ICP-MS and ICP-AES. The water trap was also found to have a damping effect on pressure fluctuations in the carrier gas stream, thus stabilising the analyte signals.

The increase in sensitivity achieved by the use of hydride generation was greater for ICP-AES than ICP-MS (sixty times compared to forty times that of pneumatic nebulisation). The reason for this was the higher hydrogen tolerance of the ICP-AES plasma, which enabled higher sample and reagent flowrates than were possible with the ICP-MS system. Despite the fact that ICP-MS is considerably more sensitive than ICP-AES, the calculated detection limits for the two techniques were remarkably similar. This is an indication that the limiting factor with respect to detection limits is the background signal arising from the reagent blank.

4.6 Publication Details

A paper based on the ICP-MS work has been submitted to the Journal of Analytical Atomic Spectrometry and is currently under review.

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CHAPTER 5. CONCLUSIONS

This study of sample manipulation and sample introduction techniques for ICP-MS and ICP-AES was undertaken with two broad objectives. The first was to extend the applicability of the instrumental techniques to situations where conventional sample introduction presents problems. The second objective was to use the sample manipulation and sample introduction methods to improve the analytical performance of the instrumental techniques, i.e. to improve the speed and efficiency of analysis, to lower the detection limits and to eliminate interferences. The success of this work can be measured in terms of the degree to which these objectives have been met in the application of each sample manipulation and sample introduction method.

5.1 Laser ablation

Laser ablation was used to extend the applicability of ICP-MS to the analysis of materials which are difficult to dissolve, since direct analysis of the solid materials was possible. Good sensitivity was achieved, as there was no dilution of the sample. Despite the problems of poor precision and memory effects which were encountered, useful analytical methods were developed. These methods were used in routine analysis for some time, but have been superseded by a dissolution method involving flow injection, which was described in Chapter 3. The flow injection method is capable of considerably better precision and is less prone to

memory effects.

5.2 Flow injection

The flow injection system has been successfully implemented in a number of applications in ICP-MS and ICP-AES. The system has been used to analyze tantalum oxide solutions with a high solid content by ICP-MS, which enabled the achievement of the required detection limits. This would not have been possible for conventional steady-state analysis because greater dilution of the sample would have been necessary. The system has also been used to increase the speed and efficiency of ICP-MS and ICP-AES analysis by reducing the time required per analysis, and by incorporating on-line dilution and internal standard addition.

The system has been used to eliminate interferences in ICP-AES by the incorporation of an on-line ion exchange column. The column was used to analyze trace levels of the platinum group metals in the presence of high levels of interfering base metals, by retaining the base metal on the column while allowing the platinum group metals to pass through to the plasma.

Evidence of the versatility of the flow injection system is given by the wide variety of situations to which it has been applied. It has therefore proved to be a highly useful sample manipulation and sample introduction method.

5.3 Hydride generation

Hydride generation has been applied to the analysis of arsenic and selenium by ICP-MS and ICP-AES, using a novel type of gas-liquid separator which achieves more efficient separation. The system was applied to the analysis of soils, in which it was used to eliminate argon chloride interferences in ICP-MS and to increase sensitivity of measurement in both techniques. The increase in sensitivity was forty-fold in ICP-MS and sixty-fold in ICP-AES. The precision of measurement was good, and good agreement with certified values was obtained for a variety of reference materials.

The hydride generation system is a useful accessory for ICP-MS and ICP-AES analysis, and is capable of producing good results. It is likely to find applications to other analytical problems involving the hydride-forming elements.

5.4 Closing comments

The sample manipulation and sample introduction methods investigated in this work are only a few of the many possible methods which could be employed. Due to the various problems associated with pneumatic nebulisation, there is great potential for research in this field. Many workers have been involved and are currently involved in the study of alternative sample manipulation and sample introduction methods for ICP-MS and ICP-AES. This work has shown that there

are numerous advantages to be obtained from investigations into these methods.

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