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TITLE
The Use of an Inductively Coupled Plasma as an Ion Source for Atomic Mass Spectrometry.

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Preamble

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THE USE OF AN INDUCTIVELY COUPLED PLASMA
AS AN ION SOURCE FOR ATOMIC MASS SPECTROMETRY

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

by

Alan L. Gray, B.Sc., F.Inst.P.

Department of Chemistry,
University of Surrey,
Guildford. December 1982
The development is described of a new ion source for atomic mass spectrometry which could lead to much wider applications of the technique.

The source is based on an atmospheric pressure high temperature inductively coupled plasma. Samples are introduced to the plasma as aqueous solutions by a pneumatic nebulizer.

Ion extraction from the plasma at temperatures up to 8000 K is based on sampling gas through an aperture placed in the tail flame. Initially apertures of 0.07 mm diameter were used which were protected from the full plasma temperature by the formation over them of a cooler boundary layer. High sensitivity and good resolution were obtained up to solute concentrations of 10 \( \mu \text{g.ml}^{-1} \), but matrix effects were severe.

Conditions were then established in which ions could be sampled direct from the plasma core without passage through a boundary layer. Continuum flow through apertures up to 0.5 mm diameter enables plasma ion populations to be frozen rapidly in the supersonic expansion, before reactions can occur to disturb the composition. Much better matrix performance is obtained in this mode and sample concentrations up to 1000 \( \mu \text{g.ml}^{-1} \) can be introduced.

Detection limits below 1 \( \text{ng.ml}^{-1} \) are obtained for a wide range of elements. Multi-element analysis is feasible at the rate of one sample per minute and isotope ratio determinations on solutions at about 30 \( \mu \text{g.ml}^{-1} \) are possible with precisions approaching 0.1% for integration times of 5 minutes.

The performance of the system is discussed theoretically and reasonable agreement demonstrated with the experimental behaviour.

The source already provides a viable analytical technique for samples introduced by any of the methods available for ICP-AES. These include solution nebulization, thermal evaporation, laser ablation and arc aerosol generation. Considerable scope exists for improving ion transport efficiency to provide sensitivity at least as high as any other routine analytical technique.
'To the greater glory of God........
.....in whom are hid all the treasures of wisdom and knowledge.'
IV

ACKNOWLEDGEMENTS

The author wishes to express his gratitude for the support of the Institute of Geological Sciences and of the Directorate General for Science, Research and Development of the European Economic Community, for the work which has led to the presentation of this thesis.

He would also like to express his appreciation of the continued support and encouragement of Dr. P.A. Sabine, Mr. P.J. Moore and Miss E. Waine of the Institute of Geological Sciences without which the ICP work would never have been started. His thanks must also go to Dr. S.H.U. Bowie F.R.S., formerly of the Institute, for his early appreciation of the potential of the technique and for preparing the ground for its eventual funding. He is further indebted to the Institute for making available the services of Dr. Alan R. Date, a most welcome and valued colleague. Most sincere personal thanks are due to Dr. Date for his unstinting involvement with the work, which contributed greatly to the results achieved.

It was a pleasure and privilege at the beginning of the work to be invited to join the ICP - MS project at the Ames Laboratory, Iowa State University for a few weeks. The author would like to thank Prof. V.A. Fassel for making this possible, and Prof. H.J. Svec and Dr. R.S. Houk for their co-operation during this mutually useful period.

In the very early days, while plans were being laid for this work, much valuable advice was received from Prof. P.F. Knewstubb and Dr. Alan N. Hayhurst of the University of Cambridge, and from Dr. J.L. Mbruuzzi of the University of Liverpool; any acknowledgement would be incomplete without mentioning them.

That this thesis has come into being is largely due to the early encouragement and advice of Prof. J.A. Elvidge of the Department of Chemistry, and the author would like to express his thanks to him for that and also for making facilities available for the work.

Grateful thanks are also due to Miss Jan Caesson whose hard work and excellent typing have greatly eased the preparation of this thesis.
ACKNOWLEDGEMENTS Contd.

And finally the author would like to record his immeasurable debt to his wife for her loyal and constant faith in the work over many years and her indispensable support during the preparation of this thesis.
Allocation of Responsibility within the Programme

This work was supported by the Institute of Geological Sciences, Gray's Inn Road, London (Contract NERC F60/A1/3P) with additional funding from The Directorate General for Science, Research and Development of the European Economic Community (Contracts 012-79-4 EXU UK and EXU-033-81-UK).

The writer was appointed project leader for the work which was carried out in the Department of Chemistry of the University of Surrey. Dr Alan R. Date was attached to the department on a part-time basis from the Institute of Geological Sciences to assist with the work with the ultimate aim of operating a second generation system at Gray's Inn Road after it had been assembled at the University following the work described herein.

During the course of the development the planning, scientific control and execution of programme on behalf of IGS was the responsibility of the writer. Dr Date contributed freely his expertise in geochemical analysis, particularly in the field of atomic emission, and was generally responsible for preparation of samples and standards and for matters relating to applications. He carried out the isotope ratio determinations in the boundary layer and continuum modes and the multi element calibration runs in the boundary layer mode which are described here for completeness. In addition when not occupied in his professional capacity he operated as a valued assistant in all stages of the work, and in addition contributed excellent draughtsmanship to the many reports and publications on the subject, some of which is reproduced herein.

Agreed

Alan K. Date
Institute of Geological Sciences.
## CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUMMARY</td>
<td></td>
<td>II</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td></td>
<td>IV</td>
</tr>
<tr>
<td>ALLOCATION OF RESPONSIBILITY WITHIN THE PROGRAMME</td>
<td></td>
<td>VI</td>
</tr>
<tr>
<td>CHAPTER ONE</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1.</td>
<td>The Need for a New Atomic Ion Source</td>
<td>2</td>
</tr>
<tr>
<td>1.2.</td>
<td>Principal Ion Sources in Use for Inorganic Samples</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1.</td>
<td>Thermal Source or Surface Ionization</td>
<td>6</td>
</tr>
<tr>
<td>1.2.2.</td>
<td>Vacuum Discharge and Spark Sources</td>
<td>7</td>
</tr>
<tr>
<td>1.2.3.</td>
<td>Secondary Ion or Ion Bombardment Sources</td>
<td>8</td>
</tr>
<tr>
<td>1.3.</td>
<td>Electrical Plasmas as Excitation and Ionization Sources</td>
<td>10</td>
</tr>
<tr>
<td>1.4.</td>
<td>The Applied Research Laboratories Project using the Capillary Arc Plasma</td>
<td>17</td>
</tr>
<tr>
<td>1.5.</td>
<td>The ICP - MS Project at the Ames Laboratory, Iowa State University, Ames, Iowa, USA</td>
<td>21</td>
</tr>
<tr>
<td>CHAPTER TWO</td>
<td>PRINCIPAL CHANGES PROPOSED TO ACCOMODATE AND USE AN INDUCTIVELY COUPLED PLASMA</td>
<td>23</td>
</tr>
<tr>
<td>2.1.</td>
<td>Sampling Apertures, Cones and Mounts</td>
<td>24</td>
</tr>
<tr>
<td>2.2.</td>
<td>Addition of an ICP</td>
<td>25</td>
</tr>
<tr>
<td>2.3.</td>
<td>Plasma Excitation</td>
<td>25</td>
</tr>
<tr>
<td>2.4.</td>
<td>Vacuum System</td>
<td>26</td>
</tr>
<tr>
<td>2.5.</td>
<td>Quadrupole Analyzer</td>
<td>26</td>
</tr>
<tr>
<td>2.6.</td>
<td>Ion Detector and Electronics</td>
<td>26</td>
</tr>
<tr>
<td>CHAPTER THREE</td>
<td>EXPERIMENTAL EQUIPMENT</td>
<td>27</td>
</tr>
<tr>
<td>3.1.</td>
<td>Vacuum System</td>
<td>28</td>
</tr>
<tr>
<td>3.2.</td>
<td>The Mass Analyzer</td>
<td>33</td>
</tr>
<tr>
<td>3.3.</td>
<td>Ion Detector</td>
<td>38</td>
</tr>
<tr>
<td>3.4.</td>
<td>Electronic and Control Equipment</td>
<td>40</td>
</tr>
<tr>
<td>3.5.</td>
<td>Data System</td>
<td>42</td>
</tr>
</tbody>
</table>
CHAPTER THREE EXPERIMENTAL EQUIPMENT Contd.

3.6. The Inductively Coupled Plasma System 45
3.7. Sample Nebulizer and Desolvator 49
3.8. Sampling Cones and Apertures 54
3.9. Expansion Stage 59

CHAPTER FOUR EXPERIMENTAL WORK 62

4.1. Initial Exploration of Plasma Behaviour and the Problems of Ion Extraction 63
4.2. Development of Boundary Layer Sampling Performance 73
4.3. Determination of Analytical Characteristics in the Boundary Layer Mode 80
4.4. Development of Operation in the Continuum Sampling Mode 86
   4.4.1. Sampling and Vacuum System Performance 86
   4.4.2. First Continuum Spectra 91
   4.4.3. System Development 98
   4.4.4. Optimization of Ion Optics 104
4.5. Determination of Operating Characteristics and Analytical Performance in the Continuum Mode 109

CHAPTER FIVE RESULTS 113

5.1. Results of Boundary Layer Sampling 114
   5.1.1. Initial Operation with ICP 114
   5.1.2. Background Signals and Spectra 119
   5.1.3. Characteristic Spectra 126
   5.1.4. Sensitivity and Dynamic Range 126
   5.1.5. Detection Limits 135
   5.1.6. Effect of Matrix Elements and Ionization Suppressants 137
   5.1.7. Isotope Ratio Determinations 140
5.2. Results Obtained by Continuum Sampling 151
   5.2.1. Source Characteristics 151
   5.2.2. Background Signals and Spectra 156
   5.2.3. Characteristic Spectra 160
   5.2.4. Sensitivity and Dynamic Range 165
CHAPTER FIVE RESULTS Contd.
5.2.6. The Effect of Ionization Suppressants 175
5.2.7. Ionization Temperature 177
5.2.8. Isotope Ratio Measurements 180

CHAPTER SIX DISCUSSION 185

APPENDICES 195

Appendix 1. Gas Dynamic Conditions 196
A.1.1. The Nature of Gas Flow through Small Apertures 196
A.1.2. Quantitative Gas Flow through the Sampling Aperture 198
A.1.3. Pumping Capacities and Working Pressures 200

Appendix 2. Ionization Equilibria in Atmospheric Pressure Plasmas 207
A.2.1. Plasma Atom Concentrations 207
A.2.2. Ionization Equilibria 210

Appendix 3. Operating Potentials of Ion Lens, Sampling and Analysis System 216

Appendix 4. Boundary Layers in Plasma Sampling 218
A.4.1. Aerodynamic and Thermal Boundary Layers 218
A.4.2. Dwell Time and Reactions of Sample in Boundary Layer 221
A.4.3. Electrical Sheath and Plasma Potential 223

TABLES
1. Vacuum Components 30
2. Pulse Counting Equipment 41
3. Inductively Coupled Plasma System 46
4. Nebulizers 53
5. Aperture Insert Materials, Inserts and Suppliers 58
6. Channel Print Out of Spectrum of Ar and ArH 78
7. Minimum Aperture Diameter for Continuum Sampling v. Temperature 87
8. Aperture Materials for Continuum Sampling 102
CHAPTER ONE

INTRODUCTION
1.1 The Need for a New Atomic Ion Source

For the analytical chemist, concerned with the determination of the elemental composition of a sample, who is faced with a variety of methods of atomic spectrometry, the first choice has rarely been that of mass spectrometry. It is only where problems exist of determination at trace and ultra trace levels of a wide range of elements, or where significant information is contained in isotope ratios, that mass spectrometry has been the preferred method. Even then it has only been accepted as a very specialised technique requiring complex and difficult sample preparation; the use of costly instruments, giving a low rate of sample throughput, and involving skilled interpretation of data. It is not therefore surprising that its use has grown far more slowly than, for example, atomic emission spectrometry in the last 40 years, a period over which there has been enormous growth in the use of instrumental methods of chemical analysis.

In the parallel field of organic mass spectrometry, however, the position is completely different. The enormous growth in the petrochemical industries in the same period has created a similar growth in the applications of mass spectrometry which has become a vital tool to the organic chemist, particularly in combination with chromatographic separation methods.

The reasons for this enormous difference in the acceptance of mass spectrometry in these two fields lie to some extent in the availability or otherwise of alternatives and in the relative scale of the demand. The mass spectrometer provides the organic chemist with a unique facility and there has been an ever growing number of laboratories which have needed it. Nothing comparable has occurred in the inorganic field. However, the more basic distinctions between the two areas lie in the different nature of the problem of sample introduction, the different types of ions required and the available methods for sample ionization.

It is rare in organic mass spectrometry for the analyst to be interested in atomic ions. The usual form of sample is a gas, vapour or volatile liquid and the degree of fragmentation of the sample molecules into smaller species is limited and usually carefully controlled. Low energy or 'soft'
ionization processes are used to ensure that characteristic molecular fragments are produced which may, on occasion, even consist of the parent molecule with a proton added or removed.

In contrast, the inorganic samples received by the mass spectroscopist for trace element or isotope ratio determination are usually in the original form of solids, or, more rarely, of solutions. The only form of inorganic sample which is as simple to handle as an organic one is a gas, and consequently there have been many applications of mass spectrometry for gas analysis. Where the sample is not gaseous, and usually consists of a mixture of molecular species, it is necessary to produce from the sample a representative cloud of free atoms which can then be ionized. If this is done at atmospheric pressure means must then be found to preserve the atomic state of the sample while transporting it into the high vacuum environment of the mass spectrometer. Ionization normally takes place in vacuo but if it occurs at atmospheric pressure the ion distribution also has to be retained. Not surprisingly the option of vaporization, dissociation and ionization at atmospheric pressure has not hitherto been accepted as a reasonable choice for routine analysis and has only been used where the nature of the problem being studied required it. Instead the alternative of preparing the sample in a suitable form and then putting it into the vacuum system for subsequent reduction to free atoms and ionization has been the normal practice.

It is important to distinguish the three separate processes which must occur in producing ions from a sample not already in gaseous form. In most of the sources used in atomic mass spectrometry it is not possible to separate them and little can be done to optimise them individually so compromise operating conditions are adopted. The characteristics of an ion source usually depend on the emphasis given to one feature or another at the expense of yet a third.

There are three basic types of vacuum atomic ion sources in routine use, Electrical Discharge Sources, Thermal or Surface Ionization Sources and Ion Bombardment Sources. The characteristics of these are summarized in the next section, but at this point it is sufficient to say that although each type has characteristics of value in specific applications, none of them offer the speed, ease of use and general all round perfor-
mance of, for example, atomic emission spectrometry and their use has consequently been limited. Nevertheless, atomic mass spectrometry does offer advantages to the analyst that can, in certain cases, offset these drawbacks. Two of these are very important, very high sensitivity for most elements of the periodic table (mainly by spark source techniques) and relatively simple spectra, especially for heavy elements which in atomic emission give very complex spectra. In addition of course isotope ratio determination is comparatively simple by mass spectrometry.

It was the attraction of these features that prompted a reassessment of methods of ion production by the author in a study made for his then employers, Applied Research Laboratories Ltd., (1). The purpose of this study was to examine the possibility of developing a new analytical instrument, based on mass spectrometry, capable of determining the atomic composition of large numbers of inorganic samples of the type produced in a mineral reconnaissance programme. For such an instrument to be practically useful it clearly had to be capable of completing useful elemental analyses of mixtures which had contained elements of interest at concentrations approaching the p.p.b. (10⁻⁹ W/w) level from a fresh sample every few minutes. Quite apart from the problems of sample preparation into a suitable form for introduction to the ion source this did not seem to be possible by development of any of the ion sources currently available. After considering a number of other ion source concepts that might merit further study, at least on paper, the report made the following comments:

"An additional method which, as far as is known, has not yet been tried, could possibly be based on a version of the aerosol generator. This is a very convenient technique for producing a submicron particulate aerosol from a large conducting sample compact in a suitable carrier gas stream. This is then injected into a plasma arc which vaporizes the particles. It should be possible to extract from this plasma neutral and ionized atoms representative of the sample. The problem then of sampling the plasma at approximately atmospheric pressure ... is similar to that of studying high temperature gas phase chemical reactions, flames and electrical discharges and a number of inlet stages have been designed for these. Some of these are based on a series of differentially pumped chambers and as such require extensive pumping systems, but those using a small orifice in a diaphragm are simpler although possibly less sensitive."
The preparation of such a report necessarily involves a review of the published work of many investigators and in its conclusions it drew heavily on their work. It is believed, however, that nowhere in the literature was there a prior suggestion that a combination of ionization in a plasma at atmospheric pressure and mass spectrometric ion sampling should be used as a technique of analysing samples introduced to the plasma. This proposal was subsequently embodied in patents which were granted to Applied Research Laboratories Ltd. (2).

Following the issue of the report this proposal was felt to merit more detailed examination, and the help of Dr P. Knewstub and Dr A.N. Hayhurst of the University of Cambridge was sought and freely given. Both had published work on flame sampling (3,4,5) and on the basis of their work they were able to quantify some of the unknowns in the proposed method.

It appeared that a plasma of the type suggested had many of the properties most desired in an ion source and if ions could be extracted using a development of flame sampling techniques there seemed to be a good chance of developing a new ion source - mass analyser combination with the most attractive advantage of sample introduction at atmospheric pressure.

A development programme was started under joint funding from Applied Research Laboratories Ltd. and the National Research and Development Corporation. The first year was occupied by a feasibility study at the University of Liverpool under Dr J.L. Moruzzi and this was followed by a further two years work at A R L Ltd. This work was described in a series of progress reports (6) and is summarised in section 1.4. The programme of work reported here started from the point reached by the A R L study at its close.
1.2 Principal Ion Sources in Use for Inorganic Samples

Inorganic samples, other than gases, are commonly presented for analysis in the form of solids or aqueous solutions. For mass spectrometric analysis using a vacuum ion source, solutions are reduced to the solid form by evaporation or plating, often directly onto a suitable electrode. Once the sample has been reduced to its constituent atomic species in vacuum subsequent ionization is straightforward and may be simply accomplished for example by electron bombardment. The major difficulties with inorganic solid samples lie with the first two steps of vaporization and dissociation. Many inorganic solids require very high temperatures for these processes to proceed rapidly and problems of containment and contamination become very severe. Simple thermal methods are only practicable in limited circumstances and two other methods of supplying the energy necessary to simultaneously vaporize, dissociate and ionize the sample, the vacuum discharge and ion bombardment, have, together with thermal sources become the principal methods of producing ions from inorganic solids. For comparative purposes the main characteristics of these sources are summarized below but the subject is fully covered in the literature (7,8). Reference 7, a good general text, also contains a useful bibliography.

1.2.1 Thermal Source or Surface Ionization

In the thermal ion source, first used by Dempster in 1918 (9), the sample is deposited, often by plating from solution, on a metal filament. This is then inserted into the vacuum system and heated electrically to a temperature of between 2000K and 3000K. Ions are formed in the space above the filament by purely thermal bombardment processes and are normally only singly ionized and have a very small energy spread. However, the ionization efficiency depends on the work function, W, of the surface, the ionization energy I of the element and the temperature, T, according to the Langmuir-Saha equation

\[
\frac{n^+}{n_o} = \exp \left[ \frac{e \times (W - I)}{kT} \right]
\]
where e is the electronic charge and k the Boltzmann constant. The ionization efficiency thus varies very widely across the periodic table and may be impractically low in some cases. Differential volatilization rates also make the source unsuitable for mixture analysis. However, the low energy spread of the ions is compatible with simple magnetic sector instruments and the source is very widely used for the analysis of specific elements in very small samples, for isotope ratio determination and for isotope dilution analysis. The time required for analysis is typically of the order of one hour. Commercial instruments often use multiposition filament turrets enabling up to 16 samples to be loaded at once and then run over a weekend (48 hours).

The thermal source has been the subject of much sophisticated development to extend its range but it remains subject to two main limitations. Considerable sample preparation is needed before the sample can be introduced and the source is unsuitable for sample mixtures, separation of the element of interest being preferable where possible.

1.2.2 Vacuum Discharge and Spark Sources

The RF Spark Ion Source also developed first by Dempster in 1934 (10) has been the most widely used source for general inorganic analysis of solids by mass spectrometry and commercial instruments have been available since about 1958. The RF spark occurs between electrodes of compressed graphite, aluminium or silver powder, one or both of which has the sample material in finely divided form incorporated in it. Ions of a wide energy range are produced and there are many multiply charged ions (up to 3 or more charges). Because of these features it is necessary to use a complex double focussing mass spectrometer of high resolution, usually using the Mattuch-Herzog geometry, which produces a fully dispersed spectrum along its focal plane. For this reason the full usefulness of the instrument is only obtained using a photographic plate as the ion detector, but although this is less convenient than a detector with electrical readout it does provide the only truly simultaneous detection over all masses. The sensitivity is high and reasonably uniform (over a range of about 10 to 1) across the periodic table. The technique is thus valuable for survey analysis
of unknown samples but quantitative precision is relatively poor.

As well as the RF spark other forms of electrical discharge are used to a lesser extent, notably a low voltage DC one, but apart from a lower ion energy spread and some differences in the distributions of multiply charged ions, the characteristics are broadly similar.

Because of the complex sample preparation and the relatively long exposures required of several hours sample throughput is low, typically one or two samples per day. In spite of these limitations, however, the technique is widely used but is limited to small sample suites.

1.2.3 Secondary Ion or Ion Bombardment Sources

This relatively new technique has attracted a lot of research effort and attention, particularly as when it was first introduced it seemed to offer a solution to the lack of a good atomic ion source, and at the same time to offer the possibility of elemental imaging by microprobe or microscope type instruments (11,12).

A relatively unprepared sample surface is required and may simply consist of a fractured rock specimen. This is mounted in vacuum and bombarded by a beam of ions produced in a conventional ion source. Typically, argon, oxygen or nitrogen ions are used but in principle any atomic ion may be chosen. The precise mechanism of ion production has been the source of extensive discussion but it is still uncertain as is the quantitative basis of the technique. However, mainly singly charged ions of an energy spread of a few hundred ev are produced and may be collected and mass analysed. Again a double focussing system is required to produce sufficient resolution although this is less complex than with the spark source. It has proved difficult to produce satisfactory quantitative analysis with this technique. The range of sensitivity over the periodic table is very large and its major application has been as a qualitative method in the imaging mode. Here it has proved very successful in producing trace element distributions in solid state material and has found its principal role as a research tool. Because of the simple sample preparation required and the ease
of introducing a solid sample the technique has a relatively high throughput of samples. Electrical ion detection is used but the analyser must be scanned through the range of masses of interest. Analysis times range from minutes to hours depending on the number of elements involved and the mode of instrument use.
1.3 Electrical Plasmas as Excitation and Ionization Sources

The use of an electrical discharge at atmospheric pressure to excite the characteristic emission lines of an unknown sample for spectroscopic analysis has a long history and is certainly older than mass spectrometry. Until comparatively recently, however, it found its main applications in the analysis of metals and alloys where the simple use of a spark or arc from a counter electrode to the sample provided the extraction of sample material from the solid, its vaporization and dissociation, and its excitation all in one simple step. As well as these four processes a fifth normally also occurred, the ionization of the sample atoms as well, excited ion lines being commonly used in spectroscopic analysis. For trace analysis, however, particularly from samples in the form of solutions, the simple electrical spark or arc is less convenient, either a film of liquid or dried residue on the counter electrode, often of carbon, being employed. This shows a close parallel with the methods used for spark source mass spectrometry where similar problems are met. For solution samples the preferred method has been to use a chemical flame to vaporize and dissociate the sample followed either by thermal excitation of emission lines or more commonly the use of the flame as an atom reservoir for atomic absorption.

Chemical flames, however, have limitations, their reactive atmospheres can lead to extensive interelement effects arising from the complex flame chemistry. Perhaps more significant, however, is the limited temperature, about 3000K, that can readily be achieved in the laboratory, and this has meant that flames have found their greatest application as atomic absorption rather than emission sources. Although extremely sensitive, however, atomic absorption is difficult to use for multielement analysis and is usually limited to sequential analysis of a small number of predetermined elements per sample, in contrast to the multi element capability of emission spectrometry.

Considerable effort has been expended, mainly in the last 30 years, to develop an emission source based on an electrical discharge which would provide a higher temperature than a flame, and thus perform better in vaporization, dissociation and excitation of the sample, while retaining the simplicity of sample introduction characteristics of flame spectroscopy.
Most of these electrical discharges have been operated in an inert gas atmosphere, usually argon, thus simplifying, although not entirely eliminating, the possible reactions in the discharge. In most cases sample introduction has been based on solution nebulization, often using nebulizers made for atomic absorption equipment.

The early work on electrical discharges was almost exclusively limited to some form of arc discharge between two electrodes. The discharge was usually unidirectional (DC) in an atmosphere of argon, typical discharge currents of between 5 and 50 amps being used, a low potential drop of a few tens of volts occurring across the arc. As a spectroscopic source such a discharge presents a number of problems. The actual current path between electrodes is usually in the form of a thin (about 1mm diameter) streamer that constantly changes position, the ends of the stream moving about on the electrodes. Quite apart from the problems of stability of the optical geometry that this causes it also means that the region of highest temperature, the most effective 'plasma' region for excitation, is the region of lower gas density and is surrounded by a strong thermal gradient against which it is very difficult to introduce a gas borne aerosol from the nebulizer. In practice therefore only a few percent of the sample ever actually reaches the true plasma core which may well be at a temperature between 5000 and 10,000K. The most likely atoms to reach the core are those from the electrodes, a source of unwelcome contamination. Many ingenious plasma geometries have been tried for DC discharges, including some which remove the electrodes from the region where the sample is introduced and the emission observed (13,14), and DC plasmas have found a place in emission spectrometry (15). The Capillary Arc Plasma (16), a small wall stabilized DC arc, was an example of these and was used, as has been described (17,18), as an ion source in the early plasma source work. In spite of all the effort extended on DC plasmas, however, the central problem of sample introduction still eludes a satisfactory solution and inadequate sample vaporization and dissociation remain the cause of extensive matrix and interelement effects.

In seeking alternative methods of exciting a discharge electrically it was natural to examine the electrodeless methods by which energy could be transferred to a plasma by radio frequency coupling. In order
to transfer energy to a non conducting gas a conducting path must first be created in it by an initiating spark discharge such as that from a Tesla coil. Once an initial supply of electrons is obtained energy may be rapidly transferred and under the correct conditions a conducting zone is formed which rapidly absorbs energy and reaches very high temperatures. The pioneering work in stabilizing and containing plasmas excited by radio frequencies in the range of 1-100MHz was done by Reed (19,20) and in about 1964 his work was further developed in two laboratories (21,22) to apply the Inductively Coupled Plasma (ICP) as an analytical excitation source. In this source, shown diagrammatically in Figure 1 a stable plasma fireball is created in the mouth of a quartz tube, typically of 20mm diameter, in a flowing stream of gas. Radio frequency energy at power levels of between 1 and 10KW is supplied to the conducting plasma by a coupling coil of a few turns around the outside of the tube. This coil is usually made of tubing and cooled by a water flow. The plasma is kept off the tube walls, which would otherwise melt, by a high velocity flow of gas directed along the inner surface of the tube which also cools it. Although argon is commonly used for both plasma and cooling gas streams, other gases may be used. Nitrogen is often preferred as coolant gas for economy as the flow required is usually between 10 and 20 litre/min^-1. In the form shown in Figure 1 the plasma contains only the plasma and coolant gases and no obvious advantage, other than the absence of electrodes and a relatively large plasma volume, is apparent over the D.C. plasmas. However, it is in the introduction of sample that this plasma shows its superiority over all other types so far described. As discussed by Greenfield (21) and Fassel (24) if sample aerosol is injected with sufficient velocity along the central axis, it is possible to punch a cooler channel through the centre of the fireball which takes on a toroidal form as shown in Figure 2. The formation of this toroidal plasma is a function of gas flows, tube geometry and operating frequency (23) but under optimum conditions the plasma can be very stable. The temperature distributions in the plasma have been extensively studied. Values as reported by Fassel (24) are shown in Figure 3. The gas temperature along the axial channel within the fireball is typically 8000K. This channel is, however, surrounded by a region which is hotter (10,000K) so that the sample is contained and all of it experiences the high temperature. The length of the fireball and the central channel gas velocity are such that all the
Fig. 1. Inductively Coupled Plasma fireball in mouth of quartz tube.

Fig. 2. Fireball formed into toroid by central sample carrying gas flow from capillary injector tube. (Figs. 1 and 2 after Fassel, ref. 13)

Fig. 3. Gas temperature in toroidal ICP. (Fassel ref. 24)
samples experience this temperature for a period of 1ms or more (24). There is thus a much more uniform high temperature region available than in any other form of plasma for sample atomization. When introduced from a nebulizer the sample aerosol is in the form of microparticulates each consisting of the dried solute content of a droplet from the nebulizer. For a given droplet size the volume of the microparticulate is proportional to concentration of the total solute, and it has a typical diameter of about $10^{-6}$cm at a concentration $1\mu g.ml^{-1}$. As they leave the mouth of the injector tube and are forced into the central channel through the toroidal energy addition region of the plasma these particles rapidly rise in temperature and begin to vaporize. Once the carrier gas leaves the plasma energy addition region and enters the tail flame the temperature starts to fall as shown in Figure 3. It is thus important that the residence time of the sample in the hottest region is sufficient for complete vaporization and dissociation of the largest particles likely to be encountered from the most concentrated solutions to be analysed. In many cases the higher concentrations are provided by the matrix elements, which may not be analytically interesting. Nevertheless the operating conditions must be chosen to accommodate these or the presence of incompletely vaporized solid particles may cause incomplete release of the elements of interest into the plasma and hence cause matrix interelement effects. The choice of carrier gas flow rate is therefore very critical. However, when the operating conditions are properly optimised the ICP, when used as an atomic emission source, shows an outstanding performance in sensitivity, dynamic range and freedom from matrix interferences that has resulted in its wide acceptance for trace analysis of solutions. As well as showing emission from excited atom lines, ion line emission is also very prominent and often provides higher sensitivity for many elements than that from atom lines.

Although the ICP has become pre-eminent as an emission source it has the drawback of being relatively expensive both to buy and to run. In attempts to find an alternative electrodeless means of exciting a plasma, considerable attention has been paid to coupling energy to it at microwave frequencies, usually 2450MHz., at power levels of up to about 200 watts. These plasma are physically very much smaller and less costly than the ICP but may still have similar power densities
in the plasma core. Although they do offer very high excitation temperatures and particularly in some recent designs (25,26) can offer very high sensitivity, they suffer from two serious drawbacks compared to the I.C.P., the plasma gas temperature rarely exceeds 2000K and so far no method has been found of creating a toroidal form. This combination of low gas temperature and cylindrical rather than annular form of the plasma column means that sample penetration and vaporization is poor and these plasmas suffer from severe matrix effects. They have found their principal application in the analysis of gases and vapours such as chromatograph elements where poor vaporization of the sample is no longer a problem.

The nature and effect on performance of the ionization equilibria in a plasma are discussed in Appendix 2. Here it is sufficient to comment that the very existence of a plasma is dependent on the presence in it of substantial numbers of ions and in the case of an electrically maintained plasma the ion population has to be large enough to carry the sustaining current. In the absence of any other atomic species these ions will be those of the plasma gas. However, in practice normal supplies of gas contain impurities such as oxygen, nitrogen and water vapour, residual and atmospheric gases, at the parts per million level so that ions of these elements are also usually present. At atmospheric pressure the collision frequency of the atoms present is very high so that the kinetic energy of the atoms and ions is rapidly equilibrated throughout the plasma. At high plasma gas temperatures as in the D.C. arc and I.C.P. a major role in the establishment of the ionization equilibria is played by purely kinetic thermal ionization processes but other mechanisms such as charge exchange, ion molecule reactions and Penning ionization through metastable states may also play a significant part. At the lower gas temperatures of the microwave plasma, processes other than thermal ionization probably dominate the mechanisms. However, whatever the precise mechanism, in a given plasma it is evident that any atoms deliberately introduced from an unknown sample will take part in the equilibria in the same way as those of the plasma gas and at atmospheric pressure will also very rapidly acquire the equilibrium kinetic energy of the plasma species $kT$, which at 10,000K is equal to 0.86eV.
It is thus possible to define the characteristics that may be expected from such a plasma used as an ion source as follows.

1. Samples are introduced at atmospheric pressure and at gas temperatures of 5000K and above are rapidly vaporized and dissociated. Few molecular species should be present in the plasma even from refractory compounds.

2. Because of the high gas temperature interelement and matrix effects should be small as demonstrated in the performances of the ICP as an emission source.

3. At temperatures between 5000K and 10,000K most elements in the periodic table will be substantially ionized, many often to 100%. At the lower temperatures doubly charged ions would be expected only from those elements with second ionization energy below 1eV.

4. Because the ionization occurs outside the vacuum system no ions will be produced from the organic molecules present from pump vapours and other organic materials present in the vacuum chamber.

5. As a consequence of 3 and 4 above spectra should contain very few peaks at fractional masses, and consist instead of simple whole number peaks.

6. The energy spread of extracted ions should be small, less than 1eV due to the plasma gas kinetic energy.

As an ion reservoir for use as the basis of an ion source such a plasma appears to be very attractive provided that the ions present can be extracted in proportions representative of the populations in the plasma and introduced into a mass analyser. It is this process that forms the subject of this thesis.
1.4 The Applied Research Laboratories Project using the Capillary Arc Plasma

This project was based on the DC Capillary Arc Plasma (CAP) developed by the American parent company of Applied Research Laboratories as an excitation source for atomic emission spectrometers (16). This source was designed to accept an aerosol of metal particles of 1µm diameter or less derived from a subsidiary discharge (the Aerosol Generator) on a metal disc sample. A diagram of the source is shown in Figure 4. The discharge column between the cylindrical anode and offset point cathode was confined in a water cooled copper cylinder of about 3mm diameter. The main plasma gas flow was directed along the tube from anode to cathode and emerged into the atmosphere at the mouth of the tube just beyond the cathode. Sample was introduced in a subsidiary argon flow midway between the electrodes and was directed tangentially to spiral along the tube with the intention of promoting mixing of the sample in the plasma gas. Spectroscopically measured temperatures at arc currents of about 11 amps at 50V. drop were between 4000K and 5000K.

Since the gas carrying the vaporized and excited sample emerged as a small tail flame into free air very shortly after leaving the hottest part of the arc column it offered an ideal physical geometry for ion sampling.

The ion sampling arrangement used is shown in Figure 5 and was based on that used by Hayhurst (5) for sampling atmospheric pressure flames. A small gas flow was extracted from the plasma by allowing the tail flame to impinge on a small aperture in the tip of a metal cone, usually made of copper. Apertures of up to 70µm diameter were used, usually drilled in platinum inserts pressed into the tip of the copper cone. The extracted ions were collected and focussed by a lens system into a second vacuum stage containing a simple quadrupole mass analyser. Ions leaving the analyser were detected by a channel electron multiplier operated as a pulse counting detector. Pulses from the detector were amplified by a conventional pulse amplifier and passed to a pulse height discriminator and ratemeter or scaler as desired.
Fig. 4. ARL Capillary Arc Plasma (16).

Fig. 5. Schematic diagram of Plasma Source Mass Spectrometer using CAP ion source.
The performance of this system using the CAP as an ion source has been described elsewhere (6,17,18,27). It was found more convenient for experimental purposes to make up test samples in the form of aqueous solutions at concentrations of about 1μg.ml⁻¹. These could then be introduced into the sample gas stream of the plasma by nebulization. At the time of this work good nebulizers which would operate at the low flow rates required (1 l.m⁻¹ of argon or less) were difficult to obtain so a batch type ultrasonic nebulizer based on a medical respiratory nebulizer was built. Using this method of sample introduction good spectra of simple test solutions could be obtained with very low background levels so that limits of detection for many elements were exceptionally low. The resolution obtained from the simple quadrupole analyser used was sufficient to enable isotope ratio measurements to be made with a precision of 0.5% or better.

Although this work effectively demonstrated that it was possible to produce representative spectra direct from aqueous solution samples in this way it also revealed that the CAP suffered from a number of severe limitations as an ion source (28). The most important of these were as follows.

1. Good sensitivity was only obtained for elements with ionization energy below about 9.0eV.

2. The system was severely non linear at total element concentrations above 1μg.ml⁻¹, the addition of one element causing a reduction in the response to others of similar ionization energy.

3. Very severe reduction in signal was caused by the addition of elements of low ionization energy.

4. Solution concentrations much above 10μg.ml⁻¹ tended to cause obstruction of the aperture by condensed solid.

These limitations were attributed to two related causes. Firstly the basic plasma temperature was too low to produce a reasonable degree of ionization in elements of ionization energy above 9 eV and secondly only a small proportion of the introduced sample actually experienced the full plasma temperature. Because the major part of the sample skirted the plasma core rather than penetrated it only a small proportion of the sample was fully
ionized. The rest was only partly ionized in the lower temperature region around the plasma column and the degree of ionization there was very dependent on the nature of the other species present. Finally at higher concentrations the combination of overall time and temperature for much of the sample aerosol was inadequate to fully vaporize the larger microparticulates so that the sample was not fully atomized and solid particles could travel right through the plasma to block the aperture.

It was appreciated that if the potential of the technique was to be realised it was necessary to use a plasma of higher temperature and better geometry. The contemporary work on the Inductively Coupled Plasma for use as an atomic emission source (29,30) was showing that this plasma was ideally suited to overcome similar problems for emission and it was evident that if ions could be extracted from this higher temperature toroidal plasma there was a real possibility of overcoming the limitations found with the CAP (28).

Accordingly proposals were prepared and submitted to the Institute of Geological Sciences in mid 1975 for a further research and development programme to continue the work using an ICP. However, before this proposal received support it was decided for reasons unconnected with the project to discontinue research in the UK branch and the A.R.L. programme closed.

After the close of the work at A.R.L. a further period of more than two years elapsed before it became apparent that support for a further development programme on the lines proposed was likely to be provided jointly by the Institute of Geological Sciences and the European Community. During this intervening period some of the basic work on ion sampling from an ICP was started in the USA and the author was invited to contribute to that programme.
1.5 The I C P-M S Project at the Ames Laboratory, Iowa State University, Ames, Iowa, U.S.A.

Shortly after the close of the work at A.R.L. in late 1975 a new project was started by R.S. Houk under Professors V.A. Fassel and J.H. Svec at the Ames Laboratory to apply the technique described by the author (17, 18, 27) to an I C P. This was a very natural development since the Ames Laboratory was one of the original locations of I C P development (22) under Professor Fassel, and Professor Svec led a very experienced mass spectrometry group.

The author became aware of this in late 1977 and was invited to visit the project. At the time of this visit ions from the plasma had been detected by a Faraday cup placed behind a sampling aperture located in the plasma flame, but these had not been mass analysed. A number of suggestions were made for modifications to the system and once these were made weak spectra of the main ions of the plasma gas were obtained.

Following this very brief visit a further visit of a month was paid in August 1978. This enabled experience to be obtained of the problems of inserting a sampling cone and aperture into the plasma flame and of the problems of aperture life. During this period of intense experimental effort weak spectra of analyte ions of transition elements introduced into the plasma at a concentration of 100μg.ml⁻¹ were obtained for the first time. Although a very great deal remained to be done at the end of this visit a start had been made from which further development could be planned. This was continued by R.S. Houk in the intervening period up to March 1979 when a further visit of two weeks was made, just after the start of the PSMS project supported by IGS at the University of Surrey. During this later visit further steps forward were made by using an intermediate baffle to isolate the central plume of the plasma which was then sampled by the aperture. Considerably greater signals were obtained and in the course of further development Houk greatly improved the performance. The development at Ames Laboratory has been described by Houk (31) and subsequently published in a more compact form (32).

Although subsequent development at Surrey diverged somewhat from that at
Ames there is no doubt that the initial experience obtained in interfacing a cone to a plasma during the August 1978 and March 1979 visits was of considerable value in the early stages of the work at Surrey. When combined with the previous experience of the Capillary Arc Plasma system it provided an excellent starting point on which to base the Surrey project.
CHAPTER TWO

PRINCIPAL CHANGES PROPOSED TO ACCOMMODATE
AND USE AN INDUCTIVELY COUPLED PLASMA
In planning a further development programme to realise the advantages hoped for from the characteristics of an I C P as an ion source it was clear that the sampling system used for the C A P was likely to prove inadequate in several respects. Limitations had also been found in both the mass analyser and ion detector used in that programme and it was evident too that a fast read out of spectra which could be provided by a multichannel scaler-data system would make assessment of performance much easier and faster.

The principal changes planned at the beginning of the work are described below. Considerable additions to the equipment were needed, some of relatively standard items but which could have long deliveries and others, mostly mechanical items, which had to be designed and manufactured. These mechanical components, particularly those of the sampling interface such as cones, cone mounts, ion lens electrodes, slide valve etc. were nearly all made outside the university to the author's sketches. This work was done by a small engineering firm who had made some of the original parts for the A.R.L. project and their excellent work greatly simplified the necessary mechanical changes that were continually required.

2.1 Sampling Apertures, Cones and Mounts

It was expected that operating conditions for the sampling apertures in the I C P would be more severe because of the higher gas temperature than in the C A P. Plasma powers of between 1000 and 1500 watts would be used compared to the C A P power of about 500 watts. Adequate water cooling would therefore be needed to stabilize the sampling cone temperature.

It was hoped to use larger aperture sizes than in the C A P project and therefore expected that a larger and hotter influx of gas would increase erosion of the aperture lip. Other aperture disc materials than the platinum originally used were therefore likely to be required.
2.2 Addition of an I C P

Although the plasma torch and flame of the proposed I C P were physically little larger than the Capillary Arc Plasma unit previously used with the vacuum housing, the CAP unit was only connected by a small cable to its power supply and could be mounted on a simple bracket in front of the sampling cone. The I C P torch, however, was mounted on one side of a relatively large and heavy housing containing the RF matching and tuning network which could not be separated from the torch. Proper access and mounting for this unit was needed so that the flame position could be adjusted in relation to the cone. This would require considerable mechanical rearrangement of the vacuum bench.

2.3 Plasma Excitation

The DC plasma previously used required only a simple high current power supply which caused no interference with either the quadrupole analyser control circuits or the ion detector pulse counting electronics. The I C P power supply which was to replace it however was effectively a 1 Kw RF transmitter operating at 27.12 MHz. When used for the purpose for which it was designed all the components in the RF circuit were well enclosed in a screened housing and the only breaks in that screening were the small tube carrying sample into the nebulizer and the window, itself screened by wire mesh, through which the light from the plasma was passed to the spectrometer. In order to extract ions the tail flame from the plasma had to emerge through the screening. Since the flame is a conductor this clearly represented a path for RF currents to the rest of the system, notably through the sampling cone. It was not clear what problems this could cause in the signal circuits fed by the ion detector which, in order to handle short pulses at rates up to several MHz, must have a band width which would include the plasma excitation frequency.
2.4 Vacuum System

The original vacuum system, pumped by a 9 inch and a 4 inch vapour pump had proved adequate to handle the gas load experienced but it was rather unsophisticated and lacked proper valves that would enable changes to be made within the vacuum vessel without allowing air into the pumps. In addition vacuum gauging was very limited and there were no proper safety trips in case of failure. It was considered essential to upgrade the system to one that was fully valved and protected so that continuous operation was possible.

2.5 Quadrupole Analyser

It was evident during the work on the CAP project that the small quadrupole used, while enabling a demonstration of feasibility to be made, had inadequate resolution and ion transmission at high masses for serious analysis and was also not sufficiently stable. A new quadrupole analyser using a larger rod assembly and having a more powerful drive system was therefore required. This would require modification of the vacuum vessel to accommodate these larger components.

2.6 Ion Detector and Electronics

The small channel electron multipliers used in the CAP project were found to lose gain very rapidly above $10^4$ counts.sec$^{-1}$ so that the system became severely non-linear for large peaks. This greatly limited the dynamic range and also the precision possible in isotope ratio measurements. A faster channel multiplier was therefore necessary. This required a new housing to mount it on the end of the analyser.

In order to handle the count rates of the new detector up to and beyond 1 MHz a fast pulse amplifier and counting chain was required. To use the system with the proposed multichannel scaler data system an interface was also necessary to couple the two.
CHAPTER THREE

EXPERIMENTAL EQUIPMENT
3.1 Vacuum System

At the start of the programme the original equipment used in the Capillary Arc Plasma project at A.R.L. was made available. This is shown in Figure 6. Since it had not been used for four years it was regarded as a set of components from which to assemble the ICP system and it was completely stripped, cleaned and rebuilt.

The vacuum vessel consisted of two stages, the first a rectangular aluminium chamber 22cm wide, 53cm long with a depth of 6cm. This shape was originally chosen to provide a reasonably short ion path through the depth of the vessel while also providing an adequate cross section for the pumping path to the Edwards E09 pump needed to handle the large incoming gas flow. Originally, this had been mounted with its long axis vertical and its small DC plasma unit was located in front of the sampling aperture above the elbow needed to connect the vessel to the pump. The ICP matching box which carried the ICP torch on one side was considerably larger than the DC plasma unit. The first stage was therefore mounted horizontally in the new arrangement and the large elbow and 9" pump mounted behind the centre line as shown in Figure 7, thus providing good access for the ICP torch box.

The Stage 2 vessel was a simple cylinder of 15 cm internal diameter 28cm long which was supported above the pump bench by a 10cm diameter tube connecting it to the E04 pump. This vessel was bolted to the outlet flange of Stage 1 and closed at its other end by a flange plate through which connections were made to the mass analyser and detector by ceramic to metal seals. Both vacuum pumps were provided with water cooled baffles and valves so that the vessels could be isolated from the pumps for modifications. Each stage was fitted with Pirani and Penning vacuum gauges.

Hydrocarbon oil was used in the vapour pump to avoid the formation of insulating deposits on electrodes and each pump was backed by an appropriate rotary pump with suitable isolation valves and safety devices. Details of the vacuum components are given in Table 1.

The original pump bench was retained, slight modifications being required to accommodate the new layout.
Fig. 6. CAP mass spectrometer system.

Fig. 7. Rearrangement of original vacuum system for use with ICP.
1. **Expansion Stage.**

First stage in continuum sampling, not used for boundary layer sampling.

EDM20A  Mechanical pump. 342 l.min.\(^{-1}\).
TCI  Thermocouple gauge.

2. **First Vapour Pumped Stage.**

Second stage in continuum sampling, used as first stage in boundary layer mode.

EO9  Oil diffusion pump fitted with H12L8 baffle and isolation valve. Combined capacity 1200 l.sec.\(^{-1}\)
ED660  Backing pump, 660 l.min.\(^{-1}\)
CP25  Penning gauge.

3. **Second Vapour Pumped Stage.**

Third stage in continuum sampling, used as second stage in boundary layer mode.

EO4  Oil diffusion pump fitted with CB4A baffle and QSB4 valve
Combined capacity 180 l.sec.\(^{-1}\)
ED100  Backing pump, 100 l.min.\(^{-1}\)
CP25  Penning gauge head.

All components manufactured by Edwards High Vacuum Ltd., Crawley, Sussex.
The flange between the two stages was fitted with the mount carrying the ion lens. This lens consisted of an assembly of electrically isolated cylinders and apertures shown in its initial form in Figure 8. Minor modifications were made to this assembly during the course of the work. The final aperture of 2mm diameter which was mounted on an insulating plate directly on the mount also formed the differential pumping aperture between the two stages. The mount and lens together could be readily removed through the front aperture of Stage 1 for modification or cleaning. Electrical connections to the lens were made through a 9 way plug and socket inside the vessel. These moulded components were considered acceptable in the relatively high pressure first stage.

The entrance aperture of the first stage was closed by a flange on which was mounted a slide valve. This valve is shown in Figure 9. The sliding plate carried the water cooled mount for the sampling cone. This relatively simple valve was adequate to enable sufficiently low pressures to be reached in Stage 1 while allowing a rapid change of the plasma sampling cone when required.

The complete vacuum system was assembled and set to pump before the arrival of the ICP system. Because of the general use of elastomer O-rings only low temperature baking was possible. Sufficient time was available, however, for a pump down period of 1 month to be given before the system had to be used. After this period when the slide valve was closed pressures of approximately $1.1 \times 10^{-2}$ Pa ($8 \times 10^{-5}$ torr) and $3 \times 10^{-4}$ Pa ($2 \times 10^{-6}$ torr) were obtained in the first and second stages. Once in full use it was possible to let the vacuum vessel up to air for modifications as required and then reach these pressures again approximately 30 minutes after recommencing to pump the vessel.
Fig. 8. Ion lens system. Approximately half size.

Fig. 9. Slide valve assembly.
3.2 The Mass Analyser

The choice of mass analyser in the original system was based on a combination of the requirements of the problem and considerations of convenience and cost. The concept of the system was based largely on flame sampling practice. Although with chemical flames an ion source at high electrical potential was not impossible it would certainly be difficult to arrange with electrical plasmas and thus ions were expected to originate from close to ground potential and because of the temperatures involved to have a small energy spread. Again because of the source temperatures few multiply charged ions were expected and thus most peaks would occur at whole mass numbers. Relatively low mass resolution was therefore required and the most appropriate analyser appeared to be of the quadrupole type.

Quadrupole mass analysers consist of a set of 4 parallel rods, usually of circular section, manufactured and mounted to very close tolerances. Opposing rods are connected together as shown in Figure 10 and the two pairs of rods fed with opposite polarities of a potential defined by

\[ U + V \cos \omega t \]

where \( U \) is a fixed DC potential and \( V \) the amplitude of an RF potential of frequency \( f = \frac{W}{2\pi} \). Ions are injected into the rod assembly along the axis and the system operates as a mass band-pass filter, only ions within a limited range about a mean mass/charge ratio \( m/z \) being transmitted. This mean transmitted ratio is given by

\[ m/z = \frac{C \cdot V}{f^2 r_o^2} \]

where \( C \) is a constant and \( r_o \) the radius of the cylinder defined by the inner surface of the rods.

The resolving power of the filter \( \frac{M}{\Delta M} \), where \( M \) is the value of \( m/z \) transmitted, is controlled by the ratio \( U/V \) and thus may be adjusted by changing electrical parameters. The transmitted mass is varied by changing \( V \), the RF amplitude, while by suitably controlling the ratio \( U/V \) the peak width \( \Delta M \) may be kept almost constant over the working mass range and the resolution is therefore often expressed as a multiple of the mass setting. The usefulness of a particular value of resolution depends on the point at which peak width is measured. Two definitions
Fig. 10. Arrangement of quadrupole analyzer rods.

Fig. 11. Twentieth Century Q806 quadrupole on flange.
are commonly used, peak width at 5% peak height (equivalent to 10% valley between equal peaks) or peak width at 50% peak height. For the nearly triangular peaks produced by a quadrupole analyzer unit mass resolution (1M) at 5% is approximately equivalent to a resolution of 2M defined at 50% peak height. However, of much greater significance for quantitative measurement is the degree of overlap between peaks caused by the departure from perfectly triangular peaks. Imperfections in rod geometry due to the use of rods of circular rather than the ideal hyperbolic cross-section, to manufacturing tolerances and to the limited number of RF cycles occurring during the ion flight along the axis all contribute to precursors and tails at the start and finish of each peak. In theory a resolving power of 2M (50% definition) should just give complete separation between adjacent peaks of successive integral mass but in fact this is not achieved in a practicable analyser. The value of U/V cannot be increased indefinitely to improve resolving power which reaches a limiting value determined by the assembly tolerances and ion entry conditions such as the diameter of the entrance aperture, angle of ion path to the axis and mean ion velocity. The effect of these limitations is most noticeable at the top of the mass range where, as the resolution is increased, a sharp drop in ion transmission occurs.

The instrument used in the CAP project was a prototype version of the 20th Century Electronics Q806. This used rods of 6mm diameter, 125mm long and was capable of approximately unity resolution (5% valley) over the mass range 0-300 amu. It was supplied with a control unit which enabled a fixed mass setting and resolution to be chosen, or alternatively, the mass setting could be scanned repetitively over any part or whole of the range at rates up to 100 scans per second. This scan cycle could be triggered either internally or externally.

The Q806 quadrupole was used for the first part of this work until the opportunity to fit a better instrument arose. It was mounted by its entrance flange onto and insulated from the removable flange carrying the ion lens system and the differential aperture which formed the boundary between the two stages, the analyser being in Stage 2. This greatly simplified alignment of the analyser and lens. The analyser is shown, mounted on this flange in Figure 11.
The rectangular box on the exit flange contains the ion detector. The analyser was originally fitted with an electron beam ion source but as the ions were produced externally in this work the source components were removed. Connections to the mass analyser were made through the rear flange of Stage 2 and the small RF generator box (RF head) of the analyser was mounted on the outside of this flange.

During the early stages of the work the supply of an improved mass analyser was discussed with VG Isotopes Ltd. and an order placed for a VG type 12-12S instrument which was subsequently fitted to the system in July 1980. This has a larger rod system, using main analysing rods of 12mm diameter, 220mm long. A set of short rods 25mm long is mounted at each end of the main rods on the same axis which act as entrance and exit filters. These rods are fed with only the AC potential so that their main effect is to control the fringe fields which otherwise occur at the field discontinuities at the ends of the analysing rods. The design of this analyser is similar to that described by Brubaker (34). The effect of the increased rod length and the entrance filter is to maintain good ion transmission up to higher masses, the normal range being 0-800 amu, and to provide a higher resolution of better than 2.5M (50%) peak height) over this mass range. In addition the better control of the fringing fields and ion entry conditions possible with this design greatly reduces the precursors and tails of the peaks so that the contribution of a peak to adjacent peaks at unit mass separation, the abundance sensitivity, is between $10^{-5}$ and $10^{-6}$ of the peak height. The larger diameter of the centre path between the rods also provides a higher total ion transmission than obtained with the smaller quadrupole.

Because of the larger size and weight of the 12-12S rod assembly it was not possible to support it from the internal flange between the stages and it was mounted instead on a flange plate which formed the end plate of Stage 2. The 12-12S quadrupole on its flange is shown in Figure 12.

The control units of both quadrupole analysers were remotely mounted. That of the Q806 was contained within a single 19 inch rack unit but the 12-12S required much larger power supplies and these were mounted in the base of a 6 ft 19 inch rack while the scan control and RF-DC unit were mounted at the top of the rack, remote from the 50Hz humfield of
the large transformers. The RF generator of the 12-12S was also much larger and was contained in a free standing case which needed to stand close to the end flange of Stage 2.

Ions were admitted to the rod systems through a circular aperture in the entrance plate of 3mm diameter in the Q806 and 5mm in the 12-12S. Both quadrupoles were fitted with a pole bias facility which enabled the mean DC rod potential with respect to earth to be varied. It was found in the earlier work that it was desirable to maintain this at between \(-2\) and \(-4\) V for optimum ion transmission and unless the entrance plate was similarly biased the transmission was greatly reduced. This was accomplished by changing the potential of the analyser body in the Q806 which was mounted on insulators from the vessel. This was too difficult with the larger 12-12S quadrupole so the entrance plate was isolated from the body and individually biased. It was also found advantageous to supply pole bias to the pre and post filter rods independently of the main rods. A bias level of a few volts negative on these rods increased signal levels by up to a factor of two.

Fig. 12. V.G.Analytical 12-12S quadrupole.
3.3 Ion Detector

In the original work a Mullard channel electron multiplier was used as an ion detector in the pulse counting mode. This operated at an electron gain of about $10^6$ at about 3.5kV EHT. Thus, for a single ion impact at the mouth producing an electron, a charge pulse of about $10^{-11}$ coulomb was produced at the output. This was fed to a pulse amplifier, pulse height discriminator and then to conventional pulse counting equipment.

This system worked well at ion counting rates up to $10^4$ counts.sec.$^{-1}$. Above this the integrated pulse current drawn through the resistive channel of the multiplier was sufficient to produce a significant drop in potential at the low potential end of the channel. This reduced the gain and thus the output pulse height resulting in counting losses at high rates as more pulses failed to reach the discriminator threshold.

In the re-assembled system a high current channel electron multiplier was therefore fitted, the Galileo Type 4800. This may be seen in Figure 13 mounted in a screened enclosure on the end of the quadrupole analyser. This multiplier was able to maintain its gain to more than $4 \times 10^7$ (at 3kV) at rates up to $10^6$ counts.sec.$^{-1}$. The multiplier was normally operated at its maximum EHT of 3.5kV at which the random background count in the absence of ions was well below 1 count.sec.$^{-1}$. Channel electron multipliers can tolerate repeated exposure to air in the absence of EHT. A discharge can occur, damaging the multiplier if EHT is left on at pressures above $10^{-2}$ Pa. A vacuum trip was therefore arranged to switch off EHT above $3 \times 10^{-3}$ Pa (approximately $2 \times 10^{-5}$ torr).
Fig. 13. Galileo CEM ion detector Type 4800 in screened housing.
3.4 Electronic and Control Equipment

Vacuum pumps and gauges were supplied with power from a mains distribution board mounted on the pump bench. A trip facility on the Stage 2 Pirani gauge was used to control supplies for channel multiplier EHT, ion lenses and quadrupole analyser which cut these off above $3 \times 10^{-3}$ Pa ($2 \times 10^{-5}$ torr). The supply for the pulse counting equipment was fed through RF filters to reduce the effect of stray noise on mains lines.

Variable potentials for the ion lens elements were provided by a series of stepped potential dividers fed by an Ortec Type 446 EHT unit. These dividers each consisted of a chain of 20 1MΩ resistors, the tapping point being selected for each element by a 20 way switch. Up to 1kV could be used across the dividers to give 50V steps but more usually 300V or 600V was used, giving 15V or 30V steps. For elements beyond the differential aperture the supply was reduced by a divider to give 1V or 2V steps.

Pulses from the ion detector were fed by coaxial cable to a pulse amplifier and discriminator which produced a standard output pulse for every input pulse which exceeded the discriminator threshold. Initially a Galileo Type PAD 400 was used suitable for rates up to 8 MHz. The output of this was fed to the ratemeter used in the original work, Nuclear Enterprises Type 5401. An analogue output from this was available to drive an X-Y plotter or recorder. When it became possible to interface the system to the multichannel scaler data system that had been ordered the Galileo amplifier-discriminator was not able to feed ratemeter and data system in parallel. It also was evident that a higher rate capacity in the ratemeter was desirable. It was decided to change to NIM modules to provide better flexibility and the system evolved to comprise the final components shown in Table 2. These provide

(a) a log/linear ratemeter display for easy optimization of focusing potentials, etc.

(b) a timing scaler display for direct reading of integrated counts in fixed ion monitoring.

(c) a multichannel scaler data system for spectrum accumulation, storage, display and computation.
Table 2.

Pulse Counting Equipment

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Amplifier Type 9302</td>
<td>EGG Ortec Ltd., Bracknell, Berks.</td>
</tr>
<tr>
<td>Ratemeter Type 449</td>
<td>John Caunt Scientific Ltd.</td>
</tr>
<tr>
<td>Scaler Timer Type 776</td>
<td>Eynsham, Oxford.</td>
</tr>
<tr>
<td>NIM - TTL Interface</td>
<td>Cannabis Instruments Ltd.</td>
</tr>
<tr>
<td>Multichannel Analyser and Scaler</td>
<td>Farringdon, Oxon.</td>
</tr>
<tr>
<td>Series 80 with TTY and X - Y</td>
<td></td>
</tr>
<tr>
<td>Plotter and cassette data storage.</td>
<td></td>
</tr>
<tr>
<td>8192 Channels.</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 14. Block diagram of pulse counting system.
(d) a linear output from the pulse amplifier which enables the nature and level of interfering signals to be observed on an oscilloscope.

The final system is capable of accepting and correctly quantifying input pulse rates of over 10 MHz. A block diagram of the counting system is shown in Figure 14.

3.5 Data System

Although in principle quantitative measurements could be made by tuning the mass analyser manually to the peaks of interest and integrating the pulse signals obtained this requires a very high degree of stability in the whole system. It is preferable to scan the mass analyser setting through the range of interest. If this is done slowly the analogue output from a ratemeter may be fed to the Y amplifier of an X-Y plotter to the X amplifier of which is fed the scan programme potential from the mass analyser control. The first few spectra plotted directly on the system were obtained in this way (Figures 31 and 32).

Since a pulse output is directly available, the rate of which is proportional at any instant to the rate of ion arrival at the detector, the system is readily interfaced to a multichannel digital store if the address corresponding to any particular mass setting can be derived from the mass analyser control. This may be achieved in a variety of ways, the most flexible being to use a small computer dedicated to this task of multichannel scaling. However, once the spectrum is stored in multichannel form in the memory considerable advantages can be gained by using microprocessor facilities to process the data and read out that of interest. These functions are normally provided in hard wired form in the sophisticated multichannel analysers developed for X ray and gamma ray analysis. Most of these analysers can also operate in a Multi Scaler mode in which, when the scan is initiated, the input pulses are directed for a fixed period, the dwell time, to successive memory channels in turn, throughout the scan period.

For this work a Canberra Series 80 Multichannel Analyser was chosen. This will operate as a Multi Scaler at data input rates up to 20 MHz. It has a memory capacity of 8192 channels, each capable of storing $10^6$
counts. This memory may be subdivided in units of 256 channels. In the
chosen mode memory groups of 1024 channels were used usually with a
dwell time of 1 millisecond. Thus a full memory scan took 1.024 seconds,
a convenient scan time for the mass analyser. When used with the Q806
analyser the data system scan was initiated by a synchronizing pulse
derived from the mass analyser at the start of each scan. Used with
the 12-12S mass analyser the data system scan was used to initiate the
mass scan. In either case it was necessary to adjust the two scans to
the same length so that the mass spectrum filled the display screen.
The multichannel analyser could be set to provide any desired number of
scans after the 'Accumulate' button was pressed. Normally 60 scans
were preselected so that the integrating time for any given spectrum was
just over 1 minute. Once the spectrum was accumulated in the active
section of the memory it could be transferred to any of three other
groups for subsequent processing, display readout or comparison on the
screen. Readout of the contents of each channel could be achieved either
on to magnetic tape for permanent storage through a cassette recorder
or on to a teletype printer. Regions of interest could be set by strobe
markers around any number of wanted peaks and the teletype output
limited only to these. The spectra stored in any memory group could be
plotted out in analogue form (as seen on the screen) on an X-Y plotter.
Spectra stored on tape could be read back into the analyser at any time
for further examination or readout.

During system development the mass analyser was usually set to scan 0-100 u
so that a single mass peak would occupy 10 channels. This provided good
peak profile on the screen whereas a scan of 0-250 u would only provide
4 channels per peak. In any case a scan as wide as this is rarely used
as it produces great congestion in the crowded regions of the spectrum.
In the normal scan where 10 channels are available for each span of 1 u
the total integrating time on any single isotope peak is only 0.6 sec.
out of the total time of 1.024 minutes for 60 scans. This emphasizes
the problem of time sharing across the spectrum in a scanning system.
However, this only affects the total integrated count for each peak, and
hence its statistical precision. It does not affect the visibility of a peak above the surroundings since the peak height in the display is
not increased if more channels are devoted to it, only its width. A
wide scan is useful therefore when searching for unknowns. The scan
may then be narrowed when better precision is required for signal/back-
ground ratio. This may be simply achieved by reducing the scan width set on the mass analyser.

The flexibility of this data system greatly simplified the work since spectra could be accumulated during a run and analysed later. During the early stages of the development its use was mainly for comparative purposes but later it became of great value in producing quantitative results.
3.6 The Inductively Coupled Plasma System

The ICP system chosen for this work was the ICP 2500A made by Plasmatherm Inc. of Plainsville, N.J., USA. It is equipped with automatic power level control which keeps the power fed to the plasma to within ±1% of the level chosen between about 0.5Kw and 2.5Kw. Automatic matching is also provided so that changes of load due to the addition of sample to the plasma are automatically corrected. The operating frequency is crystal controlled at 27.12MHz. The system was received in the form used as an optical emission source and consisted of an RF generator contained in a 6ft rack and the plasma unit which was connected to the generator by cables 4m long. This plasma unit consisted of two sections, the torch housing which contained the quartz plasma torch and beneath it the pneumatic nebulizer, and the matching unit containing the RF matching circuit and the servo controls for automatic matching. In normal use the plasma is viewed through windows in the torch housing. However, for this work access to the torch was required so the housing which provided RF screening and also contained the gas flow controls was removed and located separately on the pump bench. This left the torch in its coupling coil mounted vertically on the side of the matching network. Initially, at the suggestion of the manufacturers, a small screened housing was made for the torch so that it could be mounted remotely from the matching system and a short length (0.5m) of high power RF cable used to connect the two. This enabled the position of the torch to be adjusted in relation to the vacuum system by means of a simple translation device. However, it proved impossible to match the system properly with this design and the torch was remounted in a small housing on the side of the matching box in its original vertical position. In order to permit the closest approach of the screening box to the exciting coil, which was mounted around the mouth of the torch just inside the hole in the screen which allowed the flame to leave the box, the coil was rewound in the opposite sense so that the high potential end was remote from the earthed screen. The plasma operated well in this position with negligible reflected power up to 2.5Kw. The modified system is shown with the cover of the screening box removed in Figure 15 and with a plasma flame emerging from the aperture in the top of the box in Figure 16. With this arrangement it was necessary to move the whole matching network in order to position the torch correctly and this was achieved by mounting it on an optical bench as shown in Figure 17.
Once this was made to operate correctly this system was used throughout
the work although in order to provide different torch orientations in
relation to the sampling system a number of mounting positions and torch
housings were used. Most of the work was done with the torch mounted at
30° to the horizontal as shown in Figure 18.

Gas supplies were provided from standard argon cylinders. For most of
the work high purity argon was used but in the presence of the large
quantity of water vapour from the nebulizer no disadvantage could be seen
with commercial grade argon. Four cylinders were used in parallel to pro-
vide an adequate reserve. Initially, a two stage gas regulator was used
to drop cylinder pressure to the working pressure of 40 psig. However,
for added stability a precision regulator was later introduced for the
final reduction from 150 psig to 40 psig which reduced pressure variations
over the life of the cylinders to below 0.1 psig.

Details of the plasma system, torch and gas supplies are given in Table 3.

Table 3

Inductively Coupled Plasma System

Model ICP 2500 with APCS - 1 Automatic Power Supply and AMN - 2500E
Automatic Matching Network. Output Power 2500 watts. Crystal contr-
rolled at 27.12 MHz.

Plasma Torch Type T1.0. Load coil 3 turns ½" dia. copper tube, water
cooled.

Plasmatherm Ltd., Penge, London, SE20 7BQ.
Fig. 15. Plasma torch housing showing torch in vertical position.

Fig. 16. ICP flame emerging from housing.
Fig. 17. Plasma RF matching box and torch housing on optical bench.

Fig. 18. Housing with torch mounted at 30° to horizontal.
3.7 Sample Nebulizer and Desolvator

In conventional applications of the ICP sample is introduced from solution into the central carrier gas stream by means of a pneumatic nebulizer. A cross flow nebulizer of the type described by Kniseley et al. (38) was supplied with the plasma system and this was used in the first experiments. In this design the argon flow from a capillary tube is directed across the mouth of a second capillary at right angles to it, the lower end of which is fitted with a capillary plastic tube which dips into the sample solution. The suction created by the gas jet across the tip of the sample tube draws sample up into it which is dispersed in a fine spray by the jet. Both tubes are adjustable in position in the PTFE base and their relative position is critical to the production of a good sample mist. The adjustment is best done by observing the mist in free air. Although when correctly adjusted this nebulizer gave an adequate performance it was found to be tricky to adjust and prone to drift out of adjustment so that its performance could not be relied upon. It was therefore only used in the initial tests and was soon replaced by a non adjustable concentric glass nebulizer of the Meinhard type which was found to be far more stable. This nebulizer, however, has very fine annular clearances around the sample tube and the sample tube itself is a very fine capillary. It was found that dust particles and minute fibres caused blockages of the nebulizer so that sample delivery varied. Once blocked it was very difficult to clean because of its delicate all glass construction. It was replaced in turn after a few months of use by a new cross flow nebulizer marketed by Jarrel-Ash which had a fixed geometry and which proved both robust and stable. Occasional blockages still occurred caused by airborne dust particles or minute hairs settling on the solution but these were very easily cleared by applying back pressure to the uptake tube. Once introduced this nebulizer was used continuously for the remaining 18 months of the work. All three types of pneumatic nebulizer operated at gas pressures of between 20 and 50 psig giving a gas flow into the torch of between 0.5 and 1.0 l.min\(^{-1}\). Sample uptake varied between about 1.2 ml.min\(^{-1}\) at the lowest pressure to between 2.5 and 3 ml.min\(^{-1}\) at the highest pressure used. However, the signals observed did not increase linearly with uptake rate and it was suspected that at the higher rates the efficiency of nebulization became poorer, probably due to the formation of larger droplets which did not reach the plasma. It was usual therefore
to operate at uptake rates of 2 ml.min\(^{-1}\) or just lower. Apart from stability and freedom from blocking mentioned above there was little difference in performance between the nebulizers. All were fitted into the same type of PTFE base which fitted on the end of the Scott cloud chamber which was supplied for the original cross flow type. This provided an indirect path to the outlet to the plasma to allow larger drops to settle out and run into the drain.

These cross flow nebulizers are very convenient to use as they are self-aspirating and samples may be changed merely by transferring the uptake tube to a fresh container. This makes operation with an automatic sample changer very simple. All pneumatic nebulizers, however, are very inefficient. At convenient gas pressures and jet sizes reasonably free from clogging, most of the sample is carried in droplets of about 30|μm diameter. These are too heavy to travel far in the gas stream and fall out in the cloud chamber. Only droplets of 4|μm diameter and smaller are generally accepted as able to reach the plasma in the carrier gas and these only carry about 2% of the total sample volume (36).

Considerable attention has been paid to more efficient ways of generating aerosols of the small droplet diameter required. Several designs of ultrasonic nebulizer have been described which are up to 10 times more efficient and one of these (37) was used in the Ames Laboratory ICP-MS project (Chapter 1.5). This design may be fed to the sample solution by peristaltic pump so that it can match the pneumatic type in convenience but it is very much more costly. Batch type ultrasonic nebulizers are simpler (38) although less convenient but still provide a much higher sample delivery rate than a pneumatic nebulizer. One of these was used in the CAP programme (18). A similar nebulizer was constructed for this programme (39) by A.R. Date, using mainly standard ground glass jointed parts. The ultrasonic generator and transducer were a self contained unit made for respiratory therapy and were mounted in the base of a cup, normally filled with water to be nebulized. For use with an analyte a cloud chamber, closed at the bottom by a Mylar film containing about 10ml of sample, fitted into this cup so that the ultrasonic energy was transmitted by the intermediate water through the Mylar into the sample. The mist generated above the sample was swept out of the cloud chamber by the carrier gas flow which could be adjusted independently of the nebulization process.
For use with small sampling apertures when an intermediate boundary layer was formed between plasma and aperture, both pneumatic and ultrasonic nebulizers were used with a desolvation stage to remove as much water as possible from the mist leaving dried microparticulates to be carried to the plasma. The output tube from the cloud chamber from either type of nebulizer was coupled by a ball and cup joint to a glass heating tube 30 cm long. This and the joints at both ends were wrapped in a heating tape controlled by an energy regulator. At the full power setting the temperature of the gas leaving the tube was just over 100°C. The gas was then passed through a water cooled condenser and then to the plasma torch. Condensed water was collected in a small receiver at the lower end of the condenser.

The ultrasonic nebulizer and desolvator are shown in Figure 19 and the alternative pneumatic nebulizer and Scott chamber in Figure 20, also with the desolvator. Details of the nebulizers are given in Table 4 together with the normal operating parameters.

Measurements of the performance of the ultrasonic nebulizer and desolvator were made by A.R. Date (39). Continuous operation with an initial volume of sample of between 10 and 15 ml was possible for a period of 60-80 minutes with an aerosol output of 0.15 ml min⁻¹. In contrast at 2% efficiency a typical pneumatic nebulizer would deliver about 0.04 ml min⁻¹ to the plasma. The desolvator removed approximately 75% of the water vapour and the overall sample transport efficiency from nebulizer to plasma was greater than 60% giving final delivery to the plasma at approximately 0.1 ml min⁻¹.
Fig. 19. Ultrasonic nebulizer and desolvator.

Fig. 20. Pneumatic nebulizer and desolvator.
### Table 4

**Nebulizers**

1. **Ultrasonic Nebulizer**

   - **Transducer.** Transducer Assembly for Monaghan M250. Sandoz Products Ltd. Rugby, Warwicks.
   - **Power Supply.** Weir Type 430, 0 - 30V 2A.
   - **Glassware.** Exelo or Quickfit.
   - **Mylar Film.** Spectro-film 0.00050" (<13μm) Polaron Equipment Ltd., Watford, Herts.

2. **Crossflow Nebulizer (adjustable)**

   - **Type TNI.** Plasmatherm Ltd. (see Table 3)
     - Uptake 3.2 ml.min⁻¹ at 0.93 l.min⁻¹ argon.
     - Operating pressure 14 psig.

3. **Concentric Nebulizer (Meinhard)**

   - **Type GN1.** Plasmatherm Ltd. Uptake 1.65 ml.min⁻¹ at 1.03 l.min⁻¹ argon. Operating pressure 24 psig.

4. **Crossflow Nebulizer (fixed)**

   - **Type 09-790.** Jarrel-Ash Co., Waltham, Ma., USA. Uptake 1.53 ml.min⁻¹ at 0.5 l.min⁻¹ and 22 psig.
   - 2.30 ml.min⁻¹ at 0.65 l.min⁻¹ and 30 psig.

5. **Cloud Chamber**

   - **Scott Chamber Type Sc-2.** Plasmatherm Ltd.
3.8 Sampling Cones and Apertures

In order to extract ions from the central channel of the ICP flame it is necessary to position the small aperture, through which the gas sample passes, in the centre channel while causing the minimum disturbance to the flowing plasma. As in many chemical flame studies this is done by using an aperture in the tip of a cone, typically of 60° internal angle (40). The difference between the ICP and chemical flame studies is that although the flames are of similar volume and flow velocity the temperature of the gas to be sampled may be between 5000K and 10,000K whereas the highest chemical flame temperature is 3000K. Ideally the sampling aperture should have a thin edge, of a thickness less than the diameter, but such a thin section where aperture diameters are 0.1mm or less is very fragile in gas temperatures so far above the melting point of any material. Hayhurst (41) for flames of up to 3000K, used cones of electroformed chromium (melting point 2173K) and cones of this type were tested in the CAP programme where the DC plasma gas temperatures were 3000-4000K. They were not found very satisfactory, however, and appeared to be prone to catastrophic melting to larger diameters no doubt partly due to the negative temperature coefficient of thermal conductivity which contributed to a runaway situation. For that project a solution was found in the use of commercially available apertures of 50μm and 70μm diameter mechanically drilled in platinum discs of 2mm diameter and 0.5mm thickness. These are manufactured for electron microscope lenses and have an extremely high finish. The section of these aperture discs, of the type marketed by Agar Aids Ltd. is shown in Figure 21. Although the melting point of platinum (2042K) is slightly lower than that of chromium the discs were swaged into the tip of a sampling cone made of copper which enabled the disc temperature to be stabilized at about 600K although the thin edge of the aperture was normally much hotter. These apertures were found to be reasonably durable although catastrophic melt out could still occur if faulty thermal contact with the copper developed. The base of the copper cones was clamped to the thermal mass of the Stage 1 vessel and no water cooling was needed.

For this work the same approach was adopted but apertures of the same design made in molybdenum were used, also from Agar Aids. Molybdenum was chosen because of the higher melting point (2893K) in view of the
higher ICP temperature. Although of higher thermal conductivity than platinum this does fall as the temperature rises and molybdenum is more reactive than platinum. Although a large part of the plasma gas consists of argon the addition of the water from sample solutions introduces some 20% by volume of hydrogen and oxygen so oxidation is a possible cause of aperture damage in molybdenum. Again the apertures were swaged by hand into a recess in the tip of a copper cone. Initially cones of 60° internal angle were used but later, as described under experimental work, cones of 90° and 120° were used, the final choice being the 90° type. Whatever the angle the cones were turned from solid commercially pure copper with a 62.5mm diameter base which fitted into a recess in the water cooled mount on the slide valve on the front of Stage 1. Sections of typical cones are shown in Figure 22 and a view of a cone and aperture in Figure 23.

The apertures used were of diameters 50µm, 60µm and 70µm. As discussed under experimental work, larger apertures of this type could not be used without instant burnout. However, reasonably satisfactory performance was obtained with 70µm molybdenum apertures, aperture lifetimes of up to 10 hours being regularly obtained. Alternative aperture profiles, material and supplies were all sought at some length but at these diameters the refractory materials with desirable thermal properties are particularly difficult to drill with holes of good profile. The most promising alternative materials appear to be iridium or possibly an insulator, sapphire. These may be more suitable for a long term solution if small apertures are to be extensively used.

The properties of possible aperture insert materials are shown in Table 5.

While the 70µm apertures were used under sampling conditions which created a boundary layer across the aperture itself for a considerable part of the work, it was found, as described in Chapter 4.4, that conditions could be established in which operation with apertures of up to 400µm diameter was possible. At this diameter the holes are very much easier to drill as the drills are more robust. In addition, however, because of the greater thickness of the aperture edge that is tolerable at these diameters it is possible to use apertures drilled in lower melting point materials. It was found possible to use cones of copper, nickel, stainless steel and other materials such as the nimonic alloys, into which the
aperture was drilled direct at the tip. Because of the much larger gas flow through these large apertures and the close proximity of the skimmer to the internal cone surface internal cone angles of up to 120° were used to provide a larger pumping path. These cones were mounted on the water cooled front plate of the additional expansion stage, just as for the cones employed for boundary layer sampling. The cross sections of two different types of cone used for continuum sampling are shown in Figure 24.

Fig. 21. Cross section of aperture insert.

Fig. 22. Section of boundary layer sampling cones.
Fig. 23. $60^\circ$ Boundary layer cone and aperture insert.

Fig. 24. Cross section of continuum sampling cones.
### Table 5

**Aperture Insert Materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>M.P.</th>
<th>Thermal Conductivity $^\circ$C</th>
<th>Oxidation Resistance</th>
<th>Machinability</th>
</tr>
</thead>
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<tr>
<td>Platinum</td>
<td>1772</td>
<td>0.69</td>
<td>high</td>
<td>good</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2617</td>
<td>1.4</td>
<td>low</td>
<td>poor</td>
</tr>
<tr>
<td>Tantalum</td>
<td>2996</td>
<td>0.54</td>
<td>high</td>
<td>poor</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3410</td>
<td>1.66</td>
<td>high</td>
<td>v.poor</td>
</tr>
<tr>
<td>Iridium</td>
<td>2410</td>
<td>1.47</td>
<td>high</td>
<td>fair</td>
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<tr>
<td>Rhenium</td>
<td>3180</td>
<td>0.71</td>
<td>mod.</td>
<td>good</td>
</tr>
<tr>
<td>Saphire</td>
<td>2015</td>
<td>0.22</td>
<td>high</td>
<td>poor</td>
</tr>
<tr>
<td>Diamond</td>
<td>3550</td>
<td>10.2</td>
<td>low</td>
<td>poor</td>
</tr>
</tbody>
</table>

**Aperture Inserts and Suppliers**

- **Type A208M**
  - 50, 60 or 70 μm, Molybdenum
  - Agar Aids Ltd.
- **Type A02 P**
  - 70 μm, Platinum
- **Special Long Bore**
  - 70 μm, Platinum
  - Stansted, Essex.
- **Type 1**
  - 50 or 70 μm, Molybdenum
  - Polaron Equipment Ltd., Watford, Herts.
3.9 Expansion Stage

As described in the following chapter (4.4) it was shown that operation with large apertures up to 0.4mm diameter should be possible if a pressure of about 100 Pa (1mb or 0.75 Torr) could be maintained behind the aperture to quench the pinch discharge. At this pressure only a short ion path could be tolerated and the wanted ions should be rapidly extracted through a differentially pumped aperture into a lower pressure region if a reasonable number were to survive for mass analysis. The design of supersonic beam forming expansion stage used in molecular beam experiments is ideally suited for this purpose although normally used at rather lower pressures (42). However, use at these higher pressures had been proposed in order to enable only modest pump capacities to be used (43,44) and during the course of this work it was disclosed that such a stage had been used to sample ions from a microwave plasma (45,46).

Accordingly such an expansion stage was built along the lines described in the literature but because of the higher pressure at which the majority of the incoming gas was to be pumped away the overall dimensions were kept very compact. The stage is shown in section in Figure 25. The sampling cone and aperture is mounted on the brass water cooled front plate. The cylindrical case was fabricated from copper sheet and brazed to the front and rear flanges. The rear flange was mounted on a base plate which in turn was carried on a sliding valve plate which could replace the valve plate used to carry the cone mount for boundary layer sampling. This meant that the valve could be closed by moving the plate to one side. Since the expansion stage was pumped by its own rotary pump to the required pressure once the valve was closed it could be let up to air for modifications while leaving the main vacuum system still operating at low pressure. This facility was very important since the correct internal geometry could not be fixed on paper and a range of skimmer sizes and mounting positions was provided. Skimmers of internal angle of 55° were machined from stainless steel and nickel and a commercial type of electrodeposited nickel was also used. A range of skimmer openings were provided from 0.5mm to 2mm diameter and the skimmer to aperture spacing could be varied by interposing spacing rings from 20mm to zero. Skimmers were mounted on an insulated base so that bias could be applied, but later a metal base was also used as bias was found unnecessary and it gave better heat transfer.
O-rings were used to seal all joint faces. Great care was used to maintain concentricity of the sampling and skimmer apertures in all operating positions to better than 0.1mm. After the initial trials an extraction electrode was added inside the base of the skimmer to improve ion collection and later an insulator provided between the body of the stage and the slide valve so that the whole stage could be biased with respect to the system earth.

The stage was pumped by an Edwards EDM20A rotary pump of 342 l.min\(^{-1}\) capacity through a 25mm diameter side tube. A flexible rubber section allowed for the movement of the valve. The pressure was measured by an Edwards TCI thermocouple gauge.

The expansion stage is shown in Figures 26 and 27.

Fig. 25. Expansion Stage
Fig. 26. Expansion stage.

Fig. 27. Interior view of expansion stage.
CHAPTER FOUR

EXPERIMENTAL WORK
4.1 Initial Exploration of Plasma Behaviour and the Problems of Ion Extraction

As mentioned in Chapter 1.5 the opportunity to visit the ICP-MS project at the Ames Laboratory in Iowa provided a useful occasion to examine the phenomena occurring when a metal sample cone was introduced into the ICP flame for the purpose of extracting a gas sample into the vacuum system. At the Ames Laboratory the ICP system in use (32), very similar to the type used in this work, was a commercial version of that originally developed (22,24) at Ames for ICP-AE work. In such a system RF power, at 27.12MHz, is fed to a coupling or load coil of a few turns round the plasma torch through an automatic matching and tuning network. At power levels of 1 or 2Kw very large RF voltage swings are involved at the live end of the load coil which is normally grounded to the system chassis at its lower end, the end furthest from the mouth of the torch. When the system is operating the stable plasma fireball in the mouth of the torch and the tail flame that projects from it are electrically floating. The plasma is of course an excellent conductor and it remains a relatively good conductor by virtue of the high electron population for distances up to 20cm or more from the mouth of the torch. The first part of the flame which emits strongly in the visible region from argon recombination extends between 2 and 5cm from the torch according to the operating conditions but the remainder of the flame is still intensely hot and emits in the UV region unless elements with strong visible emissions are added when its full extent may be seen. A photograph of such a plasma flame is shown in Figure 28 where yttrium is nebulized into the plasma. Yttrium atoms and ions emit strongly in the blue-green and UV regions and where air is entrained in the flame the red band emission of yttrium oxide is also seen.

Such plasmas have long had the reputation of being difficult to approach, any object incautiously held near the flame is likely to draw an RF spark and nasty RF burns can be received by a careless user. However, this lively reputation is quite understandable if the electrical situation is considered. Quite apart from the fact that RF sparks can be produced within the screens of any operating RF power oscillator by careless intrusion, the conducting flame provides an effective RF antenna which is capacitively coupled through the torch wall to the live end of the
load coil which may well be oscillating at an amplitude of several kilovolts. As long as the flame is remote from any other conductor it has a low capacitance to ground and its RF potential is close to that of the live end of the coil. As it is approached by a conductor the RF potential distribution changes, depending on the capacitive or resistive path to ground. As long as the approach is in the remote part of the flame from the coil the effective capacitance of the sheath which forms over a surface introduced into the flame is less than that between flame and load coil and most of the potential drop is across the flame to surface gap which usually results in a strong RF spark. If, however, a grounded (and cooled) metal object is placed with a considerable area in contact with the flame near the torch mouth the impedance to the object from the flame is low and little sparking occurs. The potential drop occurs mainly across the torch wall between plasma and coil.

The early experience at Ames involved a slow approach of a sampling cone from some distance, a very natural strategy, but the consequence was a steady and spectacular discharge to the cone tip (shown in Figure 29). If the cone contained an aperture leading into the vacuum system this was often the site of a glow discharge (47) as the pressure of the gas dropped in the vicinity of the aperture. Once the situation was realized, however, the pyrotechnics were avoided and no serious problems in this work were found with placing sampling cones right up into the mouth of the torch, provided precautions were taken appropriate to operating close to high power RF conductors. Much more serious was the problem caused by circulating induced RF currents in the system structure. To allow close approach to the plasma flame it was necessary to modify the screening box round the torch and load coil, and this meant that there had to be a circular access hole at the torch mouth close to the coil (Figure 15). This represented an RF leak from the otherwise tightly screened housing which in normal use was only penetrated by an optical window usually screened with wire mesh. RF pick up on the sampling cone introduced severe noise into the counting system and quadrupole control circuits and had to be reduced. It was found helpful to reverse the load coil so that its live end was remote from the cone, and essential to provide a short low impedance path between the sampling cone mount and the torch screen near the torch mouth. Provided that this was done so that all systems had a common ground and sensible screening of signal cables was observed, the RF noise could be reduced to tolerable levels.
Fig. 28. Plasma flame while yttrium is nebulized. Y and Y⁺ emission - blue, YO emission - red.

Fig. 29. Discharge from torch to cone tip. (taken at Ames ICP-MS project).
It was found desirable also to decouple to ground with capacitors any electrodes inside the vacuum system near the sampling aperture. An unplanned advantage of the original vacuum system for this new work was the fact that the first stage closest to the plasma had thick aluminium walls, much better for RF shielding than the usual stainless steel vacuum vessel.

Thus once the ICP was delivered and modified it was found quite straightforward to approach it, when operating, with a sampling cone and insert the cone into an appropriate part of the flame. Initially the plasma torch was used in its original vertical position and the sampling cone introduced at an angle of 60° to the torch axis, as in Figure 30 so that the intense photon emission from the plasma would not produce an unacceptable background signal.

For the first experiments sampling cones of 60° internal angle (Fig. 22) were used. At first these were fitted with 50μm molybdenum apertures. When the cone was moved into the plasma flame a small RF arc occurred, just as the cone surface reached the visible part of the flame, as the plasma adjusted to the presence of the electrically grounded surface, but this quenched immediately the cone was immersed in the flame.

With the first two aperture inserts tried it was found that once fully inserted into the flame a very small but intensely bright visible discharge occurred at the aperture (47). Although the pressure in the first stage initially fell to 2.6 x 10⁻² Pa once hot argon was entering, after a few minutes the pressure began to rise to unacceptable levels above 1.3 x 10⁻¹ Pa as the aperture eroded. When removed for examination the apertures were found to have eroded to between 100μm and 150μm diameter, the holes being perfectly round and smooth with evidence of melt material on the inner surfaces. At the time it was thought that this was a consequence of the discharge in the 'pinch' as the gas entered the aperture but further work has suggested that the two phenomena are not cause and effect but rather that the 'pinch' discharge occurs after the aperture has started to enlarge and has reached a critical diameter. It was initially realised, however, that the erosion of the aperture was probably the result of simple thermal melting due to inadequate heat transfer between the insert and the sampling cone even though the source of
heat was not properly identified. Because of the aperture profile (Fig. 21) heat from the incoming gas must flow first through the thin lip at the edge of the aperture and adequate thermal contact to the base and outer circumference of the insert is vital. Much greater care was taken over the insertion of the next aperture to ensure that it was properly seated in its recess and that the copper around its edge was properly in contact, although it was also realised that because of the relative coefficients of expansion of copper and molybdenum this contact could deteriorate as the cone tip was heated. However, although this may have contributed to some instances of aperture failure it did not appear to be a major cause and the third attempt was successful. This aperture survived for over 5 hours with periods of up to 1 hour in the plasma at a time, and no pinch discharge developed.

The presence of the substantial grounded metal object presented by the sampling cone in the plasma at distances of as small as 10 mm from the end of the load coil caused no problems with plasma matching. As the cone was brought into the plasma the automatic tuning readjusted slightly and reflected power below 5 watts was normally obtained. It is thought that the very efficient matching system of this type of plasma generator contributed greatly to the general docility of the plasma in this application.

Once a stable aperture was obtained the ion lens potentials were applied and the mass analyzer and detector switched on. After some trials working settings were obtained for the lens potentials (see Appendix 3) and ion peaks were found at masses 40 and 41 from \( \text{Ar}^+ \) and \( \text{ArH}^+ \). Once these were obtained the mass analyzer was set up to scan over a mass range of about 0-100 and coupled to the X scan of an X-Y plotter. The analogue output of the ratemeter was fed to the Y scan and a 10 µg.ml\(^{-1}\) solution of cobalt nitrate in 1% nitric acid nebulized into the central channel gas flow of the plasma from the pneumatic nebulizer. When this was done the spectra shown in Figure 31 were obtained. The upper spectrum was obtained when the cone tip was positioned in the outer annulus of the flame and shows peaks at 19 (OH\(^+_3\) ) and 40 (Ar\(^+\)). These peaks were much smaller in the lower spectrum from the central channel but a large peak of about 1000 Hz was obtained at 59\( _{\text{u}} \) from \( ^{59}\text{Co}^+ \). The ultrasonic nebulizer was then substituted and a similar solution of copper introduced. This gave a spectrum with recognizable copper peaks in about the right ratio at 63 and 65\( _{\text{u}} \) and
Fig. 30. Sampling cone inserted into plasma.

Fig. 31. First spectra from outer annulus and core of plasma flame. 10μg.ml⁻¹ Co. (note scan is non-linear).
in addition large peaks at 19u, 40 and 41u and smaller peaks at 30u, 32 and 33u (figure 32).

It was found that it was usually desirable to position the aperture closer to the torch than the skew cone location permitted so changes were made to mount the plasma torch also at 30° to the horizontal as seen in Figures 33 and 35. This enabled the tip of the cone to be inserted right into the torch mouth as shown. However, an increased background count was found in this new position which was still present when ion lens potentials were switched off. It was therefore assumed to be due to direct photons from the plasma and a small circular light stop was fixed to the aperture mount to cast a shadow from the aperture onto the differential aperture at the rear of the ion lens. This reduced the photon background to a few counts per second. At this time also the scanning mode of the 20th Century mass analyser was first coupled to the multichannel analyser to enable spectra to be rapidly displayed on the VDU. The mass analyser was set to scan for a sweep length of 21 ms and the Canberra MCA set to sweep 1023 channels with a dwell time of 20μs per channel. The MCA sweep thus took 20.46 ms and finished just before the mass sweep, the start of which was used to trigger it. The MCA was set to run for 5000 sweeps taking just over one minute. Because of the high repetition rate the whole spectrum could be seen building up on the screen. At this stage up to three spectra of 1023 channels each could be stored for comparison in the analyzer and could be plotted out on an X-Y recorder or the channel contents could be printed out on teletype. This enabled a rapid visual assessment to be made of the effect of changes to the system.

Once this display system had been set up a series of experiments with sampling cones and apertures was carried out based on 50μm diameter apertures and 60° cones. An incorrectly mounted aperture would burn out immediately but provided it survived the first few seconds of warming up in the plasma the life of a 50μm molybdenum aperture was normally from 2 to 5 hours and apertures would run continuously for this period in the plasma. However, although properly inserted apertures would survive for several hours the signals obtained from the plasma varied markedly from one aperture to another. If water or solution were being nebulized it was also found that after an initial period of level res-
Fig. 32. Spectrum of 10μg.ml\(^{-1}\) Cu using ultrasonic nebulizer.

Fig. 33. Torch at 30\(^\circ\) and cone in normal relative operating positions.
ponse the signal then dropped steadily during the aperture life. It was found that the fall in signal coincided with the build up of an oxide layer on the inner surface of the cone near the tip. In severe cases this layer could be removed as a coherent black film from the inside of the cone tip. The interior of the cones could be cleaned readily either in distilled water in an ultrasonic cleaner or in stubborn cases in dilute nitric acid, but this always left a finely etched surface with the crystal structure very visible. Provided that the aperture was fresh this restored the signal although for a shorter time than for a new cone where the interior surface had been polished. However, it was found that after a few treatments of this nature of any one aperture - cone combination the signal could no longer be restored. This was attributed to oxidation of the molybdenum insert which over the period of several cone use - cleaning cycles became dull pitted and discoloured from its original bright finish, and did not respond to the same type of cleaning as the copper. It was assumed that the presence of the oxide layer on the metal surfaces allowed charges to build up which affected the electric field around the aperture. The eventual end point of aperture life was usually sudden burn out to 125\mu m diameter or more which occurred when the 50\mu m aperture had eroded, apparently by oxidation of the lip, to a diameter of 60 - 70\mu m.

In spite of these difficulties it was often possible to obtain stable operation for periods of a few hours during which the signal from a test solution would remain constant for 1 hour or more within \pm 20%. At this stage solutions of single transition elements in 1% nitric acid were used for trials at concentrations usually of 10\mu g.ml\(^{-1}\). The appearance of the experimental system at this stage is shown in the general view in Figure 34. The RF matching box is seen on the right mounted on an optical bench to provide motion relative to the vacuum system and sampling cone in three directions. On the left is the electronics rack, left centre the gas control box for the plasma and in the centre the vacuum vessel. The plasma torch mounted at 30° to the horizontal in its shielded housing is shown in Figure 35.
Fig. 34. General view of system. Data system is behind camera.

Fig. 35. Complete housing with angled torch.
4.2 Development of Boundary Layer Sampling Performance

Once the initial steps which led to ions being detected and identified from the first crude spectra had been successfully taken, it became possible to attend to the many problems that this revealed.

It was clear that one of the factors limiting cone and aperture life and the stability of measurements were the oxidation reactions occurring between the cone walls and the incoming plasma gas which contained highly reactive atomic oxygen from the nebulized solution.

The ultrasonic nebulizer described in Chapter 3.7 was introduced after the first few experiments with a cross flow nebulizer and the mist this produced was passed through a desolvation stage which removed about 75% of the water content of the droplets. It was found that using this nebulizer the rate of oxidation appeared to be slower even though the signals were about 3 times stronger. Later, however, when the larger quadrupole analyser was introduced a pneumatic nebulizer was reintroduced because of its convenience and because the lower signal levels it gave were by then acceptable. Since, however, it was then coupled to the desolvator the overall rate of water introduction was further reduced. When this change was made the nebulizer initially used was the Meinhard concentric type but later this was replaced by the Jarrel-Ash fixed geometry crossflow nebulizer. Both of these alternatives proved more stable than the initial adjustable jet crossflow type and this improved the system stability. At the same time the argon supply was improved by using four cylinders in parallel which provided greater pressure stability.

Considerable attention was then paid to aperture inserts and the supporting cones. The commercially available apertures, which are cheaply and readily available from UK suppliers (Table 5), although it is believed both buy from sources in the USA, have a similar cross section as shown in Figure 21. For the expansion of a gas jet this is quite a good shape since the diameter opens out immediately behind the aperture in the front surface. However, it was felt that a bore of constant diameter of at least 1 diameter long would provide better heat transfer from the edge and be less prone to catastrophic melting. The possibility of this and
of alternative materials was explored at length. Higher melting materials such as tungsten were attractive but nobody could be found to drill such small holes (50 or 70μm diameter) mechanically and at this stage spark erosion or laser drilling were not thought to give adequate finish, although an ultimately unproductive order was placed for spark eroded holes. At this diameter the standard apertures were only available in molybdenum and platinum but attempts were made to obtain long bore apertures as special orders from both suppliers. Only one of these, Agar Aids, successfully produced such apertures, but only in platinum, and even then took about six months each time an order was placed. However, the apertures they did produce of approximately 250μm long and 70μm diameter proved invaluable in spite of the lower melting point of platinum. Little could be done for the molybdenum apertures, however, except to replace them when they developed a pitted black surface coating. However, with care in seating the inserts in the cone tip it was found that it was possible to use routinely the larger apertures of 70μm diameter which gave a welcome increase of about 4 times in signal.

Since the heat input from the plasma flame was constant at any given power and working point in the flame, and the base of the cones was mounted on a water cooled heat sink, the temperature of the tip of the cones was a function of cone length and wall thickness. For the standard 60° cones used the tip temperature for wall thicknesses of 0.8 and 1.6mm is shown in Figure 36 plotted against plasma power. This was determined by a thermocouple cemented into the tip of a cone fitted with an insert which was closed off by the cement. The cone tip was located in the normal position level with the end of the torch and on the torch axis. At the normal operating power of 1000 watts the tip temperature of the thinner cone was 540°C. A thickness of 1mm for the wall was used in future, aiming at a tip temperature of just under 500°C.

Although copper appeared to be the ideal material from thermal considerations for the supporting cone, since its high conductivity enabled quite thin sections to be used to give an overall tip diameter of as little as 2.5mm, the severe corrosion inside presented a problem. Attempts to gold coat by evaporation were unsuccessful as the coating was too thin and quickly alloyed with the copper. Electroplating proved impracticable as it could not penetrate the extreme tip of the cone where the problem
Fig. 36. Sampling cone tip temperature v power.
was most serious. Electroless nickel plating was tried but only had limited success. Nickel was found to corrode also, a green oxide coat forming and the copper continued to oxidize underneath it. Further the nickel coating of about 20μm thickness left by this method was embrittled by the presence of the phosphide in the structure so that it tended to flake after a few thermal cycles.

At this point the angle of the cone was reconsidered, since clearly the expanding gas inside the aperture was striking the walls where they were very hot. Cones with 90° and 120° internal angle were made and showed an immediate improvement, the 120° type showing no corrosion at all. However, this resulted in an external angle that limited the approach to the torch so the 90° cone was adopted. Because of the shorter wall these ran cooler and 0.5 and 0.75mm walls were tried. The 0.75mm wall operated at between 300 and 400°C and was adopted. These still showed a little corrosion so sputter ion plating with platinum was tried, the plating being done by the Materials Group of AERE Harwell. This proved reasonably successful, a 20μm thick coating could be deposited right into the tip of the 90° cones and this gave a corrosion free life of about 25 hours. Even after corrosion appeared, however, the coating could be cleaned in dilute nitric acid and then mechanically polished and would serve for some 10 hours further.

The use of the long bore platinum apertures, which were eventually received after the change to 90° cones, provided a very stable sampling interface to the plasma, surviving long periods of operation. They appeared to produce a narrower jet of expanding gas inside the cone than short bore apertures and wall corrosion of the copper did not occur. Platinum coating was therefore not needed for cones fitted with these apertures. Their only drawback was an increase in molecular peaks in the spectrum presumably because the longer ion dwell time in close proximity to other ions and molecules encouraged ion molecule reaction processes. The most objectionable consequences of this were additional background peaks coincident with some wanted analyte ions and the addition of a hydrogen atom to some metal ions which affected isotope ratios. Their use was therefore restricted to basic system development, at this time still the major priority, and they remained clean and bright for several months of steady use before finally melting out due to erosion from the low pressure end. All attempts to obtain similar corrosion free performance by using short platinum
apertures as in the CAP programme were, however, unsuccessful. Where quantitative measurements were attempted, for example for isotope ratios, it was therefore necessary to return to short molybdenum apertures.

By the time that these reasonably reliable cones and apertures had been evolved, some problems were experienced with the control systems of the small quadrupole analyser. This was by then some ten years old and difficult to repair so as the VG 12-12S analyser was available it was installed in place of the Q806. Apart from the mechanical changes necessary to accommodate the larger electrode system and RF generator this was straightforward and excellent spectra were obtained immediately. In addition the ion transmission of this analyser was found to be some 50 times greater and consequently much larger signals were obtained.

With this analyser it was found that a small positive bias was required on the sampling cone if ions were to enter the analyser with the entrance plate grounded to the vessel even though up to 20 volts negative pole bias could be used on the main analysing rods. The best signals were obtained with a cone bias of +5 volts and pole bias of about -1 volts so that the ions entered the analysing rods with a mean energy of 6eV. However, the mean DC potential of the entrance and exit rods was still anchored to ground through a pair of resistors, their AC potential being controlled by capacitors coupled to the main rods. The lower end of those resistors was therefore isolated from ground by a decoupling capacitor and variable DC bias fed to them. It was found that this gave an appreciable increase of signal with between -5 and -10V bias and under these conditions optimum signal could be obtained with a cone potential of +1V and pole bias of -0.5V. Thus the mean energy of the ions entering the analysing rods was reduced to 1.5 eV and ions could be cut off if the pole bias was raised to +1V. This considerably improved the peak shape at the base of the peaks, the small precursor slopes and tails of the peaks being almost completely removed. With almost zero signal from plasma photons this meant that the background level between the peaks approached zero. In fact as shown in part of the print out of a spectrum in Table 6 even major peaks such as $^{40}$Ar$^+$ and $^{41}$ArH$^+$ were separated by a few channels containing no counts. The plot of a portion of a typical spectrum is shown in Figure 37.
### Table 6

Channel Print Out of Spectrum of Ar and ArH.

<table>
<thead>
<tr>
<th>CHANNEL</th>
<th>DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>416</td>
<td>0 0 0 0 0 1 102 6166</td>
</tr>
<tr>
<td>424</td>
<td>32753 23280 173 0 0 0 0 1</td>
</tr>
<tr>
<td>432</td>
<td>6 862 42994 131026 83873 700 1 1</td>
</tr>
<tr>
<td>440</td>
<td>0 0 1 1 0 0 0 0 0</td>
</tr>
</tbody>
</table>

Channel 424 Mass Number 40 Peak Rate: $545,883 \text{ c/s}$

Channel 435 Mass Number 41 Peak Rate: $2,183,767 \text{ c/s}$

Ar and ArH Peaks from Blank Solution

![Graph](image)

**Fig. 37.** Expanded spectrum showing zero channel counts between major peaks.
This analyser showed excellent stability, the channel location of the peaks in the data system memory remaining the same over operating periods of several hours. Once this had been established the real flexibility of the system began to become apparent and it became routine to operate at one scan per second for preset periods of 60 seconds. During this one minute period signals were accumulated in short term memory locations for comparison and data manipulation, including stripping one spectrum from another, ratioing one spectrum to a standard or one peak to another, and most of the other processing routines common in gamma and X ray spectrometry. In addition at this time a cassette recorder was added to the data system so that once a spectrum had been accumulated it could be stored on magnetic tape while the next was being taken. This meant that it became possible to run continuously, a fresh spectrum being taken at roughly one minute intervals for as long as desired.

At this point the emphasis of the work using small apertures sampling from within the boundary layer changed to an exploration of the analytical potential of the system.

Fig. 38. Plasma flame flowing over cone showing boundary layer. 1000μg.ml⁻¹ Y. 70μm aperture.
4.3 Determination of Analytical Characteristics in the Boundary Layer Mode

Attempts to use apertures of 100\(\mu\)m diameter or larger to sample from the plasma had always resulted in the formation of a 'pinch' discharge at the entrance to the aperture which produced such a high photon count that the spectrum was swamped. Usually also the life of larger apertures was very short; they rapidly opened out to admit more gas than the pump could handle. Much the same thing happened to 50 and 70\(\mu\)m apertures beyond a certain point as they slowly eroded in use. Once an aperture had reached about 80\(\mu\)m, attempts to use it further invariably resulted in the development of a pinch discharge and catastrophic failure.

As long as the aperture diameters remained below this value of 80\(\mu\)m however good spectra and analyte signals could be obtained even though a visible boundary layer could be seen formed across the tip of the cone. This boundary layer, intermediate in temperature between the plasma and the cone surface may be seen in Figure 38 where it is made more visible by nebulizing a solution of 1000\(\mu\)g.ml\(^{-1}\) of yttrium as for Figure 28. Where the plasma is cooled by the cone surface yttrium oxide reforms and indicates the boundary layer by its red band emission. Clearly gas entering the aperture must come from within this layer. Evidently however considerable concentrations of ions from the solution were present in the boundary layer so the performance that could be obtained by sampling from it was investigated.

Since samples were used in the form of aqueous solutions it was straightforward to prepare a wide range of elemental standards. After the first few trials these were prepared from analytical grade reagents, either BDH standards for atomic absorption or Johnson Matthey Specpure chemicals, as 1000\(\mu\)g.ml\(^{-1}\) solutions acidified to 1% with nitric acid. Analar grade nitric acid was used until its trace metal levels were found to be unacceptably high when it was replaced by the Aristar grade. Stock solutions at this level were stored in polythene bottles. Working solutions down to 1\(\mu\)g.ml\(^{-1}\) were made up and stored in the same bottles for most elements although for some such as lead and mercury these had a short life and needed frequent replacement. Solutions of lower concentrations were made fresh from 1000\(\mu\)g.ml\(^{-1}\) stock for each experiment.
Similarly solutions containing more than one element were usually made as required. After dilution all solutions were acidified to 1% HNO₃.

In general simple atomic spectra with a single peak for each isotope were obtained for the transition elements and so solutions of these were usually used at 10μg.ml⁻¹ or later 1μg.ml⁻¹ to set the system up.

Once a reasonably uniform operating procedure was established it was usual to allow the system to reach stable operating temperatures for a period of about 30 minutes after starting the plasma and bringing it into the operating position against the sampling cone. During this period distilled water would be nebulized and the mass analyser set to scan continuously so that it too could reach equilibrium operating temperatures.

The system was usually set up on monoisotopic cobalt although if work in a restricted part of the mass range remote from this was intended an element in that region would be chosen. Small differences in lens potentials were usually found at the extremes of the mass range so that either compromise settings could be used for wide mass scans, or the potentials set for the elements concerned.

Ion detector EHT potential was normally set at the recommended maximum of 3.5KV for the Galileo Type 4800 series detectors used throughout this work. Before switching this on the discriminator of the pulse amplifier was set to reject RF noise so that the scaler and ratemeter showed zero counts. The EHT was then applied and the analyser mass control set manually to the centre of a convenient peak as shown by the ratemeter. Early in the work this was usually one of the major background peaks for initial adjustment of lens potentials but once the system was in regular use only minor adjustments were needed and these were usually done on a solute ion chosen as described. The potential of the first electrode, the collector, inside the cone did appear to vary between individual sampling cones and whether short or long bore apertures were used. Once this was adjusted for peak signal the intermediate electrodes were then optimized to focus the maximum number of ions through the 2mm diameter differential aperture. Operating settings were normally found for all electrodes which showed a clear peak, although sometimes more than one combination was possible.
However, drifting settings were found at times and were taken as a sign of the development of insulating coatings on the front lens elements from pump oil vapour. These were found to stabilize when the lens elements were cleaned.

Once lens potentials were set only slight variations would occur during the normal running period. Final adjustments were made to the plasma position to give maximum analyte signal by using the micrometer adjustments on the optical bench mounting of the torch box. The cone tip was normally set level with the end of the torch or up to 2mm inside it on the torch axis.

The remaining adjustments required concerned the mass analyser. It was normally set initially to scan from 0 to 100u to include the major background peaks. Resolution was normally chosen to ensure a response which fell to background for a width of about 0.25u between adjacent peaks across the whole spectrum. This required a balance of adjustment between the low mass and high mass resolution controls. During the first six months of use the settings of these gradually drifted towards the high end of the range and adjustment of the internal preset controls was needed after this time. In general, however, there was no difficulty in setting the controls to provide the required resolution. Some adjustment of the pole bias on the analysing and prefilter rods was sometimes needed to produce the best peak shape at the base of the peaks for isotope ratio measurements.

With the operating conditions set up analytical procedure then followed a standard routine. Blank spectra were usually recorded before running test solutions and where detection limits were to be determined a series of blanks would be run and recorded to provide a value for standard deviation of blank level at the position of the peaks of interest. Since solutions were normally acidified to 1% with nitric acid the same treatment was used for the blank which was normally laboratory distilled water. Except where isotope ratios were to be determined, and a high integral peak count was required on each isotope, each run was of 60 scans of 1 second each whatever the mass range. Thus the 1023 data channels were spread across the spectrum. However, the scan was normally limited to not more than 100u giving about 10 channels per
mass unit so that reasonable definition was obtainable in the spectrum. Since the incoming counts were directed to each channel once per scan the total integrating time in a run per channel was only 0.06 secs. Thus the mean count rate represented by the total count in each channel could be obtained by dividing the total count by the total dwell time of 0.06 secs. The total available capacity of each channel was $10^6$ counts which thus represented a count rate of about 16MHz for the 1 minute run. Although the multiscaler input of the data system could in theory accept rates up to 20 MHz the preceding interface between the amplifier and the data system was limited during most of the work to about 5 MHz which itself was well above the normally accepted maximum linear rate of the channel multiplier. Although the major background peaks were seen on the scaler to exceed this rate at times the detector output rate was not a linear function of input rate above 1MHz so all these very large peaks were cramped at the top. However analyte signals were normally not above the 1MHz rate so the peaks of importance were well within the linear working range of the detecting and recording system.

Since the dwell time per channel and the number of scans remained constant, the height of peaks did not change when the scan width was reduced; peaks merely occupied more channels. Thus for isotope ratio measurements the scan was reduced to just accommodate the width of the isotope peaks required and normally also to include one peak width of base line background each side within the full 1023 channels. Where, however, full scan of the whole possible mass range of 0-250U was occasionally necessary, it was simple to reprogramme the scan of the data system to cover the mass range using 2047 or even 4095 channels and thus provide better definition of each peak. Since, however, only a total of 4095 channels of data storage were readily available this meant that data manipulation was restricted. More than 1023 channels were therefore rarely used for a scan.

Once the VG 12-12S analyser was in use pneumatic nebulizers were used because of the convenience of sample changing. This merely required that the uptake tube be transferred from one beaker to another containing the new sample solution.

Operating conditions for the two nebulizer types used for routine work
differed slightly. The concentric Meinhard nebulizer was normally operated at 22 psi when the gas flow into the injector tube of the plasma was 1.0 l.min\(^{-1}\) and the solution uptake 1.6ml.min\(^{-1}\). This was later replaced by the cross flow Jarrell-Ash nebulizer which gave an appreciably lower injector gas flow (i.e. the sample carrier flow) at a given pressure, for example at 22psi it only gave a flow into the plasma of 0.53 l.min\(^{-1}\). In spite of this, however, at this pressure the solution uptake rate was 1.5ml.min\(^{-1}\), almost as high as taken by the Meinhard type. This nebulizer, however, was normally operated at 30 psi at which the flow was 0.65 l.min\(^{-1}\) and the uptake 2.3ml.min\(^{-1}\). At this pressure an appreciably higher signal was therefore obtained with this nebulizer and it was preferred for this reason. It was not possible to achieve the same uptake with the Meinhard nebulizer without a gas flow of 1.5 l.min\(^{-1}\) which was undesirably high for plasma operation.

The mist produced from either nebulizer was then passed to the desolvator chamber.

Once the sample uptake tube was inserted into a new solution a delay of about 30 seconds elapsed before the corresponding response was seen on the analyser screen. It was usual therefore to start a scan as soon as the new sample was introduced and observe the arrival of the sample by the peak appearing on the VDU display. At the end of this scan the data was discarded and a new scan started and recorded. At the end of this scan the data would be transferred to a spare memory group from which it would be read out onto tape while the next scan was being recorded in the active accumulation memory group. This in its turn would then be transferred and read out. It was thus possible to accumulate and store repeated scans from the same sample at the rate of about 1 every 70 or 80 seconds. Read out onto tape of 1023 channels took about 30 seconds. Since the data system included programming facilities, it was possible to set it up to go through this procedure automatically for long repeated runs once the sample was introduced and the start button pressed. It was also possible to programme operation with a sample changer for totally automatic operation but for this work such a sample changer was not available.

With this operating routine the following aspects of boundary layer operation were investigated.
Background Signals and Spectra
Sensitivity and Dynamic Range
Detection Limits
Effect of Matrix-Elements and Ionization Suppressants
Measurement of Isotope Ratios.

The performance obtained is described under Results in Chapter 5.
4.4 Development of Operation in the Continuum Sampling Mode

4.4.1 Sampling and Vacuum System Performance

The original intention in adopting an ICP as a source was to improve on the temperature of the CAP at 4000K or just below and it was hoped that it would be possible to sample from a temperature of about 6000K. To sample from the bulk plasma without an intermediate boundary layer by achieving continuous flow requires an aperture Knudsen number of $10^{-2}$ or less (see Appendix 1). As shown in Table 7 for 6000K this is given by an aperture diameter of 125μm at which the gas flow into stage 1 is within the capacity of the pumps and would give a satisfactory working pressure $P_1$ of 0.11 Pa or $0.84 \times 10^{-3}$ torr.

With apertures of 70μm diameter a clearly visible boundary layer formed over the aperture, as shown in Fig. 38. However, any attempt to use apertures larger than 70μm resulted in immediate burn out of thin edged apertures in molybdenum to diameters of between 150 and 250μm at which an intense glow discharge, the pinch discharge (47), developed in the mouth of the aperture. This was accompanied by an intense photon background signal of 100K counts sec$^{-1}$ or more (present when all ion lens potentials were switched off) and very broad ion peaks and so this was regarded as an unacceptable mode of operation, particularly as a further consequence of the larger aperture was a rise in pressure in the first stage to levels above 0.13 Pa ($10^{-3}$torr) considered to be the acceptable upper limit. The pinch discharge in a 200μm aperture is shown in Figure 39. It was realised, however, that the aperture instability in this situation was probably a function of poor heat transfer from the thin edge and that apertures with bore lengths of equal to one diameter or more would be much better able to cope with the greater heat input which resulted from the admission of gas from the bulk plasma. Even if this were so, however, the pinch discharge could still be a problem. In addition the pumping capacity of the existing system was clearly marginal if the gas was to be sampled near the torch mouth where the temperature was as high as 7,500K (24,48), especially if $K_n$ was to be any lower than the limiting value of $10^{-2}$. To increase the pumping capacity of the existing first stage significantly would require major changes to the system at considerable cost. An alternative was to add an additional stage in front of the original one operating at an intermediate pressure at which
## Table 7

Minimum Aperture Diameter for Continuum Sampling v. Temperature

<table>
<thead>
<tr>
<th>Gas Temperature</th>
<th>$\lambda_0$(Ar)</th>
<th>$D_0$ for $K = 10^{-2}$</th>
<th>$P_1^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-6}$m</td>
<td>$10^{-6}$m</td>
<td>Pa $\times 10^{-3}$</td>
</tr>
<tr>
<td>4000</td>
<td>0.84</td>
<td>84</td>
<td>6.2</td>
</tr>
<tr>
<td>5000</td>
<td>1.04</td>
<td>104</td>
<td>8.5</td>
</tr>
<tr>
<td>6000</td>
<td>1.25</td>
<td>125</td>
<td>11.2</td>
</tr>
<tr>
<td>7000</td>
<td>1.46</td>
<td>146</td>
<td>14.1</td>
</tr>
<tr>
<td>8000</td>
<td>1.67</td>
<td>167</td>
<td>17.3</td>
</tr>
<tr>
<td>9000</td>
<td>1.88</td>
<td>188</td>
<td>20.7</td>
</tr>
<tr>
<td>10000</td>
<td>2.09</td>
<td>209</td>
<td>24.2</td>
</tr>
</tbody>
</table>

* First stage pressure using E09 diffusion pump in existing vessel.

---

Fig. 39. Cone tip in flame showing 'pinch' discharge in 200$\mu$m aperture. 1000$\mu$g.ml$^{-1}$ $Y$. 
a much greater mass of incoming gas could be pumped away by a modest sized pump. This technique had been reported by Campargue (43), in the context of molecular beam formation, who operated his first stage at 13 Pa (0.1 torr) using a pump capacity of 25 l.sec\(^{-1}\). Later Greene, Beachey and Milne (44) reported studies which suggested that free jet expansion into a first stage at between \(1.3 \times 10^2\) and \(1.3 \times 10^4\) Pa (1 to 100 torr) should be feasible. Calculations showed (Appendix 1) that with a conventional mechanical pump of reasonable size pressures between 13 and 133 Pa (0.1 to 1 torr) would be achievable using apertures of up to 400\(\mu\)m diameter from the ICP.

Shortly after this it was learnt that a stage of this type working at similar pressures had been used to sample ions from a microwave plasma (45,46). No pinch discharge was observed with the 400\(\mu\)m apertures used. However, the sampling conditions in the microwave plasma differed considerably from those in the ICP. The principal difference was in gas temperature. This is not known for the actual plasma used but its design was closely similar to other microwave plasmas in which the highest gas temperature reported is about 2000K. Quite apart from the effect of this on the analytical programme, the expansion conditions are very different from the ICP since the gas density is much higher. In addition the electron population in an MIP is nearer that of the CAP than that of the ICP where it is between 1 and 2 orders of magnitude higher. The pinch discharge was not observed in the CAP either even though 70\(\mu\)m apertures gave sampling conditions that were close to continuum flow at the lower gas temperature. At the time it was therefore assumed that the absence of the pinch discharge in the MIP as with the CAP was due to the lower electron population.

With this evidence of the success of continuum sampling with an intermediate pressure stage from an MIP some simple experiments were carried out using the ED 660 backing pump of stage 1 working through a cold diffusion pump to see what pressures could be attained with the ICP. A 400\(\mu\)m aperture about 3mm long was drilled in the tip of a sampling cone which had been plugged with braze metal. This was then mounted in the usual way and put into the plasma flame. The first stage pressure was found to be 93 Pa (0.7 torr), reasonably close to the expected value. In addition, however, no pinch occurred at the aperture and when a
1000 mg ml\(^{-1}\) yttrium solution was nebulized a clear path through the boundary layer into the aperture from the bulk plasma could be seen. This is shown in Figure 40. The suppression of the pinch discharge under these conditions was an unexpected but very welcome bonus to the expected confirmation that a relatively simple pump would provide the desired pressure in the first stage when sampling from the ICP with this large aperture. However, the aperture used had a very long bore (about 7 diameters) and there was no way of knowing whether it would be possible to sample ions through it successfully. It was also desirable to learn more about suppression of the pinch. A series of apertures of diameter 150, 200, 450 and 600 \(\mu\)m, all with the normal short bore profile (Figure 21) were mounted in conventional cones and together with the long bore 400 \(\mu\)m aperture used previously were examined in turn in the plasma flame. The first stage was pumped as before by the ED 660 backing pump with the diffusion pump switched off and cold. Pressure was measured by a TCI thermocouple gauge and a valve was fitted to the backing line so that the pressure could be controlled to some extent.

With all the short bore apertures a pinch formed in the entrance to the aperture when the backing valve was fully open although the pressure in the first stage was 125 Pa (0.95 torr) at 600 \(\mu\)m and 33 Pa (0.25 torr) at 150 \(\mu\)m. In each case the pressure was raised by partly closing the valve while the pinch was observed. With the two smallest apertures, 150 and 200 \(\mu\)m, the pinch discharge remained until the pressure reached full scale on the gauge at 850 Pa (6.4 torr) beyond which it extinguished. With the 400 and 600 \(\mu\)m apertures, however, the pinch discharge weakened greatly by 500 Pa (3.7 torr) and extinguished by full scale (850 Pa).

The long 400 \(\mu\)m aperture was then used. This gave no pinch discharge at any pressure down to the lowest the pump could reach, 93 Pa (0.7 torr) when in the same position in the flame as the other apertures, on the axis 10 mm from the load coil. However, it was found that when the plasma torch was moved so that the aperture, still on the axis, was withdrawn to the tip of the visible flame a weak pinch reappeared, and the same occurred if the torch was moved laterally at a distance of 10 mm from the load coil when the aperture reached the edge of the flame. On both these positions the internal pressure remained the same as it was on the axis at 10 mm and of course in all cases the pressure in front of the aperture was 1 atmosphere.
Fig. 40. Break through of boundary layer with 400µm 'long' aperture. 1000µg.ml$^{-1}$. Y.
It was difficult to draw any clear conclusions from this evidence except that in the working position in the flame the pinch discharge was suppressed at pressures inside the cone down to 100 Pa provided that the aperture had a long bore. With this condition the expansion from atmospheric to the lower pressure occurred over a distance of several hole diameters. It was not possible to extend this particular experiment as apertures of intermediate bore length were not available and for all the short apertures about 800 Pa or more was needed to quench the discharge. However, it was considered encouraging enough to build the expansion stage and test it.

When this stage was first installed it was mounted on the slide valve plate at 30° to the horizontal as with boundary layer cones to avoid the direct line of sight into the quadrupole stage. It was initially pumped through a rather long (2m) 25mm bore pipe by the ED660 backing pump of the original stage 1, a smaller pump being used for this duty instead. This worked reasonably well for the first trials but it became apparent part way through these that all these pumps needed overhauling. While this was being done a new mechanical pump of 340 l.min⁻¹ capacity was obtained and connected through a 1m long pipe to the expansion stage and the ED660 returned to its original duty. The expansion stage is described in Chapter 3.9 and shown in Figures 25, 26 and 27 where the off axis mounting on the slide plate is shown.

For this stage apertures, drilled directly in the cone tips, of 0.2, 0.3, 0.4 and 0.5mm diameter were provided. The one piece design shown in Figure 24A was later supplemented with the two piece type of Figure 24B which provided better heat transmission from the aperture edge and allowed metals of poorer thermal conductivity to be used. Aperture discs were made for the front part of this type in copper, stainless steel, and two nickel chromium alloys highly resistant to oxidation, Inconel 600 and Nimonic 75. These fitted the rear copper mount without an O-ring seal. The same range of aperture diameters was provided in both designs.

4.4.2 First Continuum Spectra

The first experiments were designed to determine whether the expansion stage met at least the physical requirements of the problem. It was found that using a 0.4mm (400μm) aperture and a 0.5mm skimmer the pressures
when sampling from the ICP and using the 660 l.m⁻¹ pump were approximately 40, 4×10⁻² and 2.6×10⁻⁴ Pa in the three stages so evidently adequate pumping capacity was available. The system appeared to operate stably without becoming too hot although on dismantling after operation it was found that the skimmer had become blue at the tip suggesting that it had been heated to several hundred degrees centigrade. The sampling cone appeared to be largely unaffected by the plasma although internally at the tip there was some evidence of sputtering. The aperture profile, however, was not affected by a few hours of operation. Since satisfactory pressures were obtained at 0.4mm the other smaller apertures were used only to check that the lower pressure they provided in the first stage offered no improvement in signal, in fact the signal was reduced by about the ratio of aperture area. During this initial period copper sampling cones were used most of the time and for the early work quite concentrated solutions of 1000μg.ml⁻¹ and 100μg.ml⁻¹ were used. With the large apertures no problems were experienced with clogging of the aperture at these concentrations even though they were run for long periods. However, even at these concentrations analyte signals were difficult to obtain. There were plenty of ions available from argon and water and many of the early spectra obtained were extremely cluttered with substantial peaks. A typical example is shown in Figure 41, no analyte peaks could be seen under these conditions even from high concentrations. The very cluttered spectra obtained initially were thought to be due to too high a pressure between the skimmer tip and the cone at the spacing of 1mm which was used initially. The pressure in the body of the expansion stage was indicated as 40 Pa but the bulk of the skimmer cone partially obstructed the gas flow from the region near its tip so the pressure in the region where it mattered could have been appreciably higher. However, increasing the spacing to 2mm gave much cleaner and more normal spectra as shown in Figure 42. Using copper cones of the type shown in Figure 24A with the 0.4mm aperture which was initially 2 diameters long no pinch discharge could be seen and the photon count was reasonable at a few hundred counts sec⁻¹. The interior of the cone immediately around the sampling aperture showed an intensely polished surface after about 1 hour of use and this eventually reduced the length of the aperture as material was sputtered away. The diameter only increased very slowly, however, so that the end point to the life of the cone occurred when the thickness of the material around the aperture was reduced to about 0.1mm and it was too fragile to be safe. Even at this point though the aperture diameter only increased to about
Fig. 41. Cluttered continuum sampling spectrum of H$_2$O.

Fig. 42. Continuum spectrum of H$_2$O with 2mm spacing.
0.5mm. The sputtered copper produced the peaks at 63 and 65u in the spectrum of Figure 42. At the usual operating position used, on the torch axis at 5mm from the load coil, no pinch discharge was observed at any stage in the life of the aperture even when worn to a very short bore. Once the expansion stage came into use the pinch discharge was no longer a problem for the aperture positions in the luminous region of the flame out to about 20mm on the axis from the load coil. Beyond that and on the extreme edges of the flame at positions close to the load coil a weak pinch discharge was visible but did not appear to contribute to the background count. It is therefore possible that a weak discharge is present all the time in the normal operating position but is not detected because the photon count is not significant and close to the load coil the intense light from the energy addition region of the plasma, the annulus in the centre of the work coil, would prevent a weak discharge being seen. In contrast, however, even in this position the discharge was always clearly visible in a burnt out small aperture with a low pressure behind it, and the photon count then was often in the region of 100 K.counts sec⁻¹.

With the spectrum of water shown in Figure 42 there seemed hope of seeing analyte peaks and attempts were made using a 100µg.ml⁻¹ cobalt solution without success. Since the pressure in the stage behind the skimmer (originally Stage 1 but now Stage 2) was quite low at 4 x 10⁻² Pa the skimmer was changed for a larger one of 0.7mm with little change of pressure. A very small peak of about 300 counts sec⁻¹ was then found, just visible above the background level. This provided something to work on to improve analyte response and the ion lens potentials were optimised afresh; (see Figure 43).

Behind the skimmer the ion lens was the same as that used behind the sampling cone in boundary layer sampling, shown in Appendix 3. The lens potentials used at the start of continuous sampling were found to optimise close to those for boundary layer sampling except that a high potential on the first cylinder or collector electrode was advantageous in its role as draw out electrode for the skimmer. When the expansion stage was added the chamber was mounted directly on the slide valve as for boundary layer cones and thus the sampling cone was still at ground potential. Experience had suggested that this was desirable for RF screening. The skimmer was mounted on an insulator and was connected to ground through a resistive RF filter of 1MΩ. This proved to develop a positive potential of about 20v
Fig. 43. First small peak of 100μg.ml⁻¹ Co by continuum sampling. Peak height 300 counts.sec⁻¹

Fig. 44. Improved response from 100μg.ml⁻¹ Co. Peak height 8500 counts.sec⁻¹.
across it so that there was a defocussing field between the skimmer and aperture. An RF choke was substituted for the resistor so that the skimmer could be connected to the body at the same potential as the cone and the response was immediately improved once the other electrode potentials were changed to allow for the new skimmer potential. The $^{59}$Co peak then increased to 8,500 counts sec$^{-1}$ for 100$\mu$g.ml$^{-1}$, clearly visible in Figure 44. Clearly if skimmer bias were to be provided, a low impedance supply would be needed capable of providing the current drawn. However, for the time being the skimmer was kept at the same potential as the cone, grounded to the vacuum system. It did not seem possible to improve the signal any further so the expansion stage was modified to allow a draw out electrode to be mounted immediately behind the skimmer to increase the extraction field for ions passing through the skimmer (Figure 45). At the same time the sampling cones were changed to the two piece design of Figure 24B because this had a wider divergence angle at the base and provided better pumping access between skimmer tip and cone. This did not increase the intensity of analyte signals much but the spectra were cleaner and contained fewer background peaks above 40$\mu$ so that analyte peaks were easier to see.

With an aperture-skimmer spacing of 8.5mm (21.25 times aperture diameter $D_a$) and skimmer diameter of 0.7mm, signals of 8000-10,000 counts sec$^{-1}$ could then be obtained for a number of elements at the 100$\mu$g.ml$^{-1}$ level.

The effect of the draw out electrode was not well defined at this stage but at the usual collector potential of about -500v a drawout electrode potential of -30v gave some increase in signal. Although these signal levels were very poor at about 100 counts sec$^{-1}$/\(\mu\)g.ml$^{-1}$ compared to those obtained in boundary layer sampling which were a factor of about 5000 better, it was observed that they showed a number of the characteristics hoped for from continuum sampling. Firstly no problems were experienced with running solutions at concentrations up to 1000$\mu$g.ml$^{-1}$. Although condensed solid was deposited around the apertures it never obstructed the aperture itself, even though quite thick layers developed on long runs at 1000$\mu$g.ml$^{-1}$.

Parts of the spectra showing cobalt, vanadium and uranium, all at 100$\mu$g.ml$^{-1}$, are shown in Figure 46. These early spectra already show one of the most important features of continuum sampling. In boundary layer sampling both vanadium and uranium show substantial oxide peaks. For vanadium $V^+$ and $VO^+$ peaks were of similar size while almost no $U^+$ metal ion was
Fig. 45. Position of draw-out or extraction electrode in relation to skimmer.

Fig. 46. Spectrum detail for Co, V and U, showing residual peaks of VO$^+$ and UO$^+$. 
detected, the main ion seen being $\text{UO}_2^+$ due to the reformation in the cooler boundary of these oxide species. In Figure 46, however, only $\text{V}^+$ can be seen and only a few percent of the uranium appears as oxide or dioxide, the metal ion peak predominates. This demonstrates that the sampled gas remains at a high temperature until it is rapidly quenched in the expansion to a temperature below that at which oxidation reactions can occur.

Similarly in Figure 47 the spectra of 100µg.ml$^{-1}$ solutions of lead are shown, one with the addition of 500µg.ml$^{-1}$ of sodium. Where the sample passed through the boundary layer this would have suppressed the lead response completely (and also of course blocked the aperture) but here it can be seen that only a depression of the response of about 20% is caused.

A further characteristic of the operation was also noticed at this stage. When a solution of barium was nebulized no ions could be found for $\text{Ba}^+$ at 138u. Instead they were all found at 69u as $\text{Ba}^{++}$. The second ionization energy of barium is the lowest of any element, 10.05eV, and evidently atoms of this ionization energy were fully ionized.

4.4.3 System Development

While this was clearly encouraging in that the boundary layer ions were much reduced, the signal levels were very low and the mass resolution was very much poorer than in boundary layer work. It appeared that although the larger apertures must allow more ions into the system a much smaller number were being transmitted to the mass analyser, and also that those that reached the analyser were of higher energy and entering it at too high a velocity.

The question of ion transmission was explored first and the bend in the ion flight path caused by the skew mounting of the expansion stage was felt to be a possible cause of ion loss. Although the background count attributed to photons was acceptably low at a few hundred per second a high potential of about -500V was needed on the first lens electrode (collector) to pull the ions into the lens. It was felt that it should still be possible to sample ions from the flame if the axis of the ex-
Fig. 47. Spectra of 100µg.ml⁻¹ Pb, showing effect of 500µg.ml⁻¹ Na.

Fig. 48. Rearrangement of expansion stage on the axis with 30° torch.
pansion stage were at an angle to the plasma axis without allowing more photons from the energy addition region of the plasma to enter the aperture. The expansion stage was therefore mounted on the slide valve on the same axis as the rest of the system (Figure 48). This produced an immediate improvement in signal levels and it was found that if the collector potential was reduced to about -150\text{V} and the potential of the draw out electrode (cylinder 1) increased to between -200\text{V} and -250\text{V} an increase in signal to about 1000 counts sec^{-1}/\mu g.ml^{-1} was obtained.

Both electrode potentials now showed clear maxima. No increase in photon counts were observed.

The effects of skimmer size and position were then explored. This raised problems of reproducibility because a change of skimmer diameter or of skimmer-aperture spacing required the plasma to be switched off and the expansion stage opened for the change to be made. However, returning to the previous settings after such a change generally gave results within ±10\% of the previous figure. It was found that an increase of skimmer diameter from 0.5 to 0.7mm doubled the response but an increase from 0.7 to 1.0mm only produced a further increase of 20\%. A further increase to 1.5mm actually reduced the response by about 40\% again possibly due to additional scattering from the resulting high pressure in the second and third stage due to the larger gas input. A 1.0mm skimmer was therefore adopted.

It had been found that attempts to operate with skimmer to aperture separations down to 3mm resulted in very cluttered spectra, thought to be due to the restriction in pumping path caused by the presence of the skimmer and it had been found preferable to operate at about 8mm separation to obtain reasonably clean spectra. Now, however, it was found that rather larger signals could be obtained in the region from 8.5 to 12.5mm although there was no clear maximum at any position. A separation of 10mm for the 1.0mm skimmer was therefore adopted. With this arrangement a variety of the available sampling cones were tried. Copper cones were generally satisfactory, being easy to clean of solid deposits and of the thin black oxidation layer that formed on the inside conical surface. They did, however, erode in the inside tip due to sputtering. Nickel cones showed less corrosion internally but formed a green oxide layer after several hours use that was much more difficult to remove. The oxide is only soluble in alkalis with some difficulty and really required
mechanical abrasion to remove it. It also formed just around the aperture on the outside and seemed to produce a rough surface which collected solid condensation from the flame. This occurred even though nickel apertures ran red hot in the centre because of their poorer thermal conductivity. Sputtering internally was similar to copper, but giving nickel background peaks in the spectrum. It was hoped that the oxidation resistant alloys, Inconel 600 and Nimonic 75 would show less corrosion. Because of their still lower thermal conductivity a rather thick section was required and this was provided in aperture discs fitting on to the copper base of Figure 24B. These were found disappointing, however. Sputtering was still high and showed the additional peaks of the alloying materials and although internally they remained clean the outer surface developed a rough black oxide coating. In addition the lip of the aperture showed melting and distortion of the profile at the edge, presumably because the conductivity was too poor to allow the edge in contact with the plasma to remain below its melting point.

For these reasons therefore a return was made to copper cones, although other materials were still considered. The properties of possible cone-aperture materials are shown in Table 8. New one piece copper cones with the same internal profile as the two piece type of Figure 24B with as sharp a tip as possible were made and found to give better signals from the flame as suggested by Hayhurst et al (49,50). They showed a much clearer peak in signal as they were moved across the flame than shallower cones, due presumably to the thinner boundary layer that formed over them which the gas flow had to penetrate. With these pointed copper cones signal levels of about 5000 counts sec⁻¹/µg.ml⁻¹ could be obtained.

After this period of operation with the axial expansion stage but skew flame it was observed that the pattern of ion burn on the skimmer tip had changed. With the stage and sampling cone on the plasma axis the tip of the skimmer and also the interior of the cone showed a series of dark rings alternating with clear patches that were symmetrical about the apertures. When the stage axis was at an angle to the cone these became tilted to suggest that the expanding jet from the aperture no longer lay along the axis of the aperture but projected above the skimmer tip. This would cause considerable loss of signal since the core of the beam would miss the skimmer. In spite of this however more signal had been obtained
Table 8

Aperture Materials for Continuum Sampling

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity $W\cdot cm^{-1} \cdot °C^{-1}$</th>
<th>M.P. $°C$</th>
<th>Machinability</th>
<th>Sputter Yield</th>
<th>Oxide Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>0.67</td>
<td>1857</td>
<td>poor</td>
<td>med.</td>
<td>poor</td>
</tr>
<tr>
<td>Copper</td>
<td>3.94</td>
<td>1083</td>
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<td>high</td>
<td>v.good</td>
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<tr>
<td>Gold</td>
<td>2.97</td>
<td>1064</td>
<td>v.good</td>
<td>high</td>
<td>-</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1.4</td>
<td>2617</td>
<td>fair</td>
<td>low</td>
<td>poor*</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.92</td>
<td>1453</td>
<td>v.good</td>
<td>high</td>
<td>poor</td>
</tr>
<tr>
<td>Niobium</td>
<td>0.52</td>
<td>2468</td>
<td>good</td>
<td>low</td>
<td>fair</td>
</tr>
<tr>
<td>Palladium</td>
<td>0.70</td>
<td>1552</td>
<td>good</td>
<td>high</td>
<td>poor</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.69</td>
<td>1772</td>
<td>v.good</td>
<td>high</td>
<td>-</td>
</tr>
<tr>
<td>Silver</td>
<td>4.18</td>
<td>962</td>
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<td>poor</td>
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<td>Tantalum</td>
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<tr>
<td>Titanium</td>
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<td>low</td>
<td>poor*</td>
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<tr>
<td>Tungsten</td>
<td>1.66</td>
<td>3410</td>
<td>v.poor</td>
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<td>poor</td>
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<tr>
<td>Zirconium</td>
<td>0.21</td>
<td>1852</td>
<td>good</td>
<td>low</td>
<td>poor</td>
</tr>
</tbody>
</table>

* Oxides are volatile.

Note 1. Alloys are not listed because of the complex sputtered background ions introduced.

Note 2. Materials of lower thermal conductivity may be used as tips to a copper base cone.
because at least the gas leaving the skimmer was now on the axis of the lens system. Evidently it was necessary to mount the plasma torch on the system axis as well. This raised the problem of avoiding the line of sight for photons from the plasma core through the aperture, skimmer and differential aperture into the quadrupole and subsequently to the detector. Up to this point the same electrode system for the ion lens was used for continuum sampling as had been adopted for boundary layer sampling where the first element, the collector of 18mm diameter, had drawn ions from the cloud formed in front of it by gas entering the small aperture. A light stop on the lower edge of this element obstructed the line of sight. The 18mm collector was now replaced by a 25mm diameter cylinder in the centre of which was mounted a 5mm diameter copper disc on four fine wires attached to the tip. This disc completely obstructed the line of sight for photons but left ample area between its edge and the cylinders for ions from the expanding cloud from the skimmer to pass. This was subsequently found to remove direct photons from the plasma completely. As a check the disc was removed without changing any other conditions and a constant rate of 150 K.counts sec\(^{-1}\) was observed with all lens potentials at zero. An ion signal from the plasma was then observed first with the disc absent and then with it replaced. The difference in signal was close to the 150 K.counts sec\(^{-1}\) observed for photons alone so evidently the obstruction of the centre of the lens element produced little loss of signal.

The first results with this axial mounting of the torch, aperture and expansion stage were disappointing, no increase of signal being found. However, it was felt that this geometry should provide the best performance since it had proved possible to remove the photon background, and the persistent low signal levels might be a consequence of poor ion focusing. The lens potentials were adjusted by individual stepped potentiometers and the lens arrangement and potentials used were still very similar to those found optimum for the low velocity ions drawn from the boundary layer.

Changes were therefore made to the biasing supplies as shown in Appendix 3. The stepped potentiometers were discarded and 3 watt multi-turn potentiometers with duodials substituted. These provided much finer control. Three controls of 0-400V negative were provided and seven controls of 0-150V which could be switched to negative or positive stabilized supply
rails. In addition a separate stabilized supply for the draw out cylinder of 0-2KV and low voltage stabilized supplies of 0-30V and 0-60V were also available for electrodes drawing more than the few microamps available from the potentiometers.

Once these changes had been made greater flexibility was available to improve both ion transmission and mass resolution.

4.4.4 Optimization of Ion Optics

One of the features of the system in boundary layer sampling was the excellent resolution obtained with the V.G. 12-12S quadrupole analyser. Even very large peaks of peak count rate of more than $10^5$ counts sec$^{-1}$ remained within the limits of 1 mass unit on the base line and for example zero background count was observed between the $^{40}\text{Ar}^+$ and $^{41}\text{Ar}H^+$ peaks. Peak precursors and tails were thus very well controlled. A very small potential drop was needed between the sampling cone and the analysing rods and ions could be cut off with only +2v on the quadrupole entrance plate.

In continuum sampling operation no changes were made to the alignment of the system and small peaks appeared reasonably well revolved. Major peaks, however, showed considerable spread at the base, the precursors and tails overlapping adjacent peaks. The spectra in Figure 49 show the region of the spectrum around mass 41 for both modes of operation, showing the spread of the peaks in continuum sampling. In order to confirm that no changes had been made inadvertently to the quadrupole system during the continuum flow work, the expansion stage was removed and a horizontal mount fitted for a boundary layer cone. This immediately gave very well resolved spectra exactly as before. The only remaining uncertainty then was that of the energy of the ions entering the quadrupole. This depended only on the difference between the effective plasma potential and the potential of the analysing rods. The plasma potential is discussed in Appendix 4 where it is shown to be the sum of the potential due to ambipolar diffusion and the Debye sheath potential across the sheath which forms in immediate contact with the sampling cone surface. The total potential is shown in Appendix 4 to be about 8 volts positive
with respect to the surface. However, such a potential difference
to a grounded sampling cone would be easily offset by raising the analyzer
pole bias to the same level so that ions would enter the rod system with
any chosen energy down to zero. It was quickly found that the
maximum pole bias of +20V had no effect on the resolution, so that if this
was the cause of the problem the ion energy must be considerably greater
than +20eV.

A rough determination of the ion energy was made by raising the potential
of the entrance plate of the quadrupole. A potential of +40V was found
to cut off the ions. This suggested that the plasma must be floating at
about this potential above the sampling cone. The sampling cone was then
isolated and biased negative so that it should have been possible to
reduce the potential difference between the plasma and the rods. However,
this had little effect, more than +30V still being required to cut off
the ions. This was resolved when the skimmer, which had remained at
ground potential, was also isolated when it was found to follow the cone
potential. Evidently the expanding plasma stream between cone and
skimmer was still a good conductor. With a grounded skimmer this may
have resulted in the plasma potential not changing with cone potential
because it was effectively tied to the skimmer. Alternatively there may
have been separate plasma potentials in front of cone and skimmer and
only the cone potential was moved. Both skimmer and cone were then
isolated and connected together.

To maintain low RF impedances in the plasma earthing leads, bypass
capacitors were fitted. It was then found that if the cone-skimmer
potential was set to -25V the ions reaching the quadrupole were cut
off when the entrance plate reached +7 volts, a total potential of 32V volts.
With the cone biassed to -20V cut off was at 13 volts, a total value of
33 volts. Thus the most energetic ions seemed to have an energy of 32
or 33 eV. A plot of the count against retarding potential for cone bias
values of 25V and -20V is shown in Figure 50. Although the most energetic
ions were at 32eV the spread of ion energy appears to be only about 10eV.
Thus by using a negative bias of 25V on the first stage the ions entered
the ion lens with a mean energy of about 4eV. This meant that all the
focus potentials were much closer to the values used for boundary layer
ions and showed more clearly defined maxima. With the lower energy ions
much better resolution was obtained although still poorer than in a good
Fig. 49. Spectra in the region of $\text{Ar}^+$ and $\text{ArH}^+$ in boundary layer and continuum sampling.

Fig. 50. Variation of response with retarding potential for 20V and 25V -ve expansion stage bias.
boundary layer system. Comparative spectra over the range from 10-48u are shown in Figure 51.

Once this question of ion energy had been resolved and the low energy of ions entering the quadrupole permitted good resolution to be obtained, two further changes were made before examining the analytical performance.

Signals were now improved to between 5000 and 8000 counts sec\(^{-1}\) for 1 ppm solutions of many elements but the background levels were still high especially at the low mass end of the spectrum. The background signal was apparently related to ions entering the system as it vanished when the ion lens potentials were switched off. Thus it could not be produced by plasma photons. However, it only varied slightly with the mass setting so it did not appear to come from ions passing through the mass analyser. It was concluded that it was probably caused by the decay of excited ions, such as the large numbers of argon ions entering the system, which entered the ions lens, possibly striking lens surfaces. It was found that although negative ion-lens potentials of several hundred volts had normally been used, especially on the collector and differential aperture, these were not really necessary and adequate focussing appeared to occur with a differential aperture potential of ~60v. The other potentials were reduced similarly, some in fact requiring low positive values. When this was done the background count of 500-1000 counts sec\(^{-1}\) was reduced to a level of 30-50 counts sec\(^{-1}\) across the spectrum.

Now that the boundary layer was no longer present across the sampling path and the interior surface of the copper sampling cone no longer formed part of a lens with the collector electrode, the two main reasons for removing as much water vapour from the sample mist entering the plasma had disappeared. The nebulizer cloud chamber was therefore mounted without a desolvator directly beneath the torch, much as it was when originally supplied for atomic emission use. However, because the torch was now horizontal a short length of tubing was still necessary between the end of the torch and the cloud chamber. This worked well and the additional water vapour seemed to have no adverse effect on performance. More oxidation of the internal cone surface was observed but as there were now no electric fields inside the expansion stage this caused no problems.
Fig. 51. Continuum spectra showing effect of expansion stage bias compared to boundary layer spectrum.
4.5 Determination of Operating Characteristics and Analytical Performance in the Continuum Mode

The determination of the system performance in the continuum sampling mode followed the pattern used for boundary layer sampling. The same sample solutions were used initially at concentrations of between 1 and 1000μg.ml⁻¹ but later these were supplemented by solutions of elements that had been avoided in boundary layer sampling, either because of their refractory oxides or because of high ionization energies.

Whereas with the rather fragile apertures used for boundary layer sampling operating power was normally limited to 1000 watts, when using the robust continuum flow apertures considerably greater freedom was felt to explore operating conditions both in different positions in the flame and at higher power levels.

Starting up and operating procedures were very similar with either mode of operation, with the exception that for continuum sampling the continuum stage pump was started just before bringing the plasma torch up to the operating position. As soon as the working pressures had stabilized, a matter of 30 seconds after opening the slide valve, lens potentials could be set on the ion of current interest. Once the problem of plasma potential had been resolved the cone-skimmer potential was normally set at -25V and not varied. The remaining potentials were set for maximum signal on an ion in the mass range of interest, just as for boundary layer operation.

Once found, settings remained reasonably stable and little change was required when starting up in the morning on the settings used the previous day.

Once the plasma had been started it was found that signals appeared higher and more reproducible if the plasma gas flow of 0.5 l.min⁻¹ necessary to start it was shut off leaving just the coolant flow of 10 l.min⁻¹ and the sample carrier gas flow running. Without the desolventor optimum signals were obtained at carrier gas (or injector) flows of from 0.5 to 0.6 l.min⁻¹, which were produced by a pressure drop across the nebulizer of 22 to 26 psig. Peak signal was obtained by adjusting plasma position horizontally and vertically once it had been brought up to the aperture. This was found necessary each time the slide valve was reopened after start-up.
In boundary layer sampling the aperture was not sampling the plasma directly but drew gas that had been delayed in the cooler layer. Greatest signals were found when the aperture was located in the mouth of the torch at 5mm from the end of the load coil and centred in the carrier flow along the axis. A sharp fall of level was found as the aperture was withdrawn from the torch along the axis. Much the same response was observed in continuum sampling except that the fall in signal was much less marked along the axis. Since there was no boundary layer intervening the signal represented more closely the true ion density in the plasma. Plasma ion density profiles along and across the flame were plotted by moving the torch box on its calibrated transverse and longitudinal carriages. The effect of plasma power on signal and background level was observed up to 1.8Kw on a copper aperture but a nickel aperture was found to melt at the tip before this power was reached. The energy distribution of the ions entering the quadrupole analyser was determined by using the entrance plate of the analyser as a retarding electrode. It was found that the response remained substantially constant as the potential was varied from a few volts negative to +2v and the signal then fell as the potential was raised until the background level was reached at +10v. These values were plotted to give the integral energy distribution plot and differential values were derived from this to give the distribution of ion energies.

From the results obtained operating parameters were selected at which to make measurements of the analytical performance. The most important of these measurements were sensitivity for elements of a range of ionization potentials and masses, background and detection limits for a range of elements, dynamic range, and the effect of matrix elements and ion suppressants. Measurements of isotope ratio on lead solutions were also made and the results compared with accepted values. The results of these and the conclusions drawn from them are discussed in Chapter 5.

The final form of the system used for continuum sampling is shown in the block diagram in Figure 52 and a diagram of the continuum sampling geometry in Figure 53. The appearance of the system during the final stages of boundary layer operation and the development of continuum sampling is shown set for boundary layer use in Figure 54, and the changes for continuum sampling showing horizontal mounting of torch and expansion stage in Figures 55 and 56.
Fig. 52. Schematic of final continuum sampling system.

Fig. 53. Detail of continuum sampling geometry.

Fig. 54. Final system for boundary layer and continuum sampling.
Fig. 55. Horizontal torch mounting. Note sample injector tube.

Fig. 56. Expansion stage mounted on latest gate valve. This allows stage and sampling aperture to remain fixed in position.
CHAPTER 5

RESULTS
5.1 Results of Boundary Layer Sampling

5.1.1 Initial Operation with the ICP

Much of the initial experimental work was devoted to achieving reasonably stable operation of the system and in particular of sample apertures in the plasma flame. However, spectra were produced early during this process and progress was largely assessed by examination of them. The first few spectra were obtained before the data system was operating and it became possible to observe the spectrum accumulating on the display. These are shown in Fig. 31 and 32 (Chapter 4.1), obtained with a simple X-Y plotter. Considering the relatively large signal of 1000 counts.sec\(^{-1}\) obtained from a 10 µg.ml\(^{-1}\) cobalt signal there is remarkably little sign of the expected peaks from argon and the other species present in the plasma in Fig. 31 even in the annulus of the flame. However, when a copper solution was introduced from the ultrasonic nebulizer a spectrum much more like those found in the earlier Capillary Arc project was obtained. Although clearly the mass analyser was resolving poorly the major peaks of \(^{19}\text{OH}_3^+\), \(^{40}\text{Ar}^+\), \(^{41}\text{ArH}^+\) are seen together with smaller ones of \(^{30}\text{NO}^+\), \(^{32}\text{O}_2^+\) and \(^{33}\text{O}_2^+\). A large peak of \(^{18}\text{OH}_2^+\) or possibly \(^{18}\text{NH}_4^+\) is not properly resolved from the \(^{19}\text{OH}_3^+\).

A major step forward was made when the plasma torch was mounted at 30° to the horizontal also so that it could be aligned on the axis of the sampling cone. At the same time the multichannel data system was coupled to the mass analyser and counting system so that spectra could be displayed as they accumulated. Two of the spectra obtained in this way and then plotted from the memory of the data system onto an X-Y plotter are shown in Figs. 57 and 58. The first of these taken from a solution containing 5 µg.ml\(^{-1}\) each of nickel and cobalt shows the spectrum over the mass range from 0-100u. Major background peaks occur at 19, 30, 32 and 41u with smaller peaks at 18, 20, 29, 33 and 40u. The relative proportions of these peaks were observed to vary considerably from run to run according to the operating conditions used, particularly in the early stages of the work. Reactions producing these ions from the main plasma constituents of argon, oxygen, nitrogen and hydrogen can occur in the fringes of the flame, the boundary layer, in the expansion through the sampling aperture and on the walls of
Fig. 57. Spectrum of 5µg.ml\(^{-1}\) each of Ni, Co. Peak count rate of \(^{59}\)Co\(^{+}\) is 11,757 counts.sec\(^{-1}\).

Fig. 58. Spectrum of 10µg.ml\(^{-1}\) Ag. Peak count rate of \(^{107}\)Ag\(^{+}\) is 29,957 counts.sec\(^{-1}\).
the sampling aperture, cone and electrodes. These ions are discussed more fully in the light of more detailed spectra taken later in the work. However, apart from these background ions there are clear peaks for the analyte ions $^{58}\text{Ni}^+$, $^{60}\text{Ni}^+$, $^{62}\text{Ni}^+$ and $^{59}\text{Co}^+$. That for cobalt reaches a peak count rate of 11,757 counts.sec$^{-1}$ or 2351 counts.sec$^{-1}$ per µg.ml$^{-1}$. The total count rate for the three peaks of nickel is rather less at 8,704 counts.sec$^{-1}$. The random background count rate is reasonably low, certainly below 100 counts.sec$^{-1}$. The spectrum shown in Fig. 58 was taken under rather better conditions with the analyser set for a rather higher resolution and for a more limited mass range across the isotopes of silver. At a solution concentration of 10 µg.ml$^{-1}$ the count rate at the $^{107}\text{Ag}^+$ peak was 29,957 counts.sec$^{-1}$ or almost 3000 counts.sec$^{-1}$ for an isotope of about 50% abundance at 1 µg.ml$^{-1}$. The ratio of these isotopes may be determined by adding the counts in each channel across the peaks for each peak, which may be done automatically in the data system by setting a region of interest around each peak. Strictly the background on a blank solution should also be recorded and subtracted but in this case, ignoring the background, the isotopic abundances found from these integrated counts are 51.97% and 48.03%. These compare well with the accepted values of 51.82% and 48.18%.

The great convenience of the synchronized scans on the mass analyser and data system is shown in Fig. 59, which is a photograph of the display of a limited scan over the isotopes of cadmium, only 28u wide. The cadmium solution was of 10 µg.ml$^{-1}$ and the signal is relatively small, the peak count rate for $^{112}\text{Cd}$ (24.07%) being only 2133 counts.sec$^{-1}$ corresponding to 8,863 for 10 µg.ml$^{-1}$ at 100% abundance. Nevertheless the peaks are clearly displayed and easily identifiable, even the small peaks of $^{106}\text{Cd}$ and $^{108}\text{Cd}$, which are only about 1% abundant. This photograph also shows the $^{112}\text{Cd}$ peak identified by markers either side of it, with its area in total counts displayed below the trace. The low background is also very evident, which resulted from the off axis position of torch, sampling aperture and detector.

During this stage of the work, using the small quadrupole, signals were gradually improved using the ultrasonic nebulizer until a 10 µg.ml$^{-1}$ solution of cobalt would produce a count rate of up to 50,000 counts.sec$^{-1}$
Fig. 59. Data system display over isotopes of cadmium at 10μg.ml⁻¹. Peak count rate in ¹¹²Cd⁺ peak (identified by markers and brightened for area measurement) is 2133 counts.sec⁻¹.
i.e. $5 \times 10^3$ counts.sec$^{-1}$ per µg.ml$^{-1}$ with background levels of about 10 counts.sec$^{-1}$. Signal levels with the pneumatic nebulizer were a factor of 3 to 4 lower so that at this stage it was used very little. This compares with signals of about $2 \times 10^4$ counts.sec$^{-1}$ per µg.ml$^{-1}$ obtained in the earlier work with the capillary arc DC plasma, the same quadrupole analyser and a similar ultrasonic nebulizer. For the same solution concentration the ion density in the ICP would be at least a factor of 2 lower because of the higher temperature alone so the two systems were not very different in sensitivity.

Once this point was reached at which results similar, at least in sensitivity, to those obtained in the capillary arc work were obtained, the next step was to introduce the higher resolution, larger V.G. 12-12S quadrupole which was one of the major intentions of the programme. By this time it had become available and was installed as described in Chapter 3.2 An immediate improvement in sensitivity was obtained of a factor of 50 and as anticipated much better resolution was available, particularly at higher masses, without the significant loss of transmission that had been a problem with the small analyser. A welcome consequence of the high signals now available was that the ultrasonic nebulizer need no longer be used and a pneumatic nebulizer of the Meinhard type was fitted to the inlet to the desolvator. Since pneumatic nebulizers are normally self aspirating this gave much greater convenience in sample changing.

At this time also the first long bore 70 µm platinum apertures were received. These proved very stable and consistent and enabled the system with the new quadrupole to be operated for long periods while the process of optimising the operating conditions was carried out. The slower rate of expansion through these apertures, however, resulted in additional ion molecule reaction peaks which were a nuisance for analysis, particularly the large peak which occurred at 59u (possibly ArH$^+$.H$_2$O). Small proton attachment peaks were also noticed next to analyte ions which were a nuisance for isotope ratio measurements. These apertures were, therefore, only used for system optimisation and setting up, and were replaced by short 70 µm molybdenum apertures in platinised cones for measurements. Signal levels were otherwise very similar with these two types of aperture. Two minor changes were made
to the ion optics during this period, which improved signals still further. The sampling cone mount was connected to ground and the entrance plate of the quadrupole analyser isolated and biased independently, and in addition a DC bias was applied to the pre filter rods of the quadrupole. The normal potentials used are shown in Appendix 3. In addition a new cone mount was fitted to the slide valve which held the sampling cone at 20° to the horizontal while the plasma torch remained at 30°. This 10° angle between the two and a small copper foil stop on the front edge of the collector electrode, obstructed the line of sight between the plasma, the sampling aperture and the differential aperture and reduced the photon signal obtained with all lens potentials off to zero. Since the random background of the electron multiplier was well below specification at one or two counts per minute the only remaining background signal detected between peaks when all operating potentials were applied was a random count of up to 10 counts/sec⁻¹ which was present over the whole mass range. This was thought to be due to photons from excited ions, mainly of argon, which decayed along the axis of the ion lens in front of the quadrupole analyser.

The performance obtained when sampling from the boundary layer once this optimization had been completed, is described in the following section 5.1.2 to 5.1.7.

5.1.2 Background Signals and Spectra

Once the large quadrupole analyser was operating with the data system it became possible to make reliable measurements. Before considering the performance of the system on analytes it was important to examine the response to a blank solution. The random background present right across the mass range consisted of a number of possible components:

(a) Random electrical noise radiated from elsewhere in the building or introduced on supply lines.
(b) RF noise from the plasma system and from the quadrupole RF generator.
(c) Pulse amplifier noise.
(d) Random detector pulses (i.e. cosmic ray background)
(e) Direct plasma photons
(f) Photons from decaying excited states of atoms and ions.

All of these were observed from time to time. Apart from careful grounding of the system and the use of filtered mains supplies little could be done about (a) but fortunately it was rare. By similar attention to screening, grounding and cable routing (b) was reduced to about twice the level of the amplifier noise (c) and the discriminator was easily set to reject this. Detector background was normally found to be very low, less than 1 count per minute, although one new detector was found to have a built-in background of 250 counts.sec\(^{-1}\) and was returned.

By the use of the light-stop and careful orientation of plasma and sampling cone (e), direct plasma photons, were completely rejected, i.e. no count was observed with all lens potentials switched off when in the normal sampling position. The remaining source of random background, excited state decay (f), contributed a total of a few hundred counts in a 1 minute integration, spread randomly across all 1023 channels of memory. Thus in a spectrum there would be many channels between peaks containing zero counts. This may be seen in Table 9 where a printout of a series of channel groups from the memory, each group of channels corresponding to a single mass peak, is shown for a 20 µg.ml\(^{-1}\) solution containing copper and zinc. The group from channel 657 to 666 corresponds to 62u and contains zero counts, as ideally it should do in the absence of a peak at that mass.

With a satisfactory random background the performance is then limited by the background which has a spectral characteristic resolvable by the mass analyser, and this is much more significant. The nature and importance of this background signal may be judged from Fig. 60 which shows the spectrum obtained from a solution of 1 µg.ml\(^{-1}\) of cobalt in 1% HNO\(_3\). A clear peak of 59u is obtained of about 7 x 10\(^5\) counts.sec\(^{-1}\) representing very high sensitivity. However, there are also many very large peaks which are produced from the plasma argon and from the constituents of the solution and their impurities. Of these large peaks only one, \(^{40}\)Ar\(^+\), can be attributed to direct ionization in the
Table 9

Print Out of Cu and Zn Peaks from 20μg.ml\(^{-1}\) Solution

<table>
<thead>
<tr>
<th>TAG NO.</th>
<th>CI SERIES 60</th>
<th>START</th>
<th>INTEGRAL</th>
<th>RATE</th>
<th>STOP</th>
<th>MASS NO</th>
<th>IDENTITY</th>
<th>PEAK COUNT RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>657</td>
<td>666</td>
<td>0</td>
<td>0.0</td>
<td>666</td>
<td>677</td>
<td>62</td>
<td>Ba</td>
<td>0 c/s</td>
</tr>
<tr>
<td>668</td>
<td>677</td>
<td>62</td>
<td>1579.4</td>
<td>677</td>
<td>688</td>
<td>64</td>
<td>Cu</td>
<td>673,633 c/s</td>
</tr>
<tr>
<td>679</td>
<td>688</td>
<td>64</td>
<td>276.0</td>
<td>688</td>
<td>699</td>
<td>65</td>
<td>Cu</td>
<td>144,050 c/s</td>
</tr>
<tr>
<td>690</td>
<td>699</td>
<td>65</td>
<td>166.8</td>
<td>699</td>
<td>710</td>
<td>66</td>
<td>Zn</td>
<td>297,667 c/s</td>
</tr>
<tr>
<td>701</td>
<td>710</td>
<td>66</td>
<td>1475</td>
<td>710</td>
<td>721</td>
<td>67</td>
<td>Zn</td>
<td>63,303 c/s</td>
</tr>
<tr>
<td>712</td>
<td>721</td>
<td>67</td>
<td>153.8</td>
<td>721</td>
<td>733</td>
<td>68</td>
<td>Zn</td>
<td>9,050 c/s</td>
</tr>
<tr>
<td>724</td>
<td>733</td>
<td>68</td>
<td>1310</td>
<td>733</td>
<td>1310</td>
<td>69</td>
<td>Zn</td>
<td>42,683 c/s</td>
</tr>
</tbody>
</table>

Fig. 60. Spectrum of 1μg.ml\(^{-1}\) solution of Co showing strong Co response and background peaks.
plasma as it is the only atomic ion. All the others are molecular ions whose binding energy is too low to survive the temperature of the plasma and which must therefore have been formed either in the boundary layer or during the expansion process by ion molecule reactions. Many such ions have been recorded in studies of ion molecule reactions (71) so their presence is to be expected. However, the size of some of these peaks clearly precludes low level detection of analyte ions that coincide with them. These major background ions are listed in Table 10 together with their probable identity and possible origin, the elemental isotopes with which they coincide and alternative isotopes for the detection of these elements where available. From this list it can be seen that there are remarkably few ions of general analytical importance whose detection is impracticable. The most serious limitations are for calcium and sulphur. Apart from these two elements, which are not really detectable at low levels, the detection limits for other elements are determined by the relationship of the concentration sensitivity (counts/sec\(^{-1}\) per \(\mu\)g.ml\(^{-1}\)) to the background level which consists of the sum of the random background and the level of any minor peaks at that mass.

That there is a considerable number of these minor peaks in the range 0-85u may be seen from the blank (1% HNO\(_3\)) spectrum shown in Figs. 61 and 62. These are the same spectrum at a full scale channel content of 16,384 and 256 counts. Also shown at one side of these is the equivalent concentration of cobalt from Fig. 60 to give the same peak height. It can be seen that down to the equivalent level of about 0.05 \(\mu\)g.ml\(^{-1}\) cobalt it is only the major peaks that cause serious interference and preclude detection at these masses. However, at levels below 0.005 \(\mu\)g.ml\(^{-1}\) the resulting small peaks could not be seen between values of 16-21u, 28-42u, 56-58u and at 33, 80 and 81u, and even between these closed areas there are few values of \(m/z\) where a background peak does not have to be subtracted. However, many of these are of a size equivalent to or below the 0.001 \(\mu\)g.ml\(^{-1}\) level and thus detection limits of this order are practicable for many elements. In addition these are the principal peaks in the range 0-100u, above 100u there are few background peaks and for many elements, therefore, a much smaller problem.

Many of these small peaks have not been identified with any certainty. Some such as those at 23u, 39u, 63u and 65u are probably contamination
### Table 10

**Boundary Layer Sampling**

**Major Background Ions, Origin, and Coincident Isotopes**

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Probable Identity</th>
<th>Origin</th>
<th>Coincident Isotope</th>
<th>Alternative Isotope</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>OH⁺</td>
<td>BL</td>
<td>O¹⁷ (0.04%)</td>
<td>O¹⁶ (99.7%)</td>
</tr>
<tr>
<td>18</td>
<td>OH₂⁺</td>
<td>BL</td>
<td>O¹⁸ (0.2%)</td>
<td>O¹⁶ (99.7%)</td>
</tr>
<tr>
<td>19</td>
<td>OH³⁺</td>
<td>BL</td>
<td>F¹⁹ (100%)</td>
<td>None</td>
</tr>
<tr>
<td>29</td>
<td>N₂H⁺</td>
<td>BL</td>
<td>Si²⁹ (4.7%)</td>
<td>Si²⁸ (92.2%)</td>
</tr>
<tr>
<td>30</td>
<td>NO⁺</td>
<td>BL</td>
<td>Si³⁰ (3.1%)</td>
<td>Si²⁸ (92.2%)</td>
</tr>
<tr>
<td>32</td>
<td>O₂⁺</td>
<td>BL</td>
<td>S³² (95%)</td>
<td>S³⁴ (4.2%)</td>
</tr>
<tr>
<td>33</td>
<td>O₂H⁺</td>
<td>BL</td>
<td>S³³ (0.8%)</td>
<td>S³⁴ (4.2%)</td>
</tr>
<tr>
<td>37</td>
<td>OH⁺⁺(H₂O)</td>
<td>AT</td>
<td>Cl³⁷ (24%)</td>
<td>Cl³⁵ (75%)</td>
</tr>
<tr>
<td>40</td>
<td>Ar⁺</td>
<td>PA</td>
<td>Ca⁴⁰ (97%)</td>
<td>Ca⁴⁴ (2.1%)</td>
</tr>
<tr>
<td>41</td>
<td>ArH⁺</td>
<td>BL</td>
<td>K⁴¹ (6.9%)</td>
<td>K³⁹ (93%)</td>
</tr>
<tr>
<td>80</td>
<td>Ar.Ar⁺</td>
<td>EX</td>
<td>Se⁸⁰ (50%)</td>
<td>Se⁷⁸ (23%)</td>
</tr>
<tr>
<td>81</td>
<td>Ar.ArH⁺</td>
<td>EX</td>
<td>Br⁸¹ (49%)</td>
<td>Br⁷⁹ (50%)</td>
</tr>
</tbody>
</table>

**BL:** boundary layer ion-molecule reaction.

**AT:** catalysed attachment of H₂O molecule to ion.

**PA:** primary ionisation in plasma.

**EX:** condensation reaction in gas expansion through aperture.
Fig. 61. Blank spectrum 0-85u showing relative height of analyte peak (Co) v. concentration. Full scale approximately 250 K.counts.sec\(^{-1}\).

Fig. 62. Same blank spectrum as in Fig. 61 but vertical scale expanded to approximately 4000 counts.sec\(^{-1}\) f.s.d.
in the blank, although the copper peaks might also be the product of sputtering of the interior of the sampling cone. A number of peaks are the minor isotopes of the major peaks of molecules containing hydrogen, oxygen, nitrogen and argon although many of these appear to be relatively too large because the major peak is not fully developed due to detector and counting system saturation. Other peaks are the consequence of cluster formation during the expansion through the sampling aperture. A well known (53,54) example of such a cluster is the dimer Ar.Ar at 80u. Mixed clusters have also been reported and could account for peaks at 54 and 56u due to Ar.N+ and Ar.O+.

Major peaks are also the result of proton and water attachment which has been extensively studied by Hayhurst (72). The attachment of water molecules to a hydrogen ion gives rise to a series H+(H2O)_n with members at 19, 37, 55, 73 and occasionally 91, although a curious feature is the absence in this work of the member at 55. Similarly, the attachment of a proton may be the source of peaks at 17(O.H+), 31(NO.H+), 41(Ar.H+) and 81(Ar.Ar.H+). Apart from the ion molecule reaction products and clusters that are reported in other work, the identification of many of the minor peaks must be uncertain, but for most purposes is not necessary. In practical analytical work while they constitute a restriction on ultimate detection limits, they can be allowed for by the normal practice of running a blank, which with this technique is very simple to do. This also allows for the variation in detail of both large and small background peaks which occurs with changes in sampling conditions, for example in the cone and aperture, and which can occur during the course of a day's run.

Although there are many small background peaks, the major areas which are unusable are fortunately not those where important analyte elements occur and the spectra are otherwise reasonably simple. There is little evidence of any peaks at fractional masses and there is no evidence of significant hydrocarbon series peaks from pump oils, which is to be expected with the ionization source outside the vacuum system. Hydrocarbon molecules could, however, form part of some cluster or attachment molecular ions.
5.1.3 Characteristic Spectra

Three main types of response have been found when solutions are nebulized. Most metals show simple metallic singly charged ion peaks at the mass number of the atomic ion, with isotopic peaks in approximately the correct ratios where there is more than one isotope. Other elements, including the alkalis, also show simple atomic spectra. Occasionally, as with iodine in Figure 64, a small proton attachment peak occurs. Typical spectra are seen in Figures 63 to 65.

A few elements, notably the alkaline earths and the rare earths, show varying degrees of double ionization. Many of these elements have second ionization energies below 12eV and some doubly charged ions are therefore seen. The spectrum of Ba$^{2+}$ ions is shown in Fig. 66, not fully resolved. The alkaline earths in particular also show a group of peaks at m/z values corresponding to the hydroxide molecule. The response for barium showing the Ba$^+$ and BaOH$^+$ ions is shown in Fig. 67.

Finally, elements with refractory oxides where the oxide dissociation energy is greater than about 6eV show substantial peaks corresponding to MO$^+$. In extreme cases where the binding energy is very high, such as uranium (7.8eV), there is practically no atomic ion and the whole response occurs as UO$^+$ and UO$_2^+$; (Fig. 68). Many elements such as yttrium and the rare earths show both atomic and monoxide peaks.

5.1.4 Sensitivity and Dynamic Range

The sensitivity and dynamic range of the system using 70 μm diameter apertures, i.e. sampling from within the boundary layer, was determined by Date (73) for a range of elements. While sensitivity expressed in count rate for a given concentration could readily be determined for elements by manually tuning to the peak concerned and noting the resulting count rate, the normal procedure was to run mixed solutions containing several elements of interest at the same concentration and within a narrow range of mass, and then setting the scan to just cover this range. The response was then integrated for the usual period of 1 minute and the integral over each peak of interest read out for that concentration.
Fig. 63. Spectrum of NBS SRM 981 at 1μg.ml⁻¹. Peak count rate $^{208}_{\text{Pb}} + 45,707$ sec⁻¹.

Fig. 64. Spectrum from solution of cadmium iodide and silver nitrate. Ag and I at 10μg.ml⁻¹, Cd at c. 5μg.ml⁻¹. Peak iodine count rate 65,617 sec⁻¹.

Fig. 65. Full spectrum from 0-230μ of 1μg.ml⁻¹Mg,Al,Co,Ag,Pb. Peak count rate $^{107}_{\text{Ag}} + 483,033$ sec⁻¹.
Fig. 66. Spectrum of $\text{Ba}^{++}$ from $10\mu\text{g.mL}^{-1}\text{Ba}$.

Fig. 67. Spectrum of $\text{Ba}^+$ and $\text{BaOH}^+$ from same solution as Fig. 66.

Fig. 68. Spectrum from $10\mu\text{g.mL}^{-1}\text{Pb and U}$, showing oxide ions $\text{UO}^+$ and $\text{UO}_2^+$.
In order to plot a calibration curve this was repeated at a range of concentrations from usually 0.001 \( \mu g.mL^{-1} \) to 10 \( \mu g.mL^{-1} \). The lower limit of this range was approaching background levels and the upper limit was restricted in practice by two problems. Where these were up to 4 elements in the solution this meant a total of 40 \( \mu g.mL^{-1} \) at the top end at which solid condensation on the cool tip of the sampling cone tended to block the sampling aperture. In addition at the sensitivities achieved pulse count rates were typically between 1 and 2MHz at 10 \( \mu g.mL^{-1} \). At this rate it became difficult to keep the channel multiplier working point on the plateau which meant a loss of linearity as the count rate increased. A combination of these effects may just be seen to cause a drop in response below the 45\(^0\) line in the calibration plots.

The energy spread of the extracted ions was very small, about 2eV positive bias on the quadrupole rods reducing the count rate to zero. This gave very good mass resolution. This may be seen in the spectrum of Chromium, Cobalt, Copper and Zinc, shown in Fig. 69, taken from one of the calibration runs. The response falls to zero for about 0.5u between the peaks. This made setting the limits for read out of the regions of interest very simple. It was found that signals from some elements, such as cadmium and zinc showed a tendency to persist after the solution was removed. This memory was attributed to the desolvator and caused a hysteresis effect between the upward and downward runs on these elements. Calibration runs were, therefore, only plotted from lowest to highest concentration. Calibration curves plotted without background correction for three groups of elements or isotopes are shown in Figs.70,71 and 72. These are almost linear over four decades of concentration but show slight deviations at high concentrations as described, and for some isotopes a departure from the 45\(^0\) slope at low concentrations due to the presence of a small peak in the blank spectrum. This is noticeable for \(^{64}\text{Zn}^{+}, \text{^{114}Cd}\) and \(\text{^{116}Cd}\). It is worth noting that \(\text{^{106}Cd}\) is only about 1% abundant yet can be followed right down to a total Cd concentration of 0.001 \( \mu g.mL^{-1} \), corresponding to \(10^{-5}\mu g.mL^{-1}\) of \(\text{^{106}Cd}\). The response to lead at the 0.001\(\mu g.mL^{-1}\) level is shown in Fig. 72. This is the spectrum taken at the lowest level in the run, clearly characteristic of lead. This spectrum was plotted by allowing the X-Y plotter to record only a dot corresponding to each
Fig. 69. Spectrum of Cr, Co, Cu and Zn at 1 μg.ml⁻¹ from calibration run. Peak count rate $^{59}$Co $\approx$ 566,900 sec⁻¹.

Fig. 70. Calibration Curves for Chromium, Cobalt, Copper and Zinc
Fig. 71. Calibration Curves for Silver and Cadmium
Spectrum of Lead at 0.001 μg.ml⁻¹ in 1% HNO₃
(Pb²⁰⁸ peak channel, 27 counts)

Fig. 72. Calibration curves for lead isotopes showing ratios at 0.1μg.ml⁻¹ and a spectrum at 0.001μg.ml⁻¹.
memory channel content instead of a continuous line. The peak channel of \( \text{Pb}^{208} \) contains 27 counts and the base line at 0 counts and the background levels of 1 and 2 counts are clearly seen. This illustrates well how the low random background contributes to low detection limits.

The sensitivity may be expressed either as concentration sensitivity in counts/sec\(^{-1}\) per \( \mu g.\text{ml}^{-1} \), which is perhaps more convenient for the analyst, or in molar sensitivity i.e. counts/sec\(^{-1}\) per unit molar concentration which is more revealing in terms of plasma ionization equilibria. Values of both these quantities, obtained during these calibration runs, are shown in Table 11 together with the ionization potentials of the elements concerned.

Although these represent a high sensitivity for these elements, they do not necessarily represent the highest attainable values. When running multi-element solutions the analyser resolution was normally set at a value that gave a response that fell to zero for a width of about 0.25u between adjacent peaks. While this simplified measurement it did not give the highest possible sensitivity. It was possible to increase signal levels by at least a factor of 2 by accepting a peak overlap of a few percent of peak height between adjacent peaks. Thus in any particular situation the sensitivity could be optimised for a portion of the spectrum of particular interest. The best compromise between sensitivity and resolution over a particular mass range could only be chosen in the light of the problem concerned. The values quoted in Table 11 represent compromises that give lower values than the best attainable.

The response to elements of closely similar mass but different ionization energy may be used to obtain a value for ionization temperature if the elements are run in the same solution at known concentrations so that variation of sensitivity with time is avoided. A convenient pair for this are silver and cadmium. The ionization potentials are 7.58eV and 8.99eV. Experimental values of the count rate taken from two of the calibration runs for Ag and Cd solutions at 10 \( \mu g.\text{ml}^{-1} \) give ratios of Cd/Ag signal of 0.50 and 0.52. The Saha equation may be used to calculate the expected ratio, i.e. the ratio of the two degrees of ionization \( \alpha_{\text{Cd}}/\alpha_{\text{Ag}} \) for a range of temperatures from which the values for
Table 11

Typical Count Rate Sensitivities for Boundary Layer Sampling

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration Sensitivity</th>
<th>Molar Sensitivity</th>
<th>Ionisation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^3$Counts.sec$^{-1}$ per µg.ml$^{-1}$</td>
<td>$10^6$Counts.sec$^{-1}$ per µM.ml$^{-1}$</td>
<td>eV</td>
</tr>
<tr>
<td>Ag</td>
<td>89.2</td>
<td>9.62</td>
<td>7.58</td>
</tr>
<tr>
<td>Al</td>
<td>27.5</td>
<td>0.74</td>
<td>5.98</td>
</tr>
<tr>
<td>Ba</td>
<td>2.3</td>
<td>0.32</td>
<td>5.21</td>
</tr>
<tr>
<td>Cd</td>
<td>26.9</td>
<td>3.03</td>
<td>8.99</td>
</tr>
<tr>
<td>Co</td>
<td>184.3</td>
<td>10.87</td>
<td>7.86</td>
</tr>
<tr>
<td>Cr</td>
<td>65.9</td>
<td>3.42</td>
<td>6.76</td>
</tr>
<tr>
<td>Cu</td>
<td>131.2</td>
<td>8.34</td>
<td>7.73</td>
</tr>
<tr>
<td>Hg</td>
<td>0.9</td>
<td>0.19</td>
<td>10.44</td>
</tr>
<tr>
<td>Li</td>
<td>6.4</td>
<td>0.04</td>
<td>5.39</td>
</tr>
<tr>
<td>Mn</td>
<td>115.7</td>
<td>6.36</td>
<td>7.43</td>
</tr>
<tr>
<td>Na</td>
<td>175.0</td>
<td>4.02</td>
<td>5.14</td>
</tr>
<tr>
<td>Ni</td>
<td>113.7</td>
<td>6.67</td>
<td>7.63</td>
</tr>
<tr>
<td>Pb</td>
<td>38.5</td>
<td>7.97</td>
<td>7.41</td>
</tr>
<tr>
<td>Rb</td>
<td>118.4</td>
<td>10.12</td>
<td>4.18</td>
</tr>
<tr>
<td>Sr</td>
<td>11.4</td>
<td>1.00</td>
<td>5.69</td>
</tr>
<tr>
<td>V</td>
<td>10.8*</td>
<td>0.55</td>
<td>6.74</td>
</tr>
<tr>
<td>Y</td>
<td>49.0*</td>
<td>4.36</td>
<td>6.53</td>
</tr>
<tr>
<td>Zn</td>
<td>3.1</td>
<td>0.20</td>
<td>9.39</td>
</tr>
</tbody>
</table>

* as monoxide.
T_i for the two cases of 6910 K and 6920 K may be deduced. Thus the effective ionization temperature is below the plasma gas temperature but still much higher than the mean boundary layer temperature and evidently little ionization reequilibration has occurred in the boundary layer. In this particular case it is not justified to assume 100% ionization for silver as at 7000 K \( \alpha_{Ag} \) is only 0.52 so the simpler calculation, assuming that the degree of ionization for cadmium is given by the ratio of cadmium to silver response, corrected for abundance and mass, cannot be used.

5.1.5 Detection Limits

Although concentration sensitivity is a useful criterion on which to evaluate system performance it does nothing to indicate the ability to detect an element unless it can be compared with the response obtained under the same conditions when the element is absent. With some slow analytical techniques this is time consuming and limits of detection are often determined on the basis of a single blank run, as the concentration equivalent to the smallest signal which would be seen above the blank response.

In atomic emission and absorption spectrometry, however, where analysis time is short, the practice has become established of quoting a detection limit in terms of the concentration equivalent to the smallest statistically significant increase in the blank level. This is normally taken as twice or three times the standard deviation of the blank level which is usually determined from a series of ten or more blank runs. In this work the concentration equivalent to 3\( \sigma \) is used, calculated from the value of \( \sigma \) for a series of blank runs and from the response to a 1 \( \mu g.ml^{-1} \) solution. Although this is a useful measure for comparison of techniques the detection limit determined in this way is still below the practicable useful limit of detection in routine work, which is better defined as the concentration equivalent to 10\( \sigma \), a quantity sometimes referred to as the Limit of Quantifiable Determination, or LQD.

The values of 3\( \sigma \) detection limit obtained in this way for a range of important elements is given in Table 12 together with values taken from the literature for ICP-AES and AAS.
Table 12

Detection Limits of Boundary Layer PSMS, ICP-AE and AAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion</th>
<th>Detection Limit ng.ml⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PSMS</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg²⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al³⁺</td>
<td>0.3</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V⁵⁺</td>
<td>0.3</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr³⁺</td>
<td>0.1</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn²⁺</td>
<td>0.06</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe⁵⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co⁹⁺</td>
<td>0.1</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu¹⁺</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn²⁺</td>
<td>2</td>
</tr>
<tr>
<td>Rubidium</td>
<td>Rb⁷⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag¹⁺</td>
<td>0.1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd¹⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba²⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg²⁺</td>
<td>2</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb²⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>Uranium</td>
<td>UO₂⁺</td>
<td>0.05</td>
</tr>
</tbody>
</table>

ICP-AES and Flame AAS values from Ref. 76.
5.1.6 Effect of Matrix Elements and Ionization Suppressants

A well documented characteristic of the ICP as an atomic emission source (74,75) is its relative freedom from interelement effects caused by the presence of relatively high concentrations (up to ca. 1000 μg.ml⁻¹) of matrix elements and/or elements such as sodium of low ionization energy which act as ionization suppressants. It is clearly desirable that as far as possible these characteristics should also be obtained in the application of the ICP as an ion source. In geochemical samples, in which a whole fraction of a rock or sediment sample has been taken into solution, concentrations of the common elements, Al, Si, Ca and Mg, which occur in great abundance in minerals, may well be at levels between 100 and 1000μg.ml⁻¹. Similarly, the common alkali elements Na and K may also occur, particularly in waters or samples of biochemical origin, at levels up to 1000 μg.ml⁻¹. Separation methods are available which enable some or all of the undesired matrix elements to be removed to reduce the interference they cause, but these are often time consuming, may also remove some of the elements of interest and may be a source of additional contamination. Wherever possible, therefore, separation is best avoided and a great advantage of ICP-AE is its ability to cope with complex matrices, even if sometimes corrections have to be applied.

This aspect of the performance of the plasma ion source is, therefore, of great importance and unfortunately, in the boundary layer mode, the behaviour has been found very disappointing.

Reference has already been made earlier in this chapter (5.1.4) to the fact that at solution concentrations much above 10 μg.ml⁻¹, solid condensation around the aperture begins to affect the flow of gas into it and reduces sensitivity. This clearly sets a limit to tolerable matrix concentration and the consequence of diluting a sample to the point where the total solids concentration is below 10 μg.ml⁻¹ would be a severe loss of trace element sensitivity in the original sample.

Solid condensation in the cooler regions of the boundary layer constitutes a form of interference that does not arise with atomic emission spectrometry although something similar can occur at very high solids contents in pneumatic nebulizers. It is, however, so
serious in the boundary layer mode of ion sampling that it makes any investigation of other mechanisms of matrix interference, such as chemical or volatilization interferences of little value since most of these normally occur at relatively high concentrations.

Another important type of matrix interference is ionization suppression in which the additional electron population, introduced by low ionization energy elements, in the plasma disturbs the equilibrium and reduces the degree of ionization of other higher ionization energy elements. For atomic emission spectrometry the ICP is normally very free of this effect since the electron concentration from argon and water in the plasma is normally so high that very little increase is produced by even very high concentrations of suppressants. Again this should be a feature available in its use as an ion source. In the boundary layer mode, however, the effect of even relatively low concentrations of sodium is severe as shown in Figure 73 for the effect of sodium on a 1 µg.ml⁻¹ solution of cobalt. Since, however, it is well established that ionization suppression is small in the bulk plasma it would not be expected to be so severe in the boundary layer because the process of ionization re-equilibration is a relatively slow one and would not be expected to occur in the short dwell time in the boundary layer (see Appendix A4). Much less severe ionization suppression is reported by Houk et al (32), for sampling further out in the tail flame, where however the total ion signals available are much lower. This suggests that the mechanism of this suppression is not electronic but is a form of volatilization interference associated with sampling ions too soon along the flight path through the plasma of the solid micro particulates which constitute the solids content of the nebulized droplets. As a consequence the release as vapour for dissociation and ionization of the cobalt atoms is delayed by the additional solid present.

Both these forms of matrix problem encountered with boundary layer sampling would prove a serious impediment to the analysis of real samples. It was considered, however, that they were essentially associated with the presence of the boundary layer which either caused recondensation or prevented full vaporization of the sample. Further investigation of these effects and a search for operating conditions which could mitigate them was deferred until sampling by continuum flow
Fig. 73. Effect of added Na on response to 1 μg.ml⁻¹ Co in boundary layer mode.
had been explored. It was hoped that avoiding the boundary layer would also avoid these effects and render further exploration of interferences in boundary layer sampling unnecessary. As will be seen later in this chapter this proved to be the case.

5.1.7 Isotope Ratio Determinations

One of the principal ultimate aims of the project funded by the Institute of Geological Sciences was a rapid method of isotope ratio determination directly on sample solutions. The form of data collection from the scanning mass analyser which was adopted was highly convenient for this and once reasonably reliable operation had been attained and the high resolution analyser was in use isotope ratio measurement was attempted. An early result of an isotope ratio run is shown in Fig. 74.

The top spectrum shows a 1 minute integration of 60 scans over a mass range of 45-70 mass units while a solution containing 1 μg.ml⁻¹ of nickel was nebulized. The central spectrum shows a similar integration while blank (1% HNO₃) solution was being nebulized. This spectrum shows the presence of ion-molecule reaction peaks at masses 54, 56, 57 and 58 which are also present in the wanted spectrum along with the nickel peaks. One of the reaction peaks at 58u (Ar⁺.H₂O?) lies under ⁵⁸Ni⁺ and would clearly interfere with the isotope ratio determination. These background peaks are removed from the top spectrum by stripping in the data system leaving the lower spectrum. The isotope abundance values determined from the peak integrals of this stripped spectrum are shown in Table 13. Although this was run at an early stage when the sensitivity was still low (only about 100,000 counts. sec⁻¹ for 1 μg.ml⁻¹nickel) the abundance values are quite close to the normally accepted, 'true', values. It is noticeable that the ⁵⁸Ni value is low, possibly due to variation in the blank mass 58 peak between runs, and this makes the other values high.

The ratios of the lead isotopes are important geologically and another early determination was carried out on three NBS lead isotope standard reference materials. Spectra of SRMs 981, 982 and 983 are shown in
Fig. 74. Spectra of 1μg.ml⁻¹ of Ni, blank 1% HNO₃, and of blank stripped from analyte.

Table 13

<table>
<thead>
<tr>
<th>Abundance %</th>
<th>Ni⁵⁸</th>
<th>Ni⁶⁰</th>
<th>Ni⁶¹</th>
<th>Ni⁶²</th>
<th>Ni⁶⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>True</td>
<td>67.88</td>
<td>26.23</td>
<td>1.19</td>
<td>3.66</td>
<td>1.08</td>
</tr>
<tr>
<td>Measured</td>
<td>67.14</td>
<td>26.73</td>
<td>1.16</td>
<td>3.88</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Total Integration Period 60 sec
Solution Concentration 1μg.ml⁻¹

Table 13. Isotope ratios of nickel from run of Fig. 74.
Fig. 75 and the ratio values obtained are compared with the certified values in Table 14. These were obtained on a 1 minute run at 1 μg.ml⁻¹ so that the total number of counts collected in each peak is relatively small. Because of the random nature of the ion formation process one of the major factors limiting available precision is the standard deviation σ of the number of counts integrated for each peak which is assumed to be given by

\[ \sigma = \sqrt{N/N} \]

On these runs the results are all within 2σ of the certified values and on the major peaks within 1σ, equivalent to an RSD of about 1%.

Once system development had reached the point where high count rate sensitivity was available it became possible to attempt more precise determinations, since with a larger number of counts available at least random errors due to count rate statistics would be reduced. However, early results did not show the improvement expected. In a general examination of the system for possible causes of poor reproducibility it was found that when set to monitor one isotope continuously and the data system was set to scan slowly through the available channels at 10 channels per second the response (for ⁵⁸Ni) shown in Fig. 76 was obtained. Quite apart from the slow drift down of about 25% in 100 seconds a sharp drop in response at regular intervals of about 7 seconds was found. In addition a small fluctuation at a period of about 0.5 seconds is present and a longer sawtooth shaped fluctuation with a period of 20-40 seconds is also visible.

For isotope ratio measurements the normal scan rate of one sweep per second through the isotope would be very sensitive to both the short period fluctuations although on a reasonable number of scans the long period sawtooth should have little effect. It was found that the 7 second fluctuation was due to the nebulizer, since it was absent on a scan taken with no sample injection flow running. This scan, shown in Fig. 77, was taken on the dimer peak ⁸⁰Ar.Ar⁺ and shows the long sawtooth very clearly. The source of the 7 second fluctuation was found to be droplet formation and release in the nebulizer cloud chamber and it was eliminated by changing the waste liquid level. The long term fluctuation was attributed to the pressure regulator on the argon supply and was also eliminated by fitting a precision regulator, after the main regulator, which held the output pressure to better
Fig. 75. Spectra of NBS SRM 981, 982 and 983 Pb standards at 1µg.ml\(^{-1}\).

Table 14
Isotope Ratios on NBS Standards from runs of Fig. 75.

<table>
<thead>
<tr>
<th>SRM</th>
<th>Abundance %</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb(^{204})</td>
<td>Pb(^{206})</td>
<td>Pb(^{207})</td>
<td>Pb(^{208})</td>
</tr>
<tr>
<td>981</td>
<td>Certified</td>
<td>1.42</td>
<td>24.14</td>
<td>22.08</td>
</tr>
<tr>
<td></td>
<td>Measured</td>
<td>1.36</td>
<td>24.38</td>
<td>21.99</td>
</tr>
<tr>
<td>982</td>
<td>Certified</td>
<td>1.09</td>
<td>40.09</td>
<td>18.72</td>
</tr>
<tr>
<td></td>
<td>Measured</td>
<td>1.23</td>
<td>40.08</td>
<td>18.45</td>
</tr>
<tr>
<td>983</td>
<td>Certified</td>
<td></td>
<td>92.15</td>
<td>6.56</td>
</tr>
<tr>
<td></td>
<td>Measured</td>
<td></td>
<td>91.87</td>
<td>6.60</td>
</tr>
</tbody>
</table>

Total Integration Period 60 sec
Solution Concentration 1µg.ml\(^{-1}\)
Fig. 76. Single ion response v. time for an analyte (1\mu g.m l^{-1} of ^{58}\text{Ni}).

Fig. 77. Single ion response on a background peak ^{80}\text{Ar}\text{Ar} with no sample injector flow.
than 10%. After these changes the RSD on single ion monitoring was reduced to below 1%, probably as low as can be expected with mechanical gas pressure regulators, a pneumatic nebulizer and plasma power supply with a power stability of about 1%.

To reduce the effect of the remaining sources of noise in the ion signal the scan rate of the mass analyser and data system was modified for isotope ratio determinations. The maximum rate of scan of the quadrupole analyser is limited ultimately by the ion transit time through the rods but before this is reached the time constants of the mass and resolution-control circuits affect the resolution obtained, and this sets a limit to about 30 ms for a full scan and 10 ms where the scan is limited to a small part of the mass range, say 10% wide. The normal minimum scan period was 300 ms so the scan unit was modified to provide scan periods at the bottom of the range of 10, 30, 100, 300 and 1000 ms. Used with the approximate dwell time settings on the data system it was then possible to run isotope ratio scans at the rate of up to 5000 per 1 minute scan.

With this high scan rate much better precision was then obtained. Table 15 shows lead isotope ratios determined by Date on NBS 981. For this set of values the practice was adopted of setting the scan to use a minimum of 100 data channels per unit mass which enabled the full spectrum of lead to be accumulated in a memory group of 1000 channels together with some background either side of the 204 and 208 peaks. At the highest scan rates the first group of 100 channels was not fully available owing to timing delays in the trigger circuits. In this case each run was 61.44 seconds (the nominal 1 minute normally used), and the solution concentration 1 µg.ml⁻¹. The total lead count integral over all four isotopes was 5 x 10⁵ counts.

For the 20 runs made the standard deviation for each ratio was calculated from the experimental results and this and the corresponding relative standard deviation are shown below the mean ratio values. The mean count error to be expected on each result is shown in the bottom line, and it can be seen that for each ratio the experimental RSD is little more than that to be expected from the counting statistics.
<table>
<thead>
<tr>
<th>Run</th>
<th>Total Count</th>
<th>204/206</th>
<th>207/206</th>
<th>208/206</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>491,142</td>
<td>0.05935</td>
<td>0.9227</td>
<td>2.185</td>
</tr>
<tr>
<td>2</td>
<td>497,831</td>
<td>0.06024</td>
<td>0.9205</td>
<td>2.176</td>
</tr>
<tr>
<td>3</td>
<td>503,645</td>
<td>0.05709</td>
<td>0.9158</td>
<td>2.167</td>
</tr>
<tr>
<td>4</td>
<td>491,459</td>
<td>0.05921</td>
<td>0.9231</td>
<td>2.179</td>
</tr>
<tr>
<td>5</td>
<td>495,229</td>
<td>0.05956</td>
<td>0.9269</td>
<td>2.188</td>
</tr>
<tr>
<td>6</td>
<td>487,182</td>
<td>0.05838</td>
<td>0.9280</td>
<td>2.183</td>
</tr>
<tr>
<td>7</td>
<td>475,346</td>
<td>0.05877</td>
<td>0.9314</td>
<td>2.201</td>
</tr>
<tr>
<td>8</td>
<td>485,816</td>
<td>0.05901</td>
<td>0.9229</td>
<td>2.196</td>
</tr>
<tr>
<td>9</td>
<td>483,665</td>
<td>0.05989</td>
<td>0.9302</td>
<td>2.201</td>
</tr>
<tr>
<td>10</td>
<td>487,903</td>
<td>0.05960</td>
<td>0.9221</td>
<td>2.190</td>
</tr>
<tr>
<td>11</td>
<td>481,101</td>
<td>0.05814</td>
<td>0.9252</td>
<td>2.184</td>
</tr>
<tr>
<td>12</td>
<td>515,956</td>
<td>0.05843</td>
<td>0.9320</td>
<td>2.205</td>
</tr>
<tr>
<td>13</td>
<td>502,241</td>
<td>0.05667</td>
<td>0.9233</td>
<td>2.189</td>
</tr>
<tr>
<td>14</td>
<td>502,590</td>
<td>0.05786</td>
<td>0.9281</td>
<td>2.193</td>
</tr>
<tr>
<td>15</td>
<td>529,737</td>
<td>0.05802</td>
<td>0.9162</td>
<td>2.177</td>
</tr>
<tr>
<td>16</td>
<td>547,837</td>
<td>0.05682</td>
<td>0.9236</td>
<td>2.184</td>
</tr>
<tr>
<td>17</td>
<td>540,608</td>
<td>0.05852</td>
<td>0.9250</td>
<td>2.197</td>
</tr>
<tr>
<td>18</td>
<td>548,662</td>
<td>0.05646</td>
<td>0.9190</td>
<td>2.196</td>
</tr>
<tr>
<td>19</td>
<td>532,352</td>
<td>0.05770</td>
<td>0.9251</td>
<td>2.200</td>
</tr>
<tr>
<td>20</td>
<td>511,832</td>
<td>0.05815</td>
<td>0.9205</td>
<td>2.179</td>
</tr>
</tbody>
</table>

Mean: 0.05839, 0.9241, 2.189

σ: 0.00109, 0.0045, 0.010

RSD (%): 1.86, 0.49, 0.46

True: 0.05904, 0.9146, 2.168

Diff. (%): -1.10, +1.04, +0.97

Mean Count (%): 1.22, 0.41, 0.35

Error
Also shown is the true value for NBS 981 and the difference between the measured and true value. The difference values show evidence of mass discrimination in favour of the heavier isotopes, values above mass 206 being high and vice versa. However, in addition the ratio of 208/206 shows a lower bias than would be expected and this is thought to be due to counting loss in the ion detection and pulse counting system. Where the pulse pair resolution of the system is $\tau$, and the pulse rate produced by the detector is $n_o$, the observed count rate will be

$$n = n_o (1 - n_o \tau)$$

In this system the pulse pair resolution of the multi-channel scaler is 50 n.sec. so that at a peak count rate of $2 \times 10^5$ counts/sec$^{-1}$, typical of these measurements for the $^{208}$Pb peak, the count rate observed would be 0.1% low. Thus although this might cause problems if the counting RSD were to be improved further by increasing the integral count, it is not very significant at RSD values of 0.46%. A more probable cause is loss of counts due to the shift of the detector plateau at high count rates. This is due to the reduction of the multiplier gain at high count rates caused by increased potential drop down the multiplier resistive coating as the integral current rises. This can only be improved by using lower discriminator settings and lower EHT levels which can only be achieved by reducing interference and noise background levels.

However, the important point demonstrated by these results is the good reproducibility obtained and that the scatter of experimental results is little more than would be expected from the level of signal collected.

The bias or mass discrimination in the results was found to be consistent and reproducible at given operating settings, but it was found to be particularly dependent on the potential used on the first electrode, the collector, which draws ions from the expanding cloud inside the sampling cone. Date found that by changing this potential the bias could be made to favour either lower or higher mass isotopes as shown in Table 16. Here the mean values for 5 runs at each of the
Variation of Isotope Ratios with Collector Potential

<table>
<thead>
<tr>
<th>NBS 981</th>
<th>10ug.ml$^{-1}$ Pb</th>
<th>30.72sec/Run</th>
<th>13 May 1981</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potential</td>
<td>Run</td>
<td>Total Count</td>
</tr>
<tr>
<td>195V</td>
<td></td>
<td>1</td>
<td>3,121,952</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>3,007,335</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>2,929,052</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>2,892,597</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>2,939,518</td>
</tr>
<tr>
<td>Mean</td>
<td>(Bias)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150V</td>
<td></td>
<td>1</td>
<td>957,654</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>991,891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1,017,825</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>1,072,152</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>1,136,338</td>
</tr>
<tr>
<td>Mean</td>
<td>(Bias)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15V</td>
<td></td>
<td>1</td>
<td>319,479</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>336,118</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>337,911</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>328,232</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>333,861</td>
</tr>
<tr>
<td>Mean</td>
<td>(Bias)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

True Values

|           | 0.05904 | 0.9146  | 2.168   |
three different collector potentials is shown and it can be seen that the discrimination favours higher masses at low collector potentials. However, unfortunately, ion collection is much less efficient at low potentials, the integrals count for 15V being only 10% of that at 195V, so this increases the scatter in the ratios. A compromise was normally chosen to give good collection efficiency with some discrimination against high masses in order to ensure good reproducibility so that the results could be corrected against the standards with some confidence. A set of results on another NBS standard SRM 982 corrected against NBS 981 is shown in Table 17 (again taken by Date). The difference between the true and measured value on these 5 minute runs is considerably less than the possible error from counting statistics. These results of Date obtained as part of the application studies on the instrument, are quoted here both for completeness and to illustrate some of the remaining problems with the technique.
Table 17

Isotope Ratios on NBS 982 Lead

<table>
<thead>
<tr>
<th>Run</th>
<th>Background ((-\text{Bkgd}))</th>
<th>Total (\text{Pb}) ((-\text{Bkgd}))</th>
<th>204/206 Ratio</th>
<th>207/206 Ratio</th>
<th>208/206 Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>467</td>
<td>433,552</td>
<td>0.02814</td>
<td>0.4647</td>
<td>0.9749</td>
</tr>
<tr>
<td>2</td>
<td>347</td>
<td>394,539</td>
<td>0.02820</td>
<td>0.4663</td>
<td>0.9725</td>
</tr>
<tr>
<td>3</td>
<td>360</td>
<td>379,191</td>
<td>0.02765</td>
<td>0.4621</td>
<td>0.9680</td>
</tr>
<tr>
<td>4</td>
<td>338</td>
<td>359,823</td>
<td>0.02792</td>
<td>0.4628</td>
<td>0.9737</td>
</tr>
<tr>
<td>5</td>
<td>392</td>
<td>342,372</td>
<td>0.02863</td>
<td>0.4629</td>
<td>0.9685</td>
</tr>
<tr>
<td>6</td>
<td>481</td>
<td>309,142</td>
<td>0.02872</td>
<td>0.4600</td>
<td>0.9671</td>
</tr>
<tr>
<td>7</td>
<td>465</td>
<td>302,194</td>
<td>0.02851</td>
<td>0.4605</td>
<td>0.9645</td>
</tr>
<tr>
<td>8</td>
<td>476</td>
<td>300,275</td>
<td>0.02844</td>
<td>0.4586</td>
<td>0.9632</td>
</tr>
<tr>
<td>9</td>
<td>382</td>
<td>288,386</td>
<td>0.02859</td>
<td>0.4627</td>
<td>0.9671</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>284,680</td>
<td>0.02837</td>
<td>0.4630</td>
<td>0.9623</td>
</tr>
</tbody>
</table>

Mean \((\bar{x})\) 0.02832 0.4624 0.9682

Standard Deviation \((\sigma)\) 0.00034 0.0022 0.0043

Relative Standard Deviation (%) 1.20 0.48 0.44

NBS 981 (Mean of 10 Runs) 0.06099 0.9056 2.099

True Value 0.05904 0.9146 2.168

NBS 982 corrected against NBS 981 0.02741 0.4670 1.00003

True Value 0.02722 0.4671 1.00016

Difference from True Value (%) +0.69 -0.021 -0.013

Counting Error (%) 1.01 0.31 0.25
5.2 Results Obtained by Continuum Sampling

The development of operation in the continuum sampling mode has been described in Chapter 4.4. Although this process started about halfway through the project progress was slow until the final few months when the stages described in 4.4.5 and 4.5 were reached. It then rapidly became possible to optimise the performance and obtain reproducible results from day to day. During the performance evaluation described below the system was frequently operated continuously without moving the plasma torch in relation to the aperture for periods of several hours at a stretch, on one occasion for 7 hours continuously. During a run of this length visible erosion of the sampling cone would occur, the aperture typically enlarging from 400 to 450 μm diameter. This would produce an increase of about 20% in signal levels. The same aperture could be used for several such sessions until after a period varying from about 30-50 hours aperture diameter had increased to about 550 μm. Apertures may be successfully used up to a diameter of at least 600 μm at which the wall thickness of the present design of copper cone becomes rather too small for safety but the performance steadily improves and no problems are found with handling the larger amount of gas admitted. However, above about 500 μm it is necessary to increase the sample flow and uptake rate to the plasma as even at 400 μm the aperture swallows half of the central channel flow. At 600 μm the gas intake was slightly greater than the sample flow and signal levels became unstable unless the flow was increased by about 50%. The final performance achieved is described below under similar headings to those used for boundary layer sampling.

5.2.1 Source Characteristics

The energy of the ions entering the mass analyser affected the resolution greatly and once the decision to operate at -25V bias on the continuum stage was taken, the energy and energy spread of the ions reaching the quadrupole was determined on a 10 μg.ml⁻¹ Co solution. The quadrupole entrance plate was used as a retardation electrode. Although not ideal for the purpose since it consisted of a single 5 mm diameter aperture rather than a grid, it was found that at negative potentials it had very
Fig. 78. Energy Distribution of Ions Obtained in Continuum Sampling.

Fig. 79  Signal and Signal-to-Background Ratio for Indium at $10\mu g . m l^{-1}$ and 10mm Load Coil to Aperture Separation
little influence on the response and only as the potential exceeded 1V positive did it reduce the signal. The differential response is shown in Fig. 78, the distribution is centered about a true potential of 6.5V. The width of the distribution at half height is 7.5V and the rod operating potential was therefore set at +4V. The bias on the pre-rods was then set to give maximum signal with the entrance plate at zero.

The variation of response with plasma power was determined on a 10 μg.ml⁻¹ solution of indium. This is a convenient element for runs of this type as it has a low first ionization potential and a second well above argon at 18.86eV so double ionization is negligible. The ¹¹⁵In isotope (95.72%) was used, and the spectrum obtained on a scan from 112u to 117u. Regions of interest were set around the 115 peak and on background either side using the same channel width, and the integrals printed out. The peak count rate for ¹¹⁵In and the ratio of ¹¹⁵In integral to the mean background integral is shown in Fig. 79 at power levels from 0.8 to 1.8KW. It can be seen that the absolute signal level reaches a plateau at 1.6KW although rising steeply before that, but the signal to noise ratio peaks at 1.4 KW. Since the plasma gas flows were not changed during this run it is possible that the signals obtained may be higher than if the recommended practice of increasing coolant flow at high power levels had been followed. However, no problems were experienced with the torch at these powers but they were used as little as possible as the heat input to the expansion stage was noticeably greater. During this run the position of the aperture at 10 mm from the load coil was unchanged and the transverse setting obtained at 1.2 KW was also left unchanged.

It is always noticeable that an unimpeded plasma flame constricts as the power level is varied and the central channel expands less rapidly along the flame so the increase in signal is presumably due to a higher ion concentration produced by this constriction, since indium would be expected to be fully ionized. From these results a normal operating power level of 1.2 KW was chosen. This gave a signal to background ratio at this time of about 10³ at 10 μg.ml⁻¹ although subsequently this was considerably improved. Profiles of the response across the flame and along the axis were also taken and are shown in Fig. 80 and Fig. 81. The transverse profiles in Fig. 80 show clearly the effect of the diffusion of the central channel into the outer annulus of the
Fig. 80. Transverse Response Profiles Across Plasma Flame at Different Distances from the Load Coil. 10 μg.ml⁻¹ In.

Fig. 81. Longitudinal Response Variation on Flame Axis. 10 μg.ml⁻¹ In.
Fig. 82. Variation of U and UO Response with Distance along the Flame Axis.

Fig. 83. Variation of U and UO Response with Power.
flame at positions further from the work coil. It is also noticeable that the flame is not quite symmetrical due to an imperfectly centred sample injector tube in the plasma torch or to misalignment of the torch itself. The half width of the flame at 5 mm is 1.6 mm. The width of the central channel from photographs of yttrium ion emission at 5 mm is 2.9 mm which corresponds to the width of the distribution at 23% of peak height. The axial longitudinal profile, Fig. 81, suggests that operation between 5 and 10 mm from the load coil yields the best signal as long as the sample is fully dissociated and ionized by then. Certainly, for uranium there is little change in the proportion of UO seen in the spectrum over the whole of the axial distance as shown in Fig. 82. Some variation in the UO level is seen to correspond with the fall in U signal at greater distances but there is evidently a substantial fraction of the UO signal that is independent of position. Similarly in Fig. 83 the UO signal varies little with plasma power. Although uranium has a low first ionization potential the second is also low (about 12.5eV - not listed) and the fall at high power may be due to an equilibrium shift between the two ionization states. However, these two plots suggest that the oxide is formed in the boundary layer rather than in the expansion as in the latter case a strong correlation with the U signal would be expected. Boundary layer is still present around the edges of the aperture and some of the gases in it will still be entrained by the ingoing gas. Fig. 82 certainly demonstrates the need to work at short axial distances to minimise oxide contributions to the response, at 20 mm this rises to 25% of the total signal.

5.2.2 Background Signals and Spectra

The causes of random background in continuum sampling are the same as those listed for the boundary mode in 5.1.2 and respond to the same treatment. The spectral background, however, is different, reflecting the different sampling mechanism. A spectrum of blank solution is shown in Fig. 84 which may be compared with Fig. 60 for the boundary layer case. Although there is a superficial resemblance there are some notable differences in the major peaks. $^{14}N^+$ and $^{16}O^+$ are much closer to the size that would be expected from their atomic
Fig. 84. Blank continuum sampling spectrum 0 - 100u.
concentrations and $^{17}\text{OH}^+$ and $^{18}\text{OH}_2^+$ are very large, but $^{19}\text{OH}_3$ is relatively small. $^{30}\text{NO}^+$ is almost absent, and $^{32}\text{O}_2^+$ is small although $^{16}\text{O}^+$ is now a large peak. The $^{40}\text{Ar}^+$ and $^{41}\text{Ar.H}^+$ peaks are similar to those in boundary layer sampling although larger; the full plot would have a full scale of 10 MHz instead of 2MHz. Significant peaks are visible at the positions of nickel and copper from sputtered ions. The dimer peak at $^{80}\text{Ar.Ar}^+$ is smaller and there is no $^{81}\text{Ar.Ar H}^+$peak. Although this spectrum looks rather cleaner than the boundary layer version this has to be related to the lower concentration sensitivity which goes with it. The real significance of the background may once again be best analysed in relation to analyte response. Expanded versions of this spectrum are shown in Figs. 85 and 86 with typical analyte concentrations shown on the vertical scale. The spectrum in Fig. 85 is on the same scale as Fig. 61 for boundary layer sampling, the height at which peaks saturate in both corresponding to 273,000 counts/sec$^{-1}$. Apart from the group of large peaks between 14 and 20u, the continuum spectrum seems no more cluttered and indeed to have some extra useful spaces, for example 31u where $^{31}\text{P}$ would occur and 35u where the major chlorine isotope would occur. The sputter peaks at 58 and 60u (Ni) and 63 and 65u (Cu) are inconvenient but can be avoided by changing materials. The peak at 56u has not yet been identified; it is possibly Ar.$^0\text{O}^+$, but a potential source of the alternative iron sputter peak has not yet been found. The most significant difference between the two spectra, however, lies in the relative analyte signals in the two cases. In Fig. 61 full scale corresponds to about 0.4 $\mu$g.ml$^{-1}$Co, whereas for Fig. 85 a cobalt concentration of about 14 $\mu$g.ml$^{-1}$ is required for a full scale peak. There is thus a ratio of about 35 between boundary layer and continuum concentration sensitivity and it is better to compare Fig. 86 with Fig. 61 where the relative equivalent full scale concentrations are 0.85 and 0.4 $\mu$g.ml$^{-1}$. The much lower sensitivity thus puts continuum sampling at a disadvantage although, as shown in Figs. 62 and 86, there is not a great difference in random background (note Fig. 62 is 4.27 k.counts.sec$^{-1}$ and Fig. 86 17.1 k.counts.sec$^{-1}$ at the peak saturation level).

These plots show that while there is still some advantage to be gained by reducing random background, particularly above 42u the major improvement needed is more efficient ion extraction from the greater flow
Fig. 85. Expanded spectrum of Fig. 84 (x4) showing equivalent analyte concentration.

Fig. 86. Further expansion of Fig. 84 (x64).
of gas entering the system in continuum sampling without a corresponding increase in background peaks. After these spectra were taken some improvement, shown in the detection limits in 5.2.5, was obtained, but much more should be possible.

5.2.3 Characteristic Spectra

The general performance of the system may be illustrated visually by a series of spectra run on mixed solutions, all elements normally being at the 10 µg.ml⁻¹ level. Fig. 87 shows a spectrum at the bottom of the mass range. The large peaks of \(^1\)H\(^+\) and \(^2\)H\(^+\) are off-scale, but \(^3\)H\(^+\) is present and well isolated peaks of \(^6\)Li\(^+\), \(^7\)Li\(^+\), \(^10\)B\(^+\) and \(^11\)B\(^+\) are seen. The peak of \(^12\)C\(^+\) is presumably from trace CO₂ in the argon, although the \(^13\)C\(^+\) peak appears slightly too large. The isotopes of boron are at about the correct ratio but \(^6\)Li\(^+\) is too small, suggesting that the Johnson Matthey lithium used had been depleted, although the suppliers had no information on this.

Fig. 88 shows the response to a solution containing silver, cadmium and indium. Small unidentified peaks may be seen at 103 and 105u, which do not correspond to any probable contaminant atoms and are thus presumably molecular ions.

The spectrum in Fig. 89 is shown over a mass range from 102 to 140u and is actually an expanded section of a much wider span. It shows peaks of Pb\(^++\), In\(^+\), U\(^++\), Te\(^+\), I\(^+\), Cs\(^+\) and La\(^+\), all from concentrations of 10 µg.ml⁻¹. The resolution is not set high enough to resolve the small lead peaks which are only 0.5u apart but is fully adequate for singly ionized atoms, \(^{127}\)I\(^+\) being quite clear of \(^{126}\)Te\(^+\) and \(^{128}\)Te\(^+\) either side of it. The \(^{139}\)La\(^+\) peak is small as most of it is doubly ionized and not visible on this scan, but the peak for \(^{238}\)U\(^{++}\) is very large, almost as large as the \(^{133}\)Cs\(^+\) peak which is probably fully ionized. A very small peak is visible in the correct position for \(^{235}\)U\(^{++}\).

Figure 90 shows a spectrum from a solution containing tungsten, gold, mercury, lead, bismuth, thorium and uranium, and illustrates well the
Fig. 87. Spectrum of Li and B in solution at 10 μg.ml⁻¹. Peak count rate $^7\text{Li}^+$, 51,282 sec⁻¹.

Fig. 88. Spectrum of mixed solution of Ag, Cd, and In, each at 10 μg.ml⁻¹. Peak count rate $^{115}\text{In}^+$ is 134,473 sec⁻¹.
Fig. 89. Expanded section of wider scan showing Pb$^{++}$, In$^+$, U$^{++}$, Te$^+$, I$^+$, Cs$^+$, and La$^+$, each at 10ug.ml$^{-1}$ of the atom.

Fig. 90. Spectrum of mixture containing W, Au, Hg, Pb, Bi, Th, and U.

Fig. 91. Expanded spectrum across W, Au, and Hg, showing peaks of $^{180}W^+$ and $^{196}Hg^+$. 
very similar response to heavy metals of different ionization energies and oxide bond strengths. Tungsten is well displayed, even the $^{180}\text{W}^{+}$, only present at 14 ng.mL$^{-1}$ is just visible on this range and can be shown as a small peak at higher gain, Fig. 91. A strong $^{197}\text{Au}^{+}$ peak is obtained, although in comparison to the $^{209}\text{Bi}^{+}$ response it can be seen not to be fully ionized. A good response for mercury is obtained although the peak of $^{196}\text{Hg}^{+}$ is not visible in this plot but can be seen in Fig. 91. Lead, although slightly doubly ionized, is well displayed as also is bismuth. Both thorium and uranium are largely doubly ionized and thus only show small peaks on this range. Both also have small oxide peaks.

The rare earth elements present severe analytical problems, partly because many have several isotopes of similar abundance and partly because they have strongly bound oxides and with most atomic ion sources produce very complex spectra. With this technique, however, the spectra are almost as simple as they could be, only the production of doubly ionized species causes complications. A mixture of 15 rare earth elements all at 10 µg.mL$^{-1}$ (from Johnson Matthey) was run to give the spectra shown in Figs. 92 and 93. Although many isotopes coincide the spectrum is remarkably simple. Only very small oxide peaks of the higher mass members are seen and evidently oxides contribute little to the main peaks. The lighter members of the group have generally lower second ionization energies than the members at the top of the group and thus appear larger in the doubly ionized spectrum in Fig. 93. This was run at a higher resolution setting so that the peaks are well resolved even though only 0.5u apart. The large peak in the centre is $^{80}\text{Ar}\text{.Ar}^{+}$ and yttrium is seen as the singly charged ion in this range as it is the only member of the group at a low mass.

These spectra are all of pure laboratory solutions although some are at quite high total concentrations, the rare earths for example being at a total of 150 µg.mL$^{-1}$. Ultimately performance on real samples is important where high matrix concentrations may be expected and the presence of sodium and potassium is common. A solution was prepared by Date to correspond to a typical rock matrix of the type frequently met at IGS. This contained the matrix elements as follows:
Fig. 92. Singly ionized spectrum of 15 rare earth elements each at 10 μg.ml⁻¹. Note Y⁺ appears in Fig. 93. Peak count rate 175Lu⁺ 96,783 sec⁻¹.

Fig. 93. Doubly ionized rare earth spectrum including Y⁺. Peak count rate 175Lu⁺⁺ 24,000 sec⁻¹.
This was then used to produce a sample solution containing these concentrations of matrix elements and in addition 5 \( \mu g.ml^{-1} \) each of Al, Co, As, Br, Rb, In, I, Te, Cs, La, W, Au, Pb, Bi, U. A control solution was also prepared with the same trace element concentrations, but without the matrix.

Figure 94 shows the full spectrum up to 100\( u \) with beneath it the residual spectrum obtained when a blank run was subtracted from it in the data system. The major matrix elements are clearly seen except for Ca. This has been lost because the response to the \( ^{40}Ar \) peak with which it coincides has become severely nonlinear at the top and the relatively small difference produced by the presence of calcium ions at the same mass is not seen. The response from 50\( u \) to 90\( u \) with and without the matrix present is shown in Fig. 95. The analyte peaks in this range are reduced in amplitude by about 30\% but the sputtered copper peaks are reduced by about 50\%. The large peak at 56\( u \) is of course the \( ^{56}Fe \) matrix element. The reduction is only about 15\% at 130\( u \) for Te and Cs and by about 200\( u \) there is actually a slight enhancement shown in Fig. 96 for W, Pb and Bi. It is difficult to visualise a mechanism that would be mass dependent but further study of this matrix effect is clearly needed. Correction would need to be made for quantitative work but certainly there were no problems in running such a matrix with over 500 \( \mu g.ml^{-1} \) dissolved solid content.

5.2.4 **Sensitivity and Dynamic Range**

As already discussed earlier in the chapter (5.1.4) the sensitivity may be expressed in either direct concentration values or may be related to molecular concentrations. The former relate more directly to the response obtained in practical analysis and are dependent on the isotopic characteristics of the element concerned and on its ionization pattern. Elements with many isotopes are often at a disadvantage even though they may be fully ionized. Totalling the signal from all the isotopes may be quite practicable but offers little advan-
Fig. 94. Spectrum from 0 - 100u of simulated mineral matrix and trace elements. Top - full spectrum, bottom - matrix elements after blank stripping.

Fig. 95. Expanded portion of Fig. 94 from 50-90u together with similar spectrum of trace solution with no matrix.
Fig. 96. Effect of matrix at high end of mass range of mixed trace spectrum showing W, Pb and Bi.

Fig. 97. Relative Ion Transmission and Concentration Response v. Mass.
Molar sensitivity values are necessary if the ionization equilibria in the plasma are to be studied but even so the values obtained are not simply determined by the ionization energy and partition function values but are also affected by mass discrimination throughout the system, which includes that of the sampling and expansion process, ion transmission through the skimmer and ion optics, transmission of the mass analyser and mass dependent response of the ion detector. All these processes play a part and may vary with changes of operating conditions. An indication of the mass dependence of overall ion transmission and detection efficiency of the system may be obtained if samples are run containing elements of a range of masses with first ionization energies of about 8eV or less and high second ionization energies. This enables the assumption of > 95% ionization to be made. Two runs over a range of about 30 elements, many of low ionization energy, were done, one, A, soon after the proper plasma potential had been established and the second, B, after the signal levels had been further improved. Values of both concentration sensitivity obtained on the most abundant isotope, i.e. the one normally chosen for detection, and molar sensitivity at 100% abundance are shown for both runs in Table 18.

The choice of resolution control balance on the mass analyser and of the lens settings may be made in a number of ways. If these are chosen to give the most uniform molar sensitivity the working concentration sensitivity becomes inconveniently low for the important heavy elements. For the first run, A, therefore, a compromise was chosen between constant molar and concentration sensitivity. This resulted in the relative ion transmission curve shown in Fig. 97, which fell away sharply to low masses where a given w/w concentration meant many atoms in the solution. The resultant relative w/w concentration response normalised for 100% abundance is also shown. This droops at both low and high masses but because of this the range of the response remains within a factor of 2 over the whole mass range.
Table 18
Concentration and Molar Sensitivities-Continuum Sampling

<table>
<thead>
<tr>
<th>Element</th>
<th>$V_i$ eV</th>
<th>Concentration Sensitivity $10^3$ counts.sec$^{-1}$/µg.ml$^{-1}$</th>
<th>Molar Sensitivity $10^3$ counts.sec$^{-1}$/µmole.ml$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Li</td>
<td>5.39</td>
<td>5.1</td>
<td>32.3</td>
</tr>
<tr>
<td>B</td>
<td>8.30</td>
<td>5.0</td>
<td>17.2</td>
</tr>
<tr>
<td>Mg</td>
<td>7.65</td>
<td>8.5</td>
<td>39.4</td>
</tr>
<tr>
<td>Al</td>
<td>5.99</td>
<td>6.7</td>
<td>26.0</td>
</tr>
<tr>
<td>Ti</td>
<td>6.84</td>
<td>28.6</td>
<td>16.3</td>
</tr>
<tr>
<td>V</td>
<td>6.74</td>
<td>3.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Cr</td>
<td>6.77</td>
<td>2.1</td>
<td>6.0</td>
</tr>
<tr>
<td>Mn</td>
<td>7.43</td>
<td>8.8</td>
<td>31.0</td>
</tr>
<tr>
<td>Fe</td>
<td>7.87</td>
<td>8.5</td>
<td>517</td>
</tr>
<tr>
<td>Co</td>
<td>7.86</td>
<td>28.6</td>
<td>16.3</td>
</tr>
<tr>
<td>Zn</td>
<td>9.39</td>
<td>3.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Ge</td>
<td>7.89</td>
<td>2.1</td>
<td>6.0</td>
</tr>
<tr>
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<td>9.82</td>
<td>5.2</td>
<td>15.5</td>
</tr>
<tr>
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<td>9.75</td>
<td>0.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Rb</td>
<td>4.18</td>
<td>6.1</td>
<td>20.7</td>
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<td>4.7</td>
<td>18.3</td>
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<tr>
<td>Cd</td>
<td>8.99</td>
<td>2.2</td>
<td>9.3</td>
</tr>
<tr>
<td>In</td>
<td>5.79</td>
<td>7.4</td>
<td>28.4</td>
</tr>
<tr>
<td>I</td>
<td>10.45</td>
<td>3.7</td>
<td>7.9</td>
</tr>
<tr>
<td>Te</td>
<td>9.01</td>
<td>1.9</td>
<td>26.0</td>
</tr>
<tr>
<td>Cs</td>
<td>3.89</td>
<td>6.2</td>
<td>25.1</td>
</tr>
<tr>
<td>Ba++</td>
<td>10.00</td>
<td>21.6</td>
<td>29.2</td>
</tr>
<tr>
<td>La++</td>
<td>11.06</td>
<td>21.6</td>
<td>29.2</td>
</tr>
<tr>
<td>Ce+++</td>
<td>10.85</td>
<td>21.6</td>
<td>29.2</td>
</tr>
<tr>
<td>W</td>
<td>7.98</td>
<td>12.9</td>
<td>7.9</td>
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<td>Au</td>
<td>9.23</td>
<td>3.3</td>
<td>19.2</td>
</tr>
<tr>
<td>Hg</td>
<td>10.44</td>
<td>1.3</td>
<td>9.4</td>
</tr>
<tr>
<td>Pb</td>
<td>7.42</td>
<td>1.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Bi</td>
<td>7.29</td>
<td>4.9</td>
<td>33.6</td>
</tr>
<tr>
<td>Th+++</td>
<td>c 12</td>
<td>27.3</td>
<td>22.4</td>
</tr>
<tr>
<td>U+++</td>
<td>c 12</td>
<td>27.3</td>
<td>22.4</td>
</tr>
</tbody>
</table>

* At 100% abundance. ++ determined on M++ ion, all others on M+ ion. All values obtained on most abundant isotope.
The second run, B, shows the improved sensitivities obtained later in the work, about 4 times better. For this run the resolution controls were set to give roughly uniform resolution over the whole range, i.e. to give peaks just fully separated to the base line, about 1% of peak height detectable by eye. The lens bias controls were then retuned for each element progressively from 7u to 209u, only slight adjustment of the quadrupole pre-rod potential usually being needed. The result is an almost linearly rising molar sensitivity and an approximately constant w/w concentration sensitivity when normalised to 100% abundance. This is a convenient operating mode for purely concentration measurements as it gives very good heavy element sensitivity. Some of this would be sacrificed if higher resolution were used for isotope ratio determination. The sensitivity of 30,000 counts. sec⁻¹ for 100% abundance of fully ionized species gives a typical line equivalent to background concentration of 1 ng.ml⁻¹ where there is only random background.

At the same time that the results of run A in Table 18 were obtained the dynamic range was determined by running a series of cobalt solutions from 1 ng.ml⁻¹ to 1000 μg.ml⁻¹, a range of 10⁶. The result is shown in Fig. 98. At concentrations above 10 μg.ml⁻¹ where the signal was just over 10⁵ counts.sec⁻¹ overall ion transmission was reduced by reducing the potential on the first electrode behind the skimmer. This gave a parallel calibration line over the top two decades and allowed the count rate to be kept within the linear range of the ion detector and electronics, below 10⁶ counts.sec⁻¹. At 10 and 1 μg.ml⁻¹ a background correction was necessary but when made gave a response close to the 45° line down to 1 μg.ml⁻¹.

A wide dynamic response and rapid sample throughout are of little value if the system has significant memory for samples. This is particularly important for rapid isotope ratio determination. In the earlier stages of the work memory effects, thought to be associated with the desolvator, were noticed. When this was discarded for work on continuum sampling it was expected that these would vanish. This did not completely happen, however, until the work had progressed to use a sharply pointed cone so that solid deposits were well away from the aperture and until the short length of plastic tube used between
the nebulizer cloud chamber and the torch was replaced by glass. The memory response was then plotted for some of the elements which had shown it most in earlier work, notably volatile elements such as lead and zinc.

The response obtained to a 10 μg.ml⁻¹ lead solution on $^{208}$Pb⁺ was monitored at a fixed mass setting. The multichannel scaler was set to operate with a 1 second dwell time per channel so that it plotted a continuous series of 1 second count integrals. The sensitivity obtained was almost 38,000 counts.sec⁻¹/μg.ml⁻¹, even higher than that shown in Table 18. The nebulizer uptake tube was allowed to remain in blank solution for a period after initially tuning to $^{208}$Pb on a low concentration solution. A full scan of 1023 seconds was then run on the blank. The uptake tube was then transferred to the sample Pb solution, allowed to remain there for about 4 minutes and then removed. The resulting response is shown in Fig. 99, showing the steep rise and slightly slower decay. The response is shown with the small background plot obtained subtracted. The decay curve is shown also on an increased scale (x 256). After 1 minute the response was just below $10^{-3}$ and it fell to $2.8 \times 10^{-4}$ after 10 minutes. This is quite adequate for isotope ratio determinations to the order of precision likely to be possible and more than adequate for concentration determinations.

Comparable decay values for zinc and barium were also obtained and were $2.2 \times 10^{-3}$ and $3.2 \times 10^{-5}$ at 1 minute.

These decay values show a much faster response than those obtained by boundary layer sampling.

5.2.5 Detection Limits

The data shown in Table 18 (columns B) were obtained by running each element separately; runs were made under the same conditions on blank solution, before introducing the analyte solution. These gave a series of 1 sec. integrals of background from which the value of standard deviation $\sigma$ was obtained. The integrals were grouped in blocks of 5 corresponding to a 5 sec. run and a minimum of 10 groups used for $\sigma$
Fig. 98. Dynamic response of continuum sampling system on cobalt solution.

Fig. 99. Response and decay on 10 µg.ml\(^{-1}\) Pb solution.
### Table 19

**Comparative Detection Limits in Boundary Layer and Continuum Modes. 3σ in ng.ml⁻¹.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion</th>
<th>Boundary Layer</th>
<th>Ion</th>
<th>Continuum Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>$^7\text{Li}^+$</td>
<td>0.4</td>
<td>$^{11}\text{B}^+$</td>
<td>5.0</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>$^{11}\text{B}^+$</td>
<td>2.0</td>
</tr>
<tr>
<td>Mg</td>
<td>$^{24}\text{Mg}^+$</td>
<td>0.2</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>Al</td>
<td>$^{27}\text{Al}^+$</td>
<td>0.3</td>
<td>$^{48}\text{Ti}^+$</td>
<td>0.5</td>
</tr>
<tr>
<td>Ti</td>
<td>$^{47}\text{V}^+$</td>
<td>0.3</td>
<td>$^{51}\text{V}^+$</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>$^{52}\text{Cr}^+$</td>
<td>0.1</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>Mn</td>
<td>$^{55}\text{Mn}^+$</td>
<td>0.06</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Fe</td>
<td>$^{56}\text{Fe}^+$</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>$^{59}\text{Co}^+$</td>
<td>0.1</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>Cu</td>
<td>$^{63}\text{Cu}^+$</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>$^{64}\text{Zn}^+$</td>
<td>2.0</td>
<td>$^{66}\text{Zn}^+$</td>
<td>4.3</td>
</tr>
<tr>
<td>Ge</td>
<td>-</td>
<td>-</td>
<td>$^{72}\text{Ge}^+$</td>
<td>1.6</td>
</tr>
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<td>As</td>
<td>-</td>
<td>-</td>
<td>$^{75}\text{As}^+$</td>
<td>11</td>
</tr>
<tr>
<td>Se</td>
<td>-</td>
<td>-</td>
<td>$^{78}\text{Se}^+$</td>
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<td>Rb</td>
<td>$^{85}\text{Rb}^+$</td>
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<td>-</td>
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</tr>
<tr>
<td>Ag</td>
<td>$^{107}\text{Ag}^+$</td>
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<td>-</td>
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<td>Cd</td>
<td>$^{114}\text{Cd}^+$</td>
<td>0.2</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>In</td>
<td>-</td>
<td>-</td>
<td>$^{115}\text{In}^+$</td>
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<td>Te</td>
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<td>-</td>
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<tr>
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<td>Ba</td>
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<td>-</td>
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</tr>
<tr>
<td>Au</td>
<td>-</td>
<td>-</td>
<td>$^{197}\text{Au}^+$</td>
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</tr>
<tr>
<td>Hg</td>
<td>$^{202}\text{Hg}^+$</td>
<td>2.0</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>Pb</td>
<td>$^{208}\text{Pb}^+$</td>
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<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>Bi</td>
<td>-</td>
<td>-</td>
<td>$^{209}\text{Bi}^+$</td>
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</tr>
<tr>
<td>Th</td>
<td>-</td>
<td>-</td>
<td>$^{232}\text{Th}^{++}$</td>
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</tr>
<tr>
<td>U</td>
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<td>$^{238}\text{U}^+$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^{238}\text{U}^{++}$</td>
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</table>
Table 20
Comparative Detection Limits by Continuum PSMS, ICP-AES and Flame A.A.S. in ng.ml⁻¹

<table>
<thead>
<tr>
<th>Element</th>
<th>PSMS</th>
<th>ICP-AES</th>
<th>Flame AAS</th>
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</thead>
<tbody>
<tr>
<td>Li</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
<td>1</td>
<td>700</td>
</tr>
<tr>
<td>Mg</td>
<td>0.7</td>
<td>0.03</td>
<td>0.1</td>
</tr>
<tr>
<td>Al</td>
<td>0.9</td>
<td>0.4</td>
<td>20</td>
</tr>
<tr>
<td>Ti</td>
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<td>0.04</td>
<td>40</td>
</tr>
<tr>
<td>V</td>
<td>0.6</td>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
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<td>0.2</td>
<td>2</td>
</tr>
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</tr>
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<td>2</td>
</tr>
<tr>
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</tr>
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<td>Ge</td>
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<td>20</td>
</tr>
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<td>100</td>
</tr>
<tr>
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<td>2</td>
<td>75</td>
</tr>
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<td>-</td>
</tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
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</tr>
<tr>
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<tr>
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</tr>
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</tr>
<tr>
<td>U</td>
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<td>11</td>
<td>30,000</td>
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</table>

ICP-AES and Flame AAS values from Ref. 76
in each case. The element response was taken from the recorded integrals at a point where the response had reached a plateau after the sample introduction. Values of concentration equivalent to 3σ blank were then calculated for each element.

These detection limits are shown in Table 19 in comparison with those obtained by boundary layer sampling. For elements of simple flame chemistry and low ionization potential the results are poorer than in the continuum mode but for many elements the results are better, B, Se and Au for example could not be detected in the boundary layer.

In Table 20 the values are compared with those currently attainable by ICP-AES and Flame AAS. It can be seen that in most cases the values are similar to or slightly worse than for ICP-AES but considerably better than those for difficult elements by optical spectrometry Te, W, Hg, Th and U. Most of the values are much lower than for Flame AAS. It should be noted, however, that the ICP-AES and Flame AAS represent the latest values after many years of development of these techniques whereas those for continuum PSMS are probably capable of considerable improvement.

5.2.6 The Effect of Ionization Suppressants

Because of the high electron population of the ICP it would not be expected that there would be any significant disturbance of the ionization equilibrium when high concentrations of elements of low ionization energy were nebulized (74,75). Thus for continuum sampling little depression of the response to analytes should occur. The response of $^{59}$Co and $^{209}$Bi to concentrations up to 1000 µg.ml$^{-1}$ of sodium is shown in Fig. 100. Some depression is seen, up to 30% for $^{54}$Co and 15% for $^{209}$Bi, most occurring above 200 µg.ml$^{-1}$ Na. These values were obtained at a sampling position of 10 mm from the work coil. Similar values obtained on $^{208}$Pb$^+$ and $^{238}$U$^+$ are shown in Table 21 for the same sampling points.
Fig. 100. Effect of Na addition on response to Co and Bi at 10 µg.ml⁻¹.
Table 21

Suppression (%) of Pb and U Response by Na

<table>
<thead>
<tr>
<th>Na (μg/ml)</th>
<th>208Pb⁺</th>
<th>238U⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1.7</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>2.5</td>
<td>1.2</td>
</tr>
<tr>
<td>100</td>
<td>18.3</td>
<td>14.1</td>
</tr>
<tr>
<td>200</td>
<td>22.6</td>
<td>18.2</td>
</tr>
<tr>
<td>500</td>
<td>15.9</td>
<td>13.0</td>
</tr>
<tr>
<td>980</td>
<td>21.1</td>
<td>18.4</td>
</tr>
</tbody>
</table>

The similarity of these values, in spite of the slight double ionization of Pb and considerable double ionization of U, to those shown in Fig. 100 for elements that do not doubly ionize, suggest that the ionization equilibria are not disturbed by the presence of sodium. The increase in \( n_e \) needed to disturb the equilibria would also reduce the degree of double ionization and \( U^+ \) would show less depression than \( Pb^+ \) or \( Bi^+ \), possibly even an enhancement. Again therefore it seems probable that the depression is caused by volatilization delay due to the high solids content at the position chosen to sample ions in the flame.

5.2.7 Ionization Temperature

As discussed in Appendix A2.2 estimates of plasma ionization temperature may be obtained from the variation of response to ionization energy for different elements. A value of \( n_e \) must be assumed in order to simplify the solution of the Saha equation for a multicomponent plasma, for continuum sampling the values at 1200 W shown in Table A4 are used. The additional information required is the ratio of response for equal molar concentrations of elements of closely similar atomic mass and widely differing ionization energy. An ideal compound for this purpose would appear to be cesium iodide since equal molar concentration is assured by stoichiometry and thus the calculation is unaffected by errors of preparing solutions and cesium has such a low ionization energy that
it may be safely assumed to be 100% ionized. A similar compound is rubidium bromide but this was not readily obtainable so a suitable solution containing both elements was prepared. However, values of partition coefficient for bromine are not listed in the compilation available so a possible error is caused by the assumption made that \( Z_I/Z_a = 1 \).

A solution containing cesium iodide, bromine and rubidium was run at a concentration of 10 \( \mu \text{g.mL}^{-1} \) and the count integrals observed from the spectra run at sampling positions of 5, 10, 15 and 20 mm from the work coil. A plot of the integral values and the consequent I/Cs and Br/Rb values is shown in Fig. 101. If it is assumed that these ratios represent the value of \( \alpha \) for iodine and bromine respectively then in spite of the reduction of \( n_e \) further along the flame they still imply a rising value for \( T_i \). This seems highly improbable. An alternative process associated with the diffusion of species from the central channel into the outer part of the flame seems more likely to account for a value of \( \alpha > 1 \).

However, where the ions are well confined in the central channel at 5 and 10 mm the ratios shown may be reasonably used to calculate the values of \( T_i \) shown in Table 22.

<table>
<thead>
<tr>
<th>Table 22</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Values of ( T_i ) Calculated from CsI, Rb and Br Response at 1200 W</strong></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
</tr>
</tbody>
</table>
| \( \begin{array}{|c|c|c|} \hline \\
| \text{CsI} & \text{Rb,Br} \\
| \hline \\
| 5 \text{ mm} & 9090 \text{ K} & 8920 \text{ K} \\
| 10 \text{ mm} & 9060 \text{ K} & 8830 \text{ K} \\
<table>
<thead>
<tr>
<th>\hline \end{array} )</th>
</tr>
</thead>
</table>

Other values for \( T_i \) may be calculated from runs made with other suitable isotope pairs and some are given in Table 23. Where full ionization cannot be assumed, as for Ag and Co, this was allowed for in making the calculation.
Fig. 101. Relative variation of response for elements of low and high ionization energy with axial distance.

Fig. 102. Relative response v. ionization energy at 10 mm.
Table 23
Ionization Temperature $T_1$ at 10 mm and 1200 W

<table>
<thead>
<tr>
<th>Thermometric Pair</th>
<th>$T_1$.K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs.Te</td>
<td>8730</td>
</tr>
<tr>
<td>Rb.Se</td>
<td>8370</td>
</tr>
<tr>
<td>Rb.As</td>
<td>8460</td>
</tr>
<tr>
<td>Ag.Cd</td>
<td>8140</td>
</tr>
<tr>
<td>Co.Zn</td>
<td>8010</td>
</tr>
</tbody>
</table>

The latter two values using Ag and Co are markedly different from the others and involved rather close values of ionization energy so are probably less reliable than the values using Cs and Rb in Tables 22 and 23. They are, however, closer to the mean value quoted by Alder et al (36) of 8070 measured at 10 mm by ICP-AES.

Values close to those in Table 22 are implied in the plot of normalised response against ionization energy shown in Fig. 102. The response values were calculated from the values for singly ionized elements given for run A in Table 18, using the overall ion transmission shown in Fig. 97 and including values for Br and Cl taken at the same time. The continuous curve was calculated from the Saha equation assuming $Z_i/Z_a = 1$ and $n_e = 4.5 \times 10^{15}$ for $T_1 = 9000$ K. The experimental values fit the calculated curve quite well, although some fall below it. A better fit would not be expected without taking account of partition functions.

From the values obtained using Cs or Rb as one of the pair the mean value of $T_1$ at 10 mm is 8690 K. This is probably the best value that can be obtained from the present data. The two values at 5 mm have a mean of 9000 K.

5.2.8 Isotope Ratio Measurements

Although the lower concentration sensitivity obtained in continuum sampling means that the collection of an adequate ion integral requires the nebulization of a larger total quantity of sample, it is compensated
by the ability to run much more concentrated solutions without aperture blocking. Thus the limitation on the speed of operation is the same as in the boundary layer mode, the loss of counts at high rates in the detector and counting system. In boundary layer sampling the integrated counts were sufficiently high and the random background so low that usually a background correction could be dispensed with, although for the data in Table 17 one was made. In continuum sampling the random background is higher and normal practice adopted by Date was to run a blank before the sample and then subtract this automatically in the data system before printing out the results. A typical run on NBS 981 in the continuum mode is shown in Table 24. Here again on the ten runs made it can be seen that the experimental value of \( \sigma \) is little bigger than the standard deviation on the integrated counts.

The mass discrimination is found for continuum sampling to be always in favour of the heavier isotope(s) and less affected by lens potentials but again there is evidence in the values in Table 24 of some count loss in the \(^{208}\)Pb peak. The total count levels for this 10 \( \mu \)g.ml\(^{-1} \) solution in a 1 minute run are about 370,000 counts compared to about 500,000 for a 1 minute run on 1 \( \mu \)g.ml\(^{-1} \) solution in Table 16, so there is little loss of precision if solutions can be run at this level, and the experimental standard deviations can be seen to be very similar.

A set of data on natural galena samples obtained by Date is shown in Table 25. These were run for 5 minutes each and were at levels varying from 5 to 35 \( \mu \)g.ml\(^{-1} \). Comparative runs were also made by thermal ionization mass spectrometry (TIMS) at IGS and the values obtained are listed for each ratio next to the PSMS value. As before NBS 981 was used to correct the PSMS values. The difference between the two values is also shown (% error) and the counting RSD. In most cases the agreement is good, rarely outside 3 times the counting RSD. The sample HA 1 is the exception to this and its behaviour has not been explained.

These results certainly suggest that the target precision of 0.1% is not an unrealistic aim. A number of the values show error values close to this. However, more understanding of the two phenomena of mass discrimination and counting loss are needed before such a precision can be
<table>
<thead>
<tr>
<th>Run</th>
<th>Peak Integral, 206Pb (blank stripped)</th>
<th>204/206 Ratio</th>
<th>207/206 Ratio</th>
<th>208/206 Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90,721</td>
<td>0.05798</td>
<td>0.9312</td>
<td>2.232</td>
</tr>
<tr>
<td>2</td>
<td>92,002</td>
<td>0.05726</td>
<td>0.9261</td>
<td>2.205</td>
</tr>
<tr>
<td>3</td>
<td>90,958</td>
<td>0.05767</td>
<td>0.9248</td>
<td>2.220</td>
</tr>
<tr>
<td>4</td>
<td>91,828</td>
<td>0.05631</td>
<td>0.9296</td>
<td>2.220</td>
</tr>
<tr>
<td>5</td>
<td>90,584</td>
<td>0.05855</td>
<td>0.9328</td>
<td>2.219</td>
</tr>
<tr>
<td>6</td>
<td>91,364</td>
<td>0.05840</td>
<td>0.9299</td>
<td>2.200</td>
</tr>
<tr>
<td>7</td>
<td>91,221</td>
<td>0.05732</td>
<td>0.9218</td>
<td>2.216</td>
</tr>
<tr>
<td>8</td>
<td>88,977</td>
<td>0.05713</td>
<td>0.9267</td>
<td>2.204</td>
</tr>
<tr>
<td>9</td>
<td>88,221</td>
<td>0.05773</td>
<td>0.9284</td>
<td>2.211</td>
</tr>
<tr>
<td>10</td>
<td>87,496</td>
<td>0.05765</td>
<td>0.9193</td>
<td>2.200</td>
</tr>
</tbody>
</table>

Mean (\(\bar{x}\)) 0.05760 0.9276 2.213

Standard Deviation (\(\sigma\)) 0.000649 0.00422 0.0105

Relative Standard Deviation (%) 1.13 0.45 0.47

Certificate Value 0.05904 0.9146 2.168

Difference from Certificate Value (%) 2.44 (low) 1.42 (high) 2.08 (high)

Counting Error on Ratio (%) 1.43 0.48 0.40
Table 25

Isotope Ratio measurements on Natural Galena Samples.

Corrected using NBS 981

<table>
<thead>
<tr>
<th>Sample</th>
<th>204/206 Ratio PSMS</th>
<th>204/206 Ratio TIMS</th>
<th>Count Error (%)</th>
<th>207/206 Ratio PSMS</th>
<th>207/206 Ratio TIMS</th>
<th>Count Error (%)</th>
<th>208/206 Ratio PSMS</th>
<th>208/206 Ratio TIMS</th>
<th>Count Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORC 16</td>
<td>0.05900</td>
<td>0.05873</td>
<td>0.46</td>
<td>0.40</td>
<td>0.9030</td>
<td>0.9003</td>
<td>0.30</td>
<td>0.14</td>
<td>2.177</td>
</tr>
<tr>
<td>ORC 17</td>
<td>0.05549</td>
<td>0.05515</td>
<td>0.62</td>
<td>0.42</td>
<td>0.8594</td>
<td>0.8568</td>
<td>0.30</td>
<td>0.14</td>
<td>2.099</td>
</tr>
<tr>
<td>ORC 18</td>
<td>0.05759</td>
<td>0.05734</td>
<td>0.44</td>
<td>0.48</td>
<td>0.8863</td>
<td>0.8837</td>
<td>0.29</td>
<td>0.16</td>
<td>2.151</td>
</tr>
<tr>
<td>TAT 4</td>
<td>0.05299</td>
<td>0.05304</td>
<td>0.09</td>
<td>0.49</td>
<td>0.8309</td>
<td>0.8318</td>
<td>0.11</td>
<td>0.16</td>
<td>2.079</td>
</tr>
<tr>
<td>LD 15</td>
<td>0.05477</td>
<td>0.05441</td>
<td>0.66</td>
<td>0.89</td>
<td>0.8487</td>
<td>0.8493</td>
<td>0.07</td>
<td>0.30</td>
<td>2.103</td>
</tr>
<tr>
<td>LD 73</td>
<td>0.05448</td>
<td>0.05438</td>
<td>0.18</td>
<td>0.38</td>
<td>0.8511</td>
<td>0.8491</td>
<td>0.24</td>
<td>0.13</td>
<td>2.086</td>
</tr>
<tr>
<td>G 31</td>
<td>0.05789</td>
<td>0.05729</td>
<td>0.89</td>
<td>0.34</td>
<td>1.026</td>
<td>1.027</td>
<td>0.10</td>
<td>0.12</td>
<td>2.348</td>
</tr>
<tr>
<td>HA 1</td>
<td>0.06801</td>
<td>0.06643</td>
<td>2.38</td>
<td>0.47</td>
<td>1.028</td>
<td>1.006</td>
<td>2.19</td>
<td>0.16</td>
<td>2.365</td>
</tr>
</tbody>
</table>

(a) Thermal Ionisation Mass Spectrometry (T.I.M.S.)
(b) Difference from TIMS Value
(c) Calculated from Counting Statistics
confidently expected. Further exploration of the discrimination over the whole mass range is required. It does not appear to follow the simple linear mass dependence predicted for molecular beam work (53,77), possibly because scattering effects are significantly higher than usual due to the high pressure in the expansion stage.
CHAPTER 6

DISCUSSION
Although at the start of this work it was well established that ions could be extracted from a small DC plasma that were reasonably representative of the introduced samples (18), it was by no means clear that the improvement required to handle real samples containing major matrix elements was attainable by the use of an ICP (27). Subsequently, it has been established both in this work and elsewhere (31,32) that by extracting samples from within the boundary layer some improvement over the performance of the CAP can be obtained by substituting an ICP. Only in the later stages of this work, however, has it been demonstrated that the problems associated with continuum sampling from the plasma can be resolved and that, therefore, performance can be obtained that corresponds closely to the properties expected of the ICP as an ion source by extracting a sample of bulk plasma, freezing its composition and analysing it on a continuous basis.

The primary problems of interfacing the plasma and sampling system were resolved first for the boundary layer mode. As discussed in Appendix 4.2 the principal problems introduced by the delay in the boundary layer when sampling with a small aperture are chemical ones. Some disturbance of the ionization equilibrium is also experienced as shown by the lower ionization temperature measured (5.1.4), but there are a number of advantages to be obtained. Because the ions are extracted from a region shielded from the full plasma potential they enter the system at low energy and very good resolution is obtained. The relatively small gas inflow enables low working pressures to be obtained with simple pumps and the simple ion optics and collimation needed give a relatively high transmission. As a result sensitivity is very high, of the order of $5 \times 10^5$ counts.sec$^{-1}$ for 1 µg.ml$^{-1}$ solutions. Low random background enables detection limits well below 1 µg.ml$^{-1}$ to be obtained for many elements. These advantages are, however, obtained at the expense of poor matrix tolerance and real difficulties in operation above concentration of 10 µg.ml$^{-1}$.

In changing to continuum sampling two main problems are met. The gas inflow for a 0.4 mm diameter aperture working from a plasma at 7,500 K is 24 times as much as admitted by the 0.07 mm boundary layer aperture and much more pumping capacity is required. Even if the continuum aperture was little above the minimum possible size at say 0.2 mm the
gas flow would still be 6 times that from the small aperture and beyond the capacity of the existing pumps. Although the solution adopted of using the intermediate expansion stage has the merit of cheapness and simplicity it is apparent that somewhere in the process of forming and introducing the beam into the mass analyser there is a considerable loss of ions. Instead of an increase of ion signal in proportion to the gas flow of 24 times there is a reduction in sensitivity of about 30 times, so compared to the boundary layer case the ion transmission has dropped a factor of 720. Remarkably enough, in spite of this, the performance does not appear to be adversely affected in other respects, in fact it is much improved in the areas required, matrix tolerance and reduced chemical or intermolecule reactions among the sampled species. Apart from the loss of sensitivity the only other disadvantages are a slightly higher random background and rather poorer resolution. Both of these would be fully acceptable, indeed are already so, if some of the lost ion transmission could be recovered. It can be seen from Tables 12 and 20 that the detection limits for many elements are similar to or better than the best alternative methods available on nebulized solutions. The crucial question is whether the lost ion transmission can be recovered without also increasing the background signals, and an answer to this can only be tentative until more information is available on the loss mechanisms.

Little change was made in the ion optics for continuum sampling, and once the question of ion energy had been resolved the lens system appeared to focus ions in the same way as before with similar sharp peaks in focussing potentials. The most uncertain part of the system must be the operation of the expansion stage and the formation of a molecular beam by the supersonic expansion through the aperture. The existing analysis (42) of free jet expansion is based on low first stage pressures where scattering is low, i.e. into pressures similar to those obtained behind the aperture in boundary layer sampling. In this case, however, the pressure is a factor of 10^3 higher and the mean free path correspondingly shorter. Many more collisions must occur since the m.f.p. is now much less than the aperture-skimmer distance, about 70 μm compared to 10 mm, whereas in most expansion stages discussed in Ref. 42 and in boundary layer sampling, the m.f.p. is nearer 70 mm. This limitation probably also applies to the region immediately inside the tip.
of the skimmer where the restricted access prevents the full pumping speed developing. This much higher scattering probability brings into question the whole matter of molecular beam formation. If a directed molecular beam were formed to produce a concentrated jet entering the skimmer the total quantity of gas entering stage 2 would be expected to be greater than in the case of simple chaotic flow through the skimmer aperture, by a factor which is the gain of the system. A gain of at least 3 or 4 would be expected. In fact, the flow into stage 2 through the skimmer shows (Appendix A1.3) good agreement with that calculated assuming chaotic flow. The experimental working pressures agree well with the calculated ones and apparently no gain is obtained.

Although the high working pressure behind the sampling aperture may prevent the proper formation of a molecular beam, it does have the advantage of suppressing the pinch discharge that forms on expansion into lower pressures from the ICP. This is an important advantage as this discharge can be a considerable source of photon background so faster pumping in the expansion stage is not an immediate answer. Although not an insuperable drawback the additional bulk and cost implied in faster pumping would also present some problems in an analytical instrument.

It is apparent that there is still a conducting gas path between the aperture and the skimmer (4.4.4) and the evident presence of a plasma in this region containing strong thermal gradients probably interferes with the normal processes of jet formation.

The relatively high ion and electron population may cause some beam spreading which will increase the scattering by the ambient gas. It is thought that this region is the most probable location of the substantial ion loss. However, the loss that occurs appears to be quite random in the choice of species affected, reasonably correct ionization temperatures are obtained, ion populations in the plasma appear correctly represented in the spectra, isotope ratios are approximately correct. The mass discrimination observed could be the result of preferential scattering of the lighter species away from the axis, although if it occurs in the expansion stage it does suggest
that there is a directed jet present. It is perhaps more likely to occur behind the skimmer where the draw out field imparts directed motion to the ions and fewer heavy ions would be lost by scattering. It seems likely, therefore, that if little dynamic focussing does occur in the expansion stage there is little point in using a skimmer with an internal angle of 60° or less and better ion collection from inside the skimmer would be obtained with a much shallower skimmer or an aperture in a flat plate.

The possibility of many collisions between aperture and skimmer also offers the opportunity of some ion molecule reactions which produce a background spectrum, i.e. the reactions occurring in the expansion are not frozen as rapidly as they should be. This is not thought to be a major source of these small background peaks (5.2.2), entrained gas from the edges of the aperture is considered a more abundant source since the reactions here are occurring in a region where the m.f.p. is much less, about 1 µm. If this is so improvements in ion transmission will affect the background peaks equally. This is supported by the weak dependence of $UO^+$ signal on sampling position in contrast to the sharp fall in $U^+$ signal found at greater distances from the load coil (5.2.1). If the oxide ions were formed in the expansion stage their concentration should be related to that of the metal ions. Cleaner, sharper aperture tip design is therefore suggested to reduce boundary layer thickness and entrainment as a means of reducing the background of molecular ions.

Although better ion transmission is highly desirable to increase the absolute numbers of ions available at low concentrations, where at present about 30 sec$^{-1}$ are detected for 1 ng.ml$^{-1}$ solutions another way of increasing the signal levels would be to make more ions available in the plasma. The present pneumatic nebulizer produces a total atom concentration $n_j$ of an element $j$ of mass 100 in the plasma of $3.16 \times 10^{10}$ cm$^{-3}$ from a solution of 1 µg.ml$^{-1}$. At this efficiency, $\varepsilon = 0.02$ (36), the concentration of hydrogen and oxygen atoms is $1.16 \times 10^{17}$ and $5.78 \times 10^{16}$ and these are the main source of the background peaks that limit detection ability, particularly below 40u. This very large population of highly reactive species in the otherwise almost inert plasma gas emphasises the ability of the system to
produce recognisable peaks in the spectrum down to concentrations of 10 ng.ml\(^{-1}\), an atom concentration of only \(3 \times 10^8\) cm\(^{-3}\), or \(10^{-8}\) of the water present.

A considerable improvement could be obtained if better means of introducing the sample were available. Ultrasonic nebulizers can certainly put 10 times as much sample into the plasma but this is only done by producing more small droplets, so, unless a desolvator is used, little improvement in the water produced background is likely to be seen.

Electrothermal vaporisation of the sample from a heated surface can produce sample atoms free of water vapour if differential heating rates are used, but this is not easy to do on a continuous basis and no commercial equipment is available. It does offer one important route to higher sensitivity and reduced background which should be explored in the future.

Apart from alternative means of sample introduction it is considered that the best route to improved sensitivity and lower background lies in further development of the aerodynamics of the sampling aperture and continuum stage. It was found that increasing the sampling aperture above 0.5 mm improved the signal considerably but around 0.6 mm instability arose as variable amounts of the central gas flow were extracted because the inflow was similar in volume to the central channel flow. At larger apertures still, say 0.7 or 0.8 mm, it should be possible to ensure that all the sample flow was extracted and the instability avoided. It is certainly desirable to increase the sample extracted as much as possible within the available pumping capacity since inflow is proportional to \(D_0^2\) whereas background from the boundary layer should be linearly related to \(D_0\).

The general behaviour of the sampling system appears to conform well to theoretical expectations and as long as sampling is confined to the immediate vicinity of the torch mouth, where the ion density in the central channel is high, plasma parameters deduced from emission spectrometry appear to account for the performance satisfactorily. However, downstream from the torch mouth where interdiffusion between the central flow and annulus becomes extensive, behaviour along the
axis is difficult to explain. The axial ion concentrations of low ionization energy species seem to fall more rapidly than those of higher energy as though they had different diffusion coefficients. It is possible that charged species produced early in the flame diffuse by coulomb repulsion to produce a more uniform concentration across the plasma and this would happen with fully ionized species without possibility of further ion production on the axis. However, along the axis there would always be atoms of a partially ionized species available to produce further ions. Thus on the axis the production of new ions of the higher energy species would distort the equilibrium to give an effective higher ionization energy. This may be the explanation of the effect shown in Fig. 101, an effective illustration of the absence of local thermal equilibrium. Certainly there is evidence from spatial profiling work by atomic emission on the distribution of ions and atoms in the plasma, to show that ion emission intensities tend to peak a few mm away from the central axis across the flame (78-81). Sampling ions with an aperture that draws gas from a radius of at least 1 mm may therefore be expected to give misleading results at positions downstream from the torch mouth, the ion densities sampled no longer having equilibrium values. This would seem to be a fruitful field for further study of ion distribution and the plasma source mass spectrometer offers the possibility of supplementing atomic emission studies in a unique way.

The nature of the ions produced by the ion extraction system has proved to be reasonably close to the initial expectations when the programme was planned, which are outlined in 1.3. It is worth commenting on these in turn.

1. The gas temperature at the sampling point is higher than expected as sampling closer to the work coil than expected proved desirable. A temperature of 7500 K is probably experienced at the sampling point. Certainly few molecular species of the introduced analyte are seen, refractory compounds are fully dissociated in the plasma, and the small oxide peaks seen probably come from gas entrained at the edges of the aperture. However, molecular species, mainly based on hydrogen and oxygen, do occur from the relatively very large quantity of water which transports the sample to the plasma, but again are probably formed around the aperture edges or in the expansion.
2. Interelement and matrix effects do occur but are small even though at present no attempts have been made to find operating conditions which minimise them.

3. So far all elements examined with ionization energies below 8eV are more than 95% ionized. 50% ionization is achieved up to about 10.5eV and better than 10% below 12 eV. Even halogens produce positive ions in accordance with the Saha equation and may be detected. The effective ionization temperature implied is about 8,700 K and in consequence elements whose second ionization energy is below that of argon may be significantly doubly ionized according to the value of $V_1^{++}$. Doubly charged species are therefore seen in some cases and can sometimes cause interference. However, in some cases their presence is an advantage permitting detection of an element whose singly charged ion coincides with a background peak. Thus (Table 19) Th$^{++}$ has a lower detection limit than Th$^+$. Because the ionization equilibrium is dominated by the argon ionization no significant ionization occurs of any species with ionization energies above that of argon, 15.76eV, whether singly or doubly charged. This means that He, F, Ne and of course Ar cannot be detected. The original upper limit of double ionization of 11eV was based on expectation of a lower ionization temperature than was found in the operating position finally adopted. No higher ionized species are seen.

4. No ions traceable to pump vapours or organic materials in the vacuum chamber have been found.

5. There are still very few peaks at fractional masses, only in the presence of significant concentrations of doubly ionized species, which are predictable from ionization energy tables. As no ion species above doubly charged are seen, only peaks at $(n + 0.5)u$ are seen. These can be resolved by the analyser at some loss of sensitivity (see Figure 93).

6. The anticipated ion energy spread of 1eV was optimistic. Only in boundary layer sampling was this approached, in continuum sampling a spread of about 7eV was found. This is within an acceptable range for the analyser but if it were possible to reduce it better abundance
sensitivity would be obtained because of the better peak profile at the base.

In general during the work the components of the system performed their functions well. The plasma unit in particular gave very reliable service and proved very consistent and stable in operation. The main limitations of the present system arise at opposite ends, sample introduction and ion detection. The former has already been discussed. It is not a problem unique to plasma ion sources. Considerable effort is being expended on improving sample introduction methods for atomic emission spectrometry and these will be directly applicable to this work. However, the present nebulizer system, although inefficient is very reliable and is directly suitable for use with an automatic sample changer. Such a device, under the control of the data system, would permit samples, blanks and calibration standards to be run at up to 1 per minute with the results, including concentration values or isotope ratios, being printed out directly.

The present ion detectors perform reasonably well, but although pulse counting detectors are essential with present ion yields to obtain adequate dynamic range, they are operating near the upper limit of their useful range. Further upward increases in ion rate will produce intolerable counting losses in channel multiplier detectors and other pulse counting detectors, such as the Daly type, will be required. However, an increase of about two decades in signal level will put the ion rates within the range of direct current detectors and problems of counting loss will be avoided and precision considerably improved. There seems to be a good chance of achieving this.

In practical terms, as it has finally evolved, the system proves easy to operate and consistent in performance. It is normally kept continuously pumped and can be put into operation in a few minutes. A full day's work can be obtained without switching off the plasma or removing it from the sampling aperture and copper apertures will operate for several days without being changed. Nickel apertures also operate reasonably well but are less easy to keep clean than copper. Other materials merit examination, metals such as molybdenum or
tantalum are attractive although difficult to machine.

There is no doubt that at present the system offers considerable scope for further development, especially in the expansion stage where the efficiency is low. In spite of this, however, the performance is consistent and shows the advantages expected from the use of an ICP. Even at its present stage of development it is a useful analytical facility for atomic mass spectrometry with an unmatched capability for handling large numbers of samples, high sensitivity, rapid response and great flexibility.
APPENDICES
Appendix 1. Gas Dynamic Conditions

A.1.1 The Nature of Gas Flow through Small Apertures

The characteristics of the flow of gas through an aperture depends on the relationship between the mean free path in the gas entering the aperture and the aperture dimensions. Between the opposite extremes of molecular flow, where the mean free path is large compared to the aperture diameter $D$, and continuum flow where the mean free path to diameter ratio is small so that the gas moves through the aperture in an undisturbed stream, a number of flow regimes are characterised by the value of the dimensionless ratio $\frac{\lambda}{D}$. This ratio is known as the Knudsen number, $K_n$, of the aperture. Above values of $K_n > 3$ the flow is molecular, below $K_n < 10^{-2}$ continuum flow occurs. The intermediate regimes of transition flow ($3 > K_n > 10^{-1}$) and slip flow ($10^{-1} > K_n > 10^{-2}$) occur in many practical cases. Detailed treatment of the flow under these conditions may be found in the standard texts (51,52).

For the purpose of extracting a representative sample of gas from an atmospheric pressure flame or plasma into a vacuum system, the continuum flow regime is the most important as it offers both the least disturbance to the sample by the boundary layer formed over the surface around the aperture, and the advantage of concentration of the incoming gas into a focussed jet along the axis. This enables a greater intensity of beam to be passed on through intermediate apertures to successive stages.

Boundary layer formation around the sampling aperture is discussed by Hayhurst et al (49,50) who show that for very small apertures the sample (in molecular or transition flow) is taken from within the boundary layer which forms over the aperture. As the aperture diameter is increased to give slip and then continuum flow, an increasing amount of the entering sample is taken from the bulk gas and the proportion of gas which has passed through the boundary layer decreases. Gas which has passed through the boundary layer has spent a significant time after leaving the plasma in a region at a considerably lower temperature. This can affect both dissociation and ionization equilibria adversely but may also be sufficiently long to enable ion molecule reactions to occur which produce molecular ion species not present in the original gas as molecules.
The mean free path \( \lambda \) in the plasma gas, which consists mainly of argon, is given by

\[
\lambda = \frac{3.107 \times 10^{-2} T}{P \cdot \delta^2}
\]

where \( T \) and \( P \) are the local temperature and pressure and \( \delta \) is the collision diameter.

For argon \( \delta = 3.83 \times 10^{-10} \) m.

So \( \lambda = 2.188 \times 10^{-5} \frac{T}{P} \) m.

In order to realise the condition for continuum sampling \( K_n \leq 10^{-2} \), the minimum aperture diameter \( 100 \lambda_T \) at a number of temperatures is shown in Table A.1.

<table>
<thead>
<tr>
<th>( T_0 ) K</th>
<th>4000</th>
<th>5000</th>
<th>6000</th>
<th>7000</th>
<th>8000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{min} ) ( \mu )m</td>
<td>84</td>
<td>104</td>
<td>125</td>
<td>146</td>
<td>167</td>
</tr>
</tbody>
</table>

At a typical sampling point 10 mm from the load coil where \( T \) is 7500 K the minimum diameter is thus 157 \( \mu \)m. Thus at this diameter and above continuum flow may be expected. At a diameter of 70 \( \mu \)m, however, continuum flow will only occur from a temperature of 3,348 K or less. Thus with an aperture of this diameter the flow from temperatures higher than this will not be strong enough to break through the boundary layer which will form across the front of the aperture. Once this occurs the gas flow occurs from within the layer, from cooler gas, so the flow takes place from an effective mean boundary layer temperature closer to that at which continuum sampling would occur for a 70 \( \mu \)m aperture. As a 70 \( \mu \)m aperture erodes in use it thus enlarges to the point at which it is just large enough to induce continuum flow and break through the layer at the mean boundary layer temperature. Immediately this occurs much hotter gas flows past the aperture lip which then melts back to a diameter of typically 150 to 200 \( \mu \)m. It is observed that this breakthrough occurs with apertures that have eroded to just over 80 \( \mu \)m. With a cone tip temperature of 350° C (623K)
the mean boundary layer temperature for a plasma temperature of 7.500 K is 4061 K for which \( D_{\text{min}} \) is 85 \( \mu \text{m} \), close to the observed value.

A.1.2 Quantitative Gas Flow through the Sampling Aperture

The gas flow through a small aperture, driven by a pressure difference \( P_0 - P_1 \) between the two sides, becomes supersonic above a critical pressure ratio \( r_c \). This critical pressure ratio is given by

\[
 r_c = \left( \frac{2}{\gamma + 1} \right)^{1/(\gamma - 1)}
\]

where \( \gamma \) is the ratio of specific heats.

For a monatomic gas such as argon \( \gamma = 1.66 \) and thus \( \frac{P_1}{P_0} = r_c = 0.49 \)

In practical plasma sampling \( \frac{P_1}{P_0} \) is normally very much lower than \( r_c \) and usually \( r = \frac{P_1}{P_0} < 10^{-3} \).

Under these conditions the quantity of gas flowing through the aperture is (51,52)

\[
 Q = A P_0 r^{1/y} \left[ \frac{2\gamma}{\gamma - 1} \cdot \frac{RT_0}{M} \left( 1 - r \cdot \frac{\gamma - 1}{\gamma} \right) \right]^{1/2}
\]

where \( A \) is the area of the aperture, \( M \) the molecular weight of the gas, \( R \) the gas constant, and \( T_0 \) the absolute temperature of the gas being sampled.

Where \( r \ll r_c \) then the aperture conductance

\[
 C = \frac{Q}{P_0}
\]

Thus for a monatomic gas where \( r \ll r_c = 0.49 \) and \( \gamma = 1.67 \)

\[
 C = 0.726 A \left( \frac{R T_0}{M} \right)^{1/4} \text{ m}^3 \text{ sec}^{-1} \quad \text{where } A \text{ is in m}^2
\]

or more conveniently

\[
 C = 0.57 D^2 \left( \frac{R T_0}{M} \right)^{1/4} \quad \text{where } D \text{ is the aperture diameter in m}
\]

Since the plasma gas is predominantly argon this reduces to

\[
 C = 8.22 D^2 (T_0)^{1/4} \text{ m}^3 \text{ sec}^{-1}
\]
Once the flow becomes supersonic at \( r \leq r_c \) no further increase occurs as \( p_1 \) is reduced. Thus this value of \( C \) is the limiting value which applies irrespective of the precise operating pressures.

To calculate the gas pressures expected from given pump size it is necessary to know the gas temperature from which the gas is sampled. This is not well characterised for the ICP, most measurements relate to excitation or ionization temperatures which in a non-equilibrium plasma are usually high. However, Human and Scott (48) have published values obtained from Doppler line broadening measurements for a similar ICP operated at 27 MHz and 1 KW. Their values are given in Table A.2

<table>
<thead>
<tr>
<th>Height above load coil (mm)</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas temperature (K)</td>
<td>7530</td>
<td>6900</td>
<td>5700</td>
</tr>
</tbody>
</table>

The position 10 mm above the load coil corresponds to the aperture position usually used in continuum sampling and for the standard plasma torch used in this work is equivalent to 5 mm beyond the torch mouth.

Thus for continuum sampling \( T_0 \) is assumed to be 7500 K. For boundary layer sampling where the sampled gas is taken from within the boundary layer it is assumed that \( T_0 \) is the mean boundary layer temperature between the plasma and sampling cone temperatures and a nominal figure of 4000 K is used.

Thus in the two cases the aperture conductance \( C \) and the quantity of gas \( Q \) entering the aperture are

**Boundary layer Sampling** - \( T_0 = 4000 \) K

\[
C = 520 \, D^2 \quad m^3 \cdot \text{sec}^{-1} \\
Q = 5.27 \times 10^7 \, D^2 \quad \text{Pa} \cdot m^3 \cdot \text{sec}^{-1}
\]

**Continuum Sampling** - \( T_0 = 7500 \) K

\[
C = 712 \, D^2 \quad m^3 \cdot \text{sec}^{-1} \\
Q = 7.21 \times 10^7 \, D^2 \quad \text{Pa} \cdot m^3 \cdot \text{sec}^{-1}
\]
A.1.3 Pumping Capacities and Working Pressures

During boundary layer sampling the first stage into which the aperture opens is pumped by an oil diffusion pump of capacity, above the baffle value, of 1.2 m³ sec⁻¹. This is connected to the chamber at the rear of the aperture by a pumping line of irregular shape approximately equivalent to 50 cm of 15 cm diameter pipe. The conductance of this pipe at room temperature is calculated as 0.69 m³ sec⁻¹ and hence the effective pumping speed at the rear of the aperture is

\[ S = \frac{0.69 \times 1.2}{0.69 + 1.2} = 0.44 \text{ m}^3 \text{ sec}^{-1} \]

Since the entering gas is cooled rapidly to room temperature the total volume pumped is reduced by the ratio of \( \frac{T_1}{T_0} \). Hence the pressure \( p_1 \) in stage 1 is given by

\[ p_1 = \frac{C \rho_0}{S} \cdot \frac{T_1}{T_0} \]

For boundary layer sampling the normal aperture diameter used was 70 μm. Hence

\[ p_1 = \frac{520 \times (7 \times 10^{-8})^2}{0.44} \times 101325 \times \frac{293}{4000} = 4.30 \times 10^{-2} \text{ Pa} \quad (3.2 \times 10^{-4} \text{ torr}) \]

This is reasonably close to the typical working pressure observed in stage 1 of 5.73 \times 10^{-2} \text{ Pa} \quad (4.3 \times 10^{-4} \text{ torr}).

In the case of continuum sampling the normal aperture used was 0.4 mm and \( T_0 \) was 7,500 K. In this case the incoming gas flow through this larger aperture was beyond the capacity of the diffusion pump on stage 1 so this was preceded by an expansion stage pumped by a mechanical pump. This was an Edwards EDM 20 A which had a capacity of 20.5 m³h⁻¹. It was connected to the expansion stage by a length of 1 m of 25 mm bore pipe. At the mean operating pressure in this pipe of \( \overline{p} \) the conductance is given by the relation
\[ C = \frac{n}{128\eta} \cdot \frac{D^2}{L} \frac{1}{p} \] for viscous flow

where \( \eta \) is the gas viscosity at room temperature, \( D \) and \( L \) pipe diameter and length.

The observed operating pressure drop across this pipe was 130 Pa (1.3 mb). At the mean pressure of 65 Pa therefore

\[ C = 2.81 \times 10^{-2} \text{ m}^3 \cdot \text{sec}^{-1} \text{ or } 101.2 \text{ m}^3 \cdot \text{h}^{-1} \]

In this case therefore the effective pumping speed

\[ S = \frac{101.2 \times 20.5}{101.2 + 20.5} \text{ m}^3 \cdot \text{h}^{-1} = 17.0 \text{ m}^3 \cdot \text{h}^{-1} = 4.72 \times 10^{-3} \text{ m}^3 \cdot \text{sec}^{-1} \]

Hence in the expansion stage the operating pressure given by

\[ P_1 = \frac{C \rho_o}{S} \cdot \frac{T_1}{T_0} \]

\[ = \frac{712 \times (4 \times 10^{-4})^2}{4.72 \times 10^{-3}} \cdot \frac{101,325}{293} \cdot \frac{7500}{101.2} \]

\[ = 95.5 \text{ Pa} \]

As already noted above the observed working pressure at 10 mm from the load coil with a 0.4 mm aperture was 130 Pa (1.3 mb).

The expansion stage was separated from the original boundary layer stage 1 by a skimmer aperture normally of 1.0 mm diameter although other diameters were investigated.

At the pressure of 95.5 Pa the mean free path \( \lambda \) is considerably larger than in front of the sampling aperture in spite of the lower temperature so the flow through the skimmer may not be continuum flow. The mean free path is given by

\[ \lambda = 2.118 \times 10^{-8} \frac{T}{p} \] for argon.
The temperature at the mouth of the skimmer is uncertain. As a result of the supersonic expansion through the aperture it should be well below ambient (see Appendix 1.4) but it is found that the skimmer tip operates at considerably above that of the expansion chamber body which is only about 320 K. For this calculation the gas temperature is assumed to be 320 K which is likely to lead to a value on the high side for skimmer conductance. At 320 K then

\[ \lambda = 7.1 \times 10^{-6} \text{ m} \]

Thus for the skimmer of 10^{-3} m diameter

\[ K_{ns} = 0.071 \]

The flow through the skimmer will thus be in the slip flow region where \( 0.1 < K_n < 0.01 \). However, for an aperture in a directed flow it is difficult to specify the flow conditions. If the flow were purely chaotic the slip flow conductance for \( K = 0.071 \) would be about 10\% less than for continuum flow (52). So using the continuum flow formula would give a high value for conductance and for the next stage pressure \( P_2 \).

Thus \[ C_s = 8.22 D^2 \left( T \right)^{\frac{1}{2}} \]

\[ = 1.47 \times 10^{-4} \text{ m}^3 \text{ sec}^{-1} \]

Hence \[ P_2 = \frac{C_s P_1}{S_2} \] as the temperature is assumed to be the same both sides

\[ = 3.19 \times 10^{-2} \text{ Pa}. \quad (2.40 \times 10^{-4} \text{ torr}) \]

The observed pressure in stage 2 under these conditions is 3.3 \times 10^{-2} \text{ Pa} (2.5 \times 10^{-4} \text{ torr}). The use of the continuum flow conductance for the skimmer thus seems reasonably justified although if the observed stage 1 pressure had been used instead of the calculated value the agreement would have been less good, giving \( P_2 = 4.34 \times 10^{-2} \text{ Pa} \) (3.26 \times 10^{-4} \text{ torr}). However, since the gauges on the system were not calibrated in absolute pressure this agreement is probably as good as can be expected.

In boundary and layer and continuum sampling cases the pressure calculated for the first of the vapour pumped stages is therefore 4.30 \times 10^{-2} \text{ Pa and}
$3.19 \times 10^{-2}$ Pa respectively. The final stage pressure $p_3$ will be determined by molecular flow through the differential aperture of 2 mm diameter since at these pressures the mean free path

$$\lambda = 1.67 \times 10^{-1} \text{ m}$$

so that $K_n = 167$ well into the molecular flow regime.

For molecular flow in argon

$$C = 4.52 D^2 (T)^{\frac{1}{2}} \text{ m}^3 \cdot \text{sec}^{-1}$$

$$= 3.09 \times 10^{44} \text{ m}^3 \cdot \text{sec}^{-1}$$

Hence $p_3 = p_2 \frac{C}{S_3} = p_2 \cdot \frac{3.09 \times 10^{-4}}{S_3}$

The pumping capacity of the second vapour pump at the mouth of its baffle and valve was 0.2 m$^3$/sec. It was coupled to the vessel by a length of 0.45 m of 0.1 m diameter tube. The conductance of a pipe for argon in molecular flow is

$$C_p = 6.02 \frac{D^3}{L} T^{\frac{1}{2}} \text{ m}^3 \text{ sec}^{-1}$$

where $D$ and $L$ are diameter and length in metres.

Thus $C_p = 0.229 \text{ m}^3 \text{ sec}^{-1}$

and $S_3 = \frac{0.2 \times 0.229}{0.429} \text{ m}^3 \text{ sec}^{-1}$

$$= 0.107 \text{ m}^3 \text{ sec}^{-1}$$

Hence $p_3 = p_2 \cdot 2.89 \times 10^{-3}$

$$= 1.24 \times 10^{-4} \text{ Pa (9.34 x 10}^{-7} \text{ torr) for boundary layer sampling}$$

$$= 9.22 \times 10^{-5} \text{ Pa (6.93 x 10}^{-7} \text{ torr) for continuum sampling}.$$

Both these pressures are below the observed working values for this stage but this is probably because the lower value realised even with no gas input to the system and the slide valve closed is approximately $9.3 \times 10^{-5}$ Pa ($7 \times 10^{-7}$ torr).
A.1.4 Supersonic Expansion through the Sampling Aperture

The pressure ratio across the sampling aperture for $D = 400 \, \mu m$ is $1.3 \times 10^{-3}$ (observed pressure) well below the critical ratio for argon of 0.49. The flow beyond the aperture is thus supersonic for continuum flow operation and a free jet is formed. The theory and practice of the expansion and jet formation process has been discussed in the literature (53,54,55,56) and a recent review gives a very useful summary of theory and applications (42). In all these treatments, however, the free jet expansion is considered to occur into a much lower pressure than used here so that the gas density in the first stage is much lower and the mean free path at the skimmer is of the same order as the skimmer diameter whereas in this work the value of $K_{ns}$ is $<<1$. No analysis of a similar kind appears to have been published for the high gas density case corresponding to expansion stage pressures of the order of 100 Pa ($\approx$ 1 torr) although the possibility of such a system has been discussed (44). It is not therefore considered justifiable to take the analysis for this system very far but it is useful to develop the main parameters of the expansion on the assumption that the theory as outlined in reference 42 can be applied at these pressures.

The free jet flow field is bounded by a shock system consequent on the presence of the gas in the expansion region. The shock front normal to the flow, the Mach disc, occurs at a position given by

$$X_m = 0.67 \, \frac{D_0}{\left(\frac{P_o}{P_f}\right)^{\frac{1}{2}}}$$

where $X_m$ is the distance from the aperture, diameter $D_0$, and $P_o$ and $P_f$ the initial and final pressures. In this system therefore at the pressures observed

$$X_m = 0.67 \cdot 0.4 \left(\frac{101325}{130}\right)^{\frac{1}{2}} \, m.m.$$

$$= 7.48 \, mm.$$  

At the Mach disc the gas density in the jet becomes equal to that of the background gas and beyond it the gas motion becomes randomized and the beam becomes attenuated. Closer to the aperture, however, the axial velocity of the gas reaches a limit at the terminal Mach number $M_t$. 
This is given by the relation

$$M_t = 1.17 K_0 \frac{\gamma - 1}{\gamma}$$  \hspace{1cm} (55)$$

For argon expanding from 7,500 K through a 0.4 mm diameter aperture $\lambda_0$, the mean free path is $1.57 \times 10^{-3}$ mm and $\gamma$, the ratio of specific heats, is 1.67.

Hence

$$K_0 = \frac{\lambda_0}{D_0} = \frac{1.57 \times 10^{-3}}{0.4} = 3.92 \times 10^{-3}$$

and

$$M_t = 1.17 \left(3.92 \times 10^{-3}\right)^{0.64} = 10.74.$$

The points at which this terminal Mach number is reached may be calculated from the relation which expresses Mach number on the axis in terms of the aperture diameter $D_0$

$$M = A \left(\frac{X}{D_0}\right)^{\gamma - 1}$$  \hspace{1cm} (42)$$

For argon $\gamma = 1.67$ and $A = 3.26$ (42)

Thus

$$X = D_0 \cdot \left(\frac{M}{3.26}\right)^{\frac{1}{2}}$$

Hence

$$X_t = D_0 \cdot \left(\frac{10.74}{3.26}\right)^{\frac{1}{2}} = 5.98 D_0$$

$$= 2.39 \text{ mm for } D_0 = 0.4 \text{ mm.}$$

During the expansion from the aperture the gas temperature falls rapidly until the distance $X_t$ at which $M_t$ is reached, beyond which it remains constant. The temperature along the axis is related to the Mach number by the equation

$$\frac{T}{T_0} = \left[1 + \frac{\gamma - 1}{2} M^2\right]^{-1} = \left[1 + \frac{1}{3} M^2\right]^{-1}$$

for argon.

Thus at $X_t$ from the aperture

$$T = 7500 \left[1 + \frac{10.74^2}{3}\right]^{-1}$$

$$= 190 \text{ K}$$
At distances greater than $X_t$ the gas continues to expand (56) but the beam intensity falls in proportion to the inverse square of the distance. Further along the axis beyond the shock front at the Mach disc the beam intensity is attenuated by gas collisions and shock wave effects. It is thus generally accepted that the skimmer should be located between the Mach disc and the distance $X_t$ where freezing occurs, preferably as close to $X_t$ as possible. In this system this is therefore between 2.39 and 7.48 mm.

However, these values are calculated from the theory derived for expansion into considerably lower pressures where collisions are much less significant and where at the skimmer the mean free path is comparable to the skimmer diameter. It seems probable therefore that at the higher pressures experienced the beam formation process is hampered by scattering due to collisions with the background gas and that this will considerably modify the shock wave effects.

During the expansion to the point $X_t$ at about 6 aperture diameters downstream, the very rapid cooling of the entering gas is very important to freeze reactions taking place in the sample. However, it seems very unlikely that the calculated temperature of 190 K is reached since the skimmer becomes very hot during operation.
Appendix 2. Ionization Equilibria in Atmospheric Pressure Plasmas

A.2.1 Plasma Atom Concentrations

The carrier gas flow entering the plasma consists principally of argon with the other major constituent being water vapour. In addition to these there are also present the trace impurities of the argon, water vapour, oxygen, nitrogen and carbon dioxide, and the analyte present in the solution. Where the nebulizer mist has been passed through a desolvator the water vapour content will be reduced and the analyte will normally be in the form of dry microparticulates. For the calculation of equilibrium ion concentrations the argon impurities may be neglected in the presence of the water vapour. Since the sample solutions are normally acidified to 1% with nitric acid some nitrogen is also carried into the plasma.

For the purposes of calculation it is assumed that all the material carried from the nebulizer cloud chamber by the carrier gas is fully desolvated, vaporized, and dissociated as the flow passes through the centre of the energy addition region where the gas temperature is reported to be between 8,000 K and 10,000 K (24).

When the gas leaves the energy addition region within the work coil it cools and at 10 mm from the end of the coil the temperature is reported to be 7,500 K (48 and Table A.2). Up to this point it is assumed that the central injector gas flow from the nebulizer remains undisturbed by and separate from the surrounding coolant gas. This is probably justified out to 10 mm from the work coil but as can be seen in Figure 28 further out the injector flow and the outer annulus expand and diffuse into one another.

For each individual element present in the dissociated gas the total concentration \( n \) is the sum of the concentrations of ions \( n_i \) and of the remaining unionized atoms \( n_a \).

Within the region where the injection flow is undisturbed the argon concentration is given by

\[
n_{Ar} = n_{iAr} + n_{aAr} = \frac{\rho_{Ar}}{40} \cdot n_A \cdot \frac{273}{T_0} \cdot \text{cm}^{-3}
\]
where \( \rho_{Ar} \) = density of argon at s.t.p. in gr. cm\(^{-3}\)  
\( N_A \) = Avogadro's number = 6.022 \( \times \) \( 10^{23} \)  
\( T_o \) = Gas temperature (at sampling point)

At 10 mm where \( T_o \) = 7500 K then

\[
n_{Ar} = 9.75 \times 10^{17} \text{cm}^{-3}
\]

in the absence of nebulized water or solution.

When water is nebulized into the injector gas flow the concentration of water molecules prior to dissociation is given by

\[
n_{H_2O} = \frac{s \cdot e}{18} \cdot \frac{N_A}{f \cdot 10^3} \cdot \frac{273}{T_o}
\]

where

- \( s \) = nebulizer uptake rate in ml.min\(^{-1}\)
- \( e \) = nebulizer efficiency
- \( f \) = injector flow rate in l.min\(^{-1}\)

and \( N_A \) and \( T_o \) are as above.

Where a desolvator is used the value of \( n_{H_2O} \) is reduced by the fraction of water vapour transmitted. For the desolvator used this was measured as 0.25.

In the two operating modes used in this work, boundary layer and continuum sampling, slightly different injector flow rates were normally used but insufficient information is available about the detailed effect of this on the gas temperature so the same value of \( T_o \) is assumed for both cases. Similar problems exist in assigning values from the literature to \( n_e \) (see next section). So only approximate values of atom and ion populations can be calculated.

At a gas temperature of 7500 K the water is assumed to be fully dissociated giving a total atom and ion concentration of \( 2n_{H_2O} \) of hydrogen and \( n_{H_2O} \) of oxygen.

In the presence of water the argon concentration adjusts to accommodate the hydrogen and oxygen. In the two operating modes the concentrations
of the three major constituents are shown in Table A.3 for 10 mm from the load coil (48).

Table A.3

<table>
<thead>
<tr>
<th>Mode</th>
<th>$f$</th>
<th>$s$</th>
<th>$Ar$</th>
<th>$H$</th>
<th>$O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary</td>
<td>0.65</td>
<td>2.30</td>
<td>$9.14 \times 10^{17}$</td>
<td>$4.04 \times 10^{16}$</td>
<td>$2.02 \times 10^{16}$</td>
</tr>
<tr>
<td>Continuum</td>
<td>0.53</td>
<td>1.53</td>
<td>$8.02 \times 10^{17}$</td>
<td>$1.16 \times 10^{17}$</td>
<td>$5.78 \times 10^{16}$</td>
</tr>
</tbody>
</table>

Analyte atoms from the nebulized solution form minor additions to these populations and do not significantly disturb them.

The concentration of analyte $n_j$ resulting from a concentration of $c \mu g.mL^{-1}$ in the solution is given by

$$n_j = n_{aj} + n_{ij} = \frac{C.S.E.N_A}{f.4.10^{10} \cdot \frac{273}{T_0}}$$

An example of the total concentration of an analyte species may be calculated for an atom of atomic weight 100 in solution at $1 \mu g.mL^{-1}$. In the boundary layer mode where $s = 2.3 \ mL.min^{-1}$ and $f = 0.65 \ l.min^{-1}$ then

$$n_j = 3.88 \times 10^{10} \ cm^{-3}$$

In the continuum mode with $s = 1.53 \ mL.min^{-1}$ and $f = 0.53 \ l.min^{-1}$ then

$$n_j = 3.16 \times 10^{10} \ cm^{-3}$$

These populations of analyte species are then distributed between the various stages of ionization according to the equilibria discussed in the next section.

Where solutions are acidified to 1% v.v. with nitric acid, as was normal practice to stabilize them, then the concentration of nitrogen in sample solutions was

$$C_N = 3.35 \times 10^3 \ \mu g.mL^{-1}$$
Thus nitrogen concentration in the gas for the two modes are

- Boundary layer: $1.30 \times 10^{14}$ cm$^{-3}$
- Continuum: $1.06 \times 10^{14}$ cm$^{-3}$

**A.2.2 Ionization Equilibria**

A plasma is usually considered to exist in a gas when it is ionized to a substantial extent. In practical terms this condition is usually maintained in a stable state by the passage of a continuous electrical discharge of some kind which supplies the energy necessary to maintain the ionization which itself is necessary to permit the passage of the discharge. Continuous discharges of this sort are not usually self initiating at atmospheric pressure since the mean free path of electrons is too short in the cold condition to enable the discharge to start with the normal running potentials available. An auxiliary spark discharge such as that from a Tesla coil is usually used to start them.

Once established the equilibria in the plasma are conveniently described in terms of the temperature but in most cases the numerical value of the temperature obtained will depend on the parameter used to define it (59).

In a fully dissociated gas consisting only of atoms, ions and electrons, four different temperatures may be defined as follows:

1. Gas temperature defined by the kinetic energy of the neutral atom population; $T_g$.
2. Electron temperature defined by the kinetic energy of the electron population; $T_e$.
3. Excitation temperature defined by the population of the energy levels of excited states; $T_{exc}$.
4. Ionization temperature defined by the population of the various states of ionization; $T_i$.

If molecular species are present in the gas further temperatures may be defined from consideration of degree of dissociation, rotational energy levels and vibrational energy levels.
The plasma is said to be in thermal equilibrium if all these various definitions of temperature agree. In a practical case a plasma cannot be fully in equilibrium with its surroundings because it is unlikely to exist at temperatures that could be survived by any containment material. However, a limited state of local thermal equilibrium can be recognized if conditions are substantially uniform over the span of a few mean free paths of the phenomena being considered. Thus the centre of an arc column or the central channel of a toroidal ICP are regions where local thermal equilibrium might be discussed.

In atomic gases such as argon or helium, however, it has been argued that thermal equilibrium is only achieved at high current densities (59) and in low power inductively coupled plasmas there have been several demonstrations (60,61) that thermal equilibrium is not achieved.

In considering the behaviour of a plasma as an ion source, however, the important parameters are the gas temperature and the ionization temperature and it is not necessary that thermal equilibrium is achieved. It is, however, important that the gas temperature is sufficiently high to vaporize and dissociate all the introduced sample before the resultant atoms are ionized. It is then preferable that the ionization temperature is sufficiently high to fully ionize to the singly charged state all atoms of interest while not being so high that significant quantities of doubly charged ions are produced.

The equilibrium between neutral atoms, ions and electrons in a plasma at a temperature \( T \) is described by the Saha equation

\[
\frac{n_{ij} \cdot n_e}{n_{aj}} = S_{nj} = \frac{(2 \pi m k T)^{3/2}}{h^3} \cdot \frac{2 Z_{i}^{2}}{Z_{aj}} \cdot \exp \left(-\frac{\varepsilon_{ij}}{kT} \right) \tag{1}
\]

using the notation of Boumans (59) where

- \( n_{ij}, n_{aj} \) = atom or ion concentration of species \( j \) in \( \text{cm}^{-3} \)
- \( n_e \) = electron concentration, \( \text{cm}^{-3} \)
- \( S_{nj} \) = ionization constant for species \( j \)
- \( m \) = electron mass

\( k \) = Boltzmann constant

\( \varepsilon_{ij} \) = excitation energy
\[ k = \text{Planck constant} \]
\[ Z_a, Z_i = \text{partition function of atom or ion} \]
\[ \varepsilon = \text{ionization energy} \]

Substituting numerical values for the constants this reduces to

\[ S_{nj} = 4.83 \times 10^{15} T^{1/2} \cdot \frac {Z_{ij}} {Z_{aj}} \cdot 10^{-\left(\frac {5040} {T}\right) V_{ij}} \]  \hspace{1cm} (2)

where \( V_i \) is the ionization energy in electron volts, or

\[ \log S_{nj} = \frac {3} {z} \log T - \frac {5040} {T} \cdot V_{ij} + \log \frac {Z_{ij}} {Z_{aj}} + 15.684 \]  \hspace{1cm} (3)

The degree of ionization \( \alpha_j \) is the ratio of ion concentration to the total concentration, i.e.

\[ \alpha_j = \frac {n_{ij}} {n_j} \]  \hspace{1cm} (4)

where \( n_j = n_{aj} + n_{ij} \)  \hspace{1cm} (5)

Since the ionization is the only source of electrons \( n_e = n_i \).

From equations (1) (4) and (5) then

\[ \alpha_j = \frac {S_{nj}(T)} {n_e + S_{nj}(T)} \]  \hspace{1cm} (6)

Thus the value \( \alpha_j \) can be calculated for a species if both \( n_e \) and \( S_{nj}(T) \) are known, and the latter requires a knowledge of \( T_i \), the ionization temperature of the plasma. For a practical multicomponent plasma the value of \( n_e \) is the sum of the contributions from the ionization of each component for which

\[ n_i = \alpha \cdot n = \frac {n \cdot S_{n}(T)} {n_e + S_{n}(T)} \]

Thus \( n_e = \sum n_i = n_{ij} + n_{ik} + \ldots \ldots \]

\[ = \frac {n_j \cdot S_{nj}(T)} {n_e + S_{nj}(T)} + \frac {n_k \cdot S_{nk}(T)} {n_e + S_{nk}(T)} + \ldots \ldots \]  \hspace{1cm} (7)
Even if the value of $T$ is known for the plasma the calculation of $n_e$ is difficult and can only be performed by an iterative process except in certain simple or limited cases. However, there is no direct method of determining $T$ which in this case is the ionization temperature $T_i$ and it can only be calculated from measurements made on the ionization of species in the plasma with a knowledge of $n_e$. Fortunately, $n_e$ may be determined from optical measurements on the plasma, of $H_\beta$ line broadening, and also from the absolute intensity of the argon recombination continuum. Recent measurements of the values of $n_e$ have been reported (36,57) for plasmas of similar geometry, one at a power level of 1000 watts and the other at 1200 watts. From the two sets of data the $n_e$ values shown in Table A.4 may be deduced for a flow rate of 0.6 l.min$^{-1}$, close to the mean value for this work.

**Table A.4**

| Values of Electron Concentration $n_e$ from (36,57) in units of $10^{15}$ cm$^{-3}$ |
|----------------------------------|---------|---|---|---|---|
| Position mm | 5 | 10 | 15 | 20 | 25 |
| 1200 W | 7 | 4.5 | 4 | 3 | 2 |
| 1000 W | 4.5 | 3 | 2 | 1.5 | 1 |

Note - Position is measured from the end of the load coil.

Injector flow 0.6 l.min$^{-1}$

In the particular case of an argon plasma containing dissociated water vapour an approximate solution of equation (7) can be obtained since at the temperatures in the range below 9000 K the values of $S_n$ are only a few percent or less of $n_e$ and may be ignored in the denominator for an approximate result. If this is done using the atom populations given in Table A.3, the resulting values of $n_e$ obtained at three ionization temperatures are shown in Table A.5.

Values of $n_e$ calculated for argon alone without water are also shown, demonstrating that the presence of water vapour, because of the lower ionization energies of hydrogen and oxygen, does increase the value of $n_e$ significantly. Experimental demonstration has been given by Alder et al (36).
Table A.5

Calculated Values of the $n_e$ in Units of $10^{15}$ cm$^{-3}$

<table>
<thead>
<tr>
<th>Operating Mode</th>
<th>Ionization Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8000 K</td>
</tr>
<tr>
<td>Argon alone</td>
<td>1.5</td>
</tr>
<tr>
<td>Boundary layer</td>
<td>1.7</td>
</tr>
<tr>
<td>Continuum</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Thus by comparing Tables A.4 and A.5 it may be seen that the measured value of $n_e$ at 1000 watts and 10mm correspond to an ionization temperature of about 8,400 K.

Once the value of $n_e$ for the plasma is available it is possible to calculate the value of $c_j$ for any element from equation 6 for a range of possible temperatures since the variation of $S_{nj}$ with temperature is expressed by the Saha relation 3. Values of the partition functions $Z_a$ and $Z_i$ are required for this and are tabulated for most atoms (58,62). Measurement of $T_i$ by direct determination of $c_j$ from the plasma is not possible by mass spectrometry since no direct value can be obtained for $n_a$, the atom population.

However, several other methods are available. The most direct is to make measurements of the ratio of intensities of singly and doubly charged ions of the same element and then calculate temperature from the Saha equations for the two species. This is not available for all elements with an ICP source as many do not doubly ionize significantly. However, it is open to a more serious objection that the peaks for the two types of ions occur in different regions of the spectrum and the correction for intensity requires an accurate knowledge of mass discrimination effects. An alternative is to use known concentrations of two elements of similar mass that do not doubly ionize but have widely different ionization energies, one preferably being low enough that it may be assumed to fully ionize. Convenient elements are Br, Rb, Ag, Cd, In, I, Cs. An ideal thermometric pair for this purpose is found in the compound caesium iodide where the relative concentrations are fixed by the composition and thus do not need to be known precisely,
the masses are 133 (Cs) and 127 (I) and ionization energies are 3.89eV and 10.46eV respectively. All these atoms have high second ionization potentials, the lowest of which for cadmium is 16.90eV. Thus the number of doubly charged ions produced will be less than 0.1% of the population which may be neglected.

A third method is to determine the relative response to the same concentration of a number of elements over a wide range of ionization potential. When corrected for mass discrimination the relative response may be plotted against ionization energy. The calculated response may then also be plotted for a series of values of \( T_1 \) producing a family of curves against which the experimental plot may be compared to give a value for \( T_1 \).
Appendix 3. Operating Potentials of Ion Lens, Sampling and Analysis System.

The electrically significant elements of the ion lens, sampling and analysis system are shown below. The location and name of each element are given together with an identification code relating to the potential values listed overleaf.

<table>
<thead>
<tr>
<th>Location</th>
<th>Name</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ions</td>
<td>Sampling Cone-Aperture</td>
<td>SA</td>
</tr>
<tr>
<td></td>
<td>Skimmer</td>
<td>Sk</td>
</tr>
<tr>
<td></td>
<td>Draw-out Electrode (Cylinder 1)</td>
<td>DE</td>
</tr>
<tr>
<td></td>
<td>Collector</td>
<td>Co</td>
</tr>
<tr>
<td></td>
<td>Plate</td>
<td>P1</td>
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<td></td>
<td>Cylinder 2</td>
<td>C2</td>
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<tr>
<td></td>
<td>Cylinder 3</td>
<td>C3</td>
</tr>
<tr>
<td></td>
<td>Differential Aperture</td>
<td>DA</td>
</tr>
<tr>
<td></td>
<td>Cylinder 4</td>
<td>C4</td>
</tr>
<tr>
<td></td>
<td>Entrance Plate</td>
<td>EP</td>
</tr>
<tr>
<td></td>
<td>Pre Rods</td>
<td>Pre.R</td>
</tr>
<tr>
<td></td>
<td>Main Rods</td>
<td>R</td>
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<tr>
<td></td>
<td>Post Rods</td>
<td>Pst.R</td>
</tr>
<tr>
<td></td>
<td>Exit Plate</td>
<td>XP</td>
</tr>
</tbody>
</table>

Detector
Typical Potential Distribution

The potential, in volts, given below for each element refers to the steady bias potential used to provide accelerating and focussing fields in the system. Operating potentials of the quadrupole are not included with the exception of the main rod pole bias R, although this is derived from the RF/DC control unit. It is included because it is only concerned with acceleration and focussing and plays no part in the mass analysis function. Four typical cases are shown as representative of early and late practice in both boundary layer and continuum operation. Not all the electrodes were present all the time. A dash indicates when an electrode was omitted.

<table>
<thead>
<tr>
<th>Code</th>
<th>Early Work</th>
<th>Final System</th>
<th>Early Work</th>
<th>Final System</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>+5</td>
<td>+1</td>
<td>0</td>
<td>-25</td>
</tr>
<tr>
<td>Sk</td>
<td>--</td>
<td>--</td>
<td>0</td>
<td>-25</td>
</tr>
<tr>
<td>DE</td>
<td>--</td>
<td>--</td>
<td>-30</td>
<td>-230</td>
</tr>
<tr>
<td>Co</td>
<td>-600</td>
<td>-600</td>
<td>-300</td>
<td>-20</td>
</tr>
<tr>
<td>Pl</td>
<td>-90</td>
<td>-90</td>
<td>-75</td>
<td>0</td>
</tr>
<tr>
<td>C2</td>
<td>-90</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C3</td>
<td>0</td>
<td>-30</td>
<td>-60</td>
<td>+8</td>
</tr>
<tr>
<td>DA</td>
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<td>-90</td>
<td>-255</td>
<td>-60</td>
</tr>
<tr>
<td>C4</td>
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<td>-6</td>
<td>-125</td>
<td>+5</td>
</tr>
<tr>
<td>EP</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>P.R.</td>
<td>0</td>
<td>-6</td>
<td>-11</td>
<td>-7</td>
</tr>
<tr>
<td>R</td>
<td>-2</td>
<td>-1</td>
<td>-3</td>
<td>+6</td>
</tr>
<tr>
<td>Pst.R</td>
<td>0</td>
<td>-6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>XP</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Appendix 4. Boundary Layers in Plasma Sampling

A.4.1 Aerodynamic and Thermal Boundary Layers

Whenever a flowing gas is intercepted by a stationary surface the flow is deflected to pass round or over it. Immediately adjacent to the surface the flow becomes zero and at points successively further from the surface the flow increases until at some distance from the surface it remains undisturbed. The subject of the formation and behaviour of the boundary layer between the undisturbed region of the flow and the surface constitutes a major topic in fluid dynamics. A simple treatment in the restricted case of a flame playing against a flat surface is given by Hayhurst et al (49) on which the following discussion is based.

A simplified model is assumed in which a steady axisymmetric flow is incident normally onto an infinite surface. In the practical case of sampling a plasma flame of a total diameter of 15 mm playing on the flat tip of a cone of 3 mm diameter there are obviously considerable departures from the model but the area of interest is the aperture of 70 μm diameter in the centre of the 3 mm disc and the faster central channel of the flame also has a diameter of 3 mm. For this the infinite flat plate model may be expected to provide an upper limit for the layer thickness which may be compared with the visible effect.

Hayhurst shows that for this case the aerodynamic or momentum boundary layer thickness $\delta$ is given by

$$\delta = 3.0 \left( \frac{\nu}{2c} \right)^{1/4}$$  \hspace{1cm} (1)

where $\nu$ is the kinematic viscosity of the gas and $c$ is a constant given by

$$W_0 = cD$$  \hspace{1cm} (2)

where $D$ is flame diameter and $W_0$ axial velocity.

Kinematic viscosity $\nu$ is the ratio of dynamic viscosity $\eta$ to density

$$\nu = \frac{\eta}{\rho}$$

The value of $\nu$ varies with temperature as both $\eta$ and $\rho$ are temperature
dependent.

At a temperature $T_2$

$$n_2 = n_1 \left( \frac{T_1 + C}{T_2 + C} \right)^{3/2} \left( \frac{T_2}{T_1} \right)^{3/2}$$

where $n_1$ is a known value at $T_1$ and $C$ is Sutherland's constant (Ref.63) (142 for Ar).

Thus at a temperature $T_2$

$$n_2 = \frac{n_1}{\rho_1} \left( \frac{T_1 + C}{T_2 + C} \right)^{3/2} \left( \frac{T_2}{T_1} \right)^{3/2}$$

In the hot plasma flame the momentum boundary layer will also be accompanied by a thermal boundary layer since the surface (cone tip) must be kept cooler than the plasma and hence there is a temperature gradient across the layer. The thickness $\tau$ of the thermal boundary layer is related to that of the momentum layer by the Prandtl number $P_r$, the ratio of the kinematic viscosity to the thermal diffusivity.

Thus

$$\tau = P_r \delta$$

where $P_r = \frac{4Y}{9Y - 5}$

(Ref.64)

For argon where $\gamma$, the ratio of specific heats, = 1.67

$$P_r = \frac{2}{3}$$

The temperature distribution across the thermal boundary layer is approximately linear (49), hence the best value of kinematic viscosity for the calculation of boundary layer thickness $\delta$ will be that at the mean boundary layer temperature. For the sampling cones used the tip temperature was approximately 623 K (350°C) so that for a plasma temperature of 8.000 K (at 5 mm from the coil) the mean temperature was 4812K. Hence

$$\nu_2 = \frac{n_1}{\rho_1} \cdot 92.4$$

(5)

where $n_1$ and $\rho_1$ are the values at 273 K.
The velocity of the sample gas in the central channel in which the sampling aperture is placed is calculated to be the equivalent at room temperature of 613 cm.sec\(^{-1}\) at the injector tube mouth which has a diameter of 1.5 mm. By a position 5 mm from the coil, the normal operating position in boundary layer sampling, where the temperature has risen to approximately 8000 K, the diameter of the central channel, measured from photographs such as Figure 28, has increased to 3 mm. If the reasonable assumption is made that little mixing with the slower coolant gas flow in the annulus has yet occurred then the velocity at this point is 41.8 m.sec\(^{-1}\). Little experimental data has been published on velocity profiles in small plasma torches of this type but this value is not in conflict with computer simulation values (65) and is compatible with figures quoted for residence time of analyte species in the central channel (24). The velocity of the gas (coolant gas) in the outer annular channel is just half that in the central channel for typical operating conditions so that it is reasonable to treat the central channel as the flame of diameter 3 mm, and ignore the annular flow.

With these assumptions then from equations 1, 2 and 5

\[ \delta = 3.0 \left( \frac{92.4 n_1}{2 \rho_1 \frac{D}{W_0}} \right)^{\frac{1}{2}} \]

\[ = 0.59 \text{ mm} \]

This value of the momentum boundary layer thickness may be compared with the visual evidence from photographs taken of the plasma flowing over the tip of the cone where the central channel is made visible by nebulizing a yttrium solution as in Figures 38 to 40. The thickness of the red YO layer over the tip of a cone at the mouth of the torch is equivalent to 0.3 mm. In the absence of a cone red YO emission is first seen in the centre of the plasma flame at a distance of about 30 mm from the work coil where the gas temperature has fallen to about 5000 K. It is therefore reasonable to assume that this is the temperature at the outer edge of the visible red YO in the boundary layer. Since the outer edge of the thermal boundary layer is at 8000 K the thickness of the thermal boundary layer is then

\[ \tau = \frac{8}{5} \cdot 0.3 \text{ mm} = 0.48 \text{ mm}. \]
Since $\tau = P_T \delta$ and $P_T = 2/3$ for argon then $\delta = 0.72 \text{ mm}$.

This measured value of $\delta$ is in reasonably good agreement with the calculated value of $0.59 \text{ mm}$. Closer agreement would be obtained if mixing between the central and annular flows had not been neglected as this would reduce the value of $W_o$.

A.4.2 Dwell Time and Reactions of Sample in the Boundary Layer

In a boundary layer at a mean temperature of 4312 K the mean free path at atmospheric pressure is $9 \times 10^{-7} \text{ m}$ or 0.9 $\mu\text{m}$.

The arithmetic average atomic velocity of argon atoms at this temperature is given by

$$V_a = \left( \frac{8 kT}{m \text{m}} \right)^{1/2}$$

(ref. 52)

where $m$ is the atomic mass and $k$ and $T$ have their usual meaning. Thus

$$V_a = 1.51 \times 10^3 \text{ m sec}^{-1}$$

compared to which the flame velocity $W_o$ is negligible. The average time between collisions is therefore

$$\approx 6 \times 10^{-10} \text{ secs.}$$

If the effect of the aperture is neglected the shortest possible path to the tip of the cone through the boundary layer thus involves a number of collisions

$$= \delta/\lambda$$

occupying a minimum dwell time of

$$t_d = \frac{\delta \cdot 6 \times 10^{-16}}{\lambda} \text{ secs.}$$

$$= 4 \times 10^{-7} \text{ secs.}$$
The effect of a small sampling aperture of 70μm diameter on the dwell time will be relatively small, and in practice the mean dwell time will be several times the minimum value of $t_d$ because of the random nature of collisions so a period of several microseconds is most probable. This value is similar to that deduced by Hayhurst et al (50) for sampling from flames with similar apparatus. Even though these small apertures are not able to draw enough gas to break through the boundary layer about 9 diameter thick, they still produce supersonic flow of the expanding gas although it will be drawn from within the layer. The terminal Mach number for a 70μm diameter aperture is reached at about 3 diameters downstream and by this point, which is reached in 0.23μs (42), the composition is effectively frozen. With these small apertures therefore the dwell time in the boundary layer is the most significant period, providing opportunities for reactions to occur which will change the composition of the plasma gas. Hayhurst et al (50,66) classify such reactions according to their relaxation times, fast reactions with times of 1μs or less and slow ones where the relaxation times are greater than 5μs. The fast reactions will be able to re-equilibrate during the dwell time in the boundary layer and less so in the expansion and thus will modify the sample in the process. Typical of this type of fast reactions are the hydration reactions such as

$$H_3O^+ + H_2O \rightarrow H_3O^{+}.H_2O$$

and three body hydration reactions of metal ions

$$M^+ + H_2O + X \rightarrow M^+.H_2O + X$$

Three body reactions are slower than bi-molecular ones and thus will proceed less far during sampling than the simple hydration of $H_3O^+$. Important fast reactions for the alkaline earths are of the class

$$M^+ + H_2O \rightarrow MOH^+ + H$$

Among the slow reactions that cannot follow the cooling in the boundary layer and expansion and are thus effectively frozen even in boundary layer sampling are the very important processes of ion formation and recombination.

$$M + X \rightarrow M^+ + e^- + X$$

and
The presence of the boundary layer may thus be expected to cause little change in the concentrations of atomic ions in the sample and the relative intensities of ions measured by the mass spectrometer should reasonably represent the plasma composition.

In the context of reaction processes occurring during sampling it is relevant to note that in a continuum expansion through a 0.4 mm diameter aperture where the boundary layer cannot form over the aperture, the time to reach the terminal Mach number is just 1μs. The extent to which reactions can follow this expansion will depend on just how fast they are.

A.4.3 Electrical Sheath and Plasma Potential

Much of the literature on the sampling of ions from electrical plasmas is devoted to the diagnosis of low pressure electrical discharges and ionospheric plasmas. In these studies ion effusion through very small holes at $K_n >> 1$ is normally used. Work at atmospheric pressure using large apertures, $K_n < 0.1$, is usually limited to chemical flames and the electrical conditions in these circumstances, which are much closer to the ICP sampling case, are not usually discussed. Diagnosis of high pressure plasmas is more often conducted with electrical probes (67) in which the current voltage characteristics of the probe are measured. This, however, requires either a second large area electrode in the plasma or a double probe to complete the measuring circuit. The ICP is essentially an electrodeless plasma, which, from contamination considerations, is a highly desirable feature, and although the insertion of a sampling cone is necessary for ion extraction, any further electrodes are both undesirable and mechanically inconvenient. In these circumstances the plasma potential is therefore floating in relation to sampling cone and aperture, and on balance the use of a potential to influence the extraction is probably best avoided, apart from being difficult to achieve. Under these conditions the net current flow to a floating cone will be zero. A convenient treatment of the electrical sheath that forms across a surface in a plasma is given in Ref. 68, and

$$M^+ + e^- + X \rightarrow M + X$$
When a surface is immersed in a plasma which is electrically neutral \((n_i = n_e)\) the surface acquires a potential \(\phi_0\) which develops to maintain a balanced flux of ions and electrons to the surface. In the absence of this potential the electron flux would predominate due to the much higher thermal velocity of electrons and the surface potential thus becomes negative with respect to the plasma. A sheath region is therefore formed over the surface in which the electron population is depleted and charge neutrality no longer obtains. The thickness of the sheath is approximately the same as the Debye length given by

\[
\lambda_D = 69.0 \left( \frac{T}{n_e} \right)^{\frac{1}{2}} \text{m}
\]

where \(n_e\) is electron density in \(\text{m}^{-3}\).

In this relation \(T\) is strictly the electron temperature, \(T_e\) which in the absence of LTE is not the same as \(T_i\) or \(T_g\). \(T_e\) is not commonly measured for the ICP but for a similar plasma at 10 mm from the work coil, Alder et al deduce a value of about 8,500 K. For 5 mm a value of 9,000 K is therefore assumed (36).

Thus, for boundary layer sampling conditions

\[
\lambda_D = 9.8 \times 10^{-6} \text{m}
\]

The value of the potential \(\phi_0\) across this sheath is given by

\[
\phi_0 = k \frac{T_e}{e} \ln \left( \frac{m_i}{m_e} \right)^{\frac{1}{2}}
\]

where \(m_i\) and \(m_e\) are ion and electron masses.

For an argon plasma this yields

\[
\phi_0 = 4.35 \text{ V}
\]

This value is linearly dependent on the value of \(T\) used and would therefore have been little different had gas temperature or ion temperature been used in the ICP. For low pressure plasmas, however, \(T_e\) may well be between \(10^9\) and \(10^5\) K and sheath thickness and potential would be consequently increased.
In a collision dominated plasma such as the ICP the additional process of ambipolar diffusion along the gradients in plasma properties also contributes to the floating plasma potential. The potential due to diffusion in the main body of the plasma falls to zero at the edge of the sheath and then the total floating potential is the sum of the Debye sheath potential $\phi_o$ and that due to diffusion.

The potential drop due to ambipolar diffusion alone is given by

$$\left( \phi_o - \phi_b \right)_{\text{amb}} = \frac{kT_e}{e} \ln \frac{n_e^*}{n_{eb}}$$

where $n_e^*$ is the electron concentration in the body of the plasma remote from walls and surfaces and $n_{eb}$ is that at the sheath boundary.

The ratio $\frac{n_e^*}{n_{eb}}$ is shown in Ref. 68 to be approximated by the expression

$$\frac{\pi}{\sqrt{2}} \cdot \frac{\lambda_e}{\lambda_R}$$

where $\lambda_e$ is the electron mean free path and $\lambda_R$ the mean distance travelled by an ion before it recombines, a measure of the distance which the disturbance created by the surface extends into the plasma. Its value is given by the relation

$$\lambda_R = \frac{D_a}{n_e^* \cdot \alpha}$$

where $D_a$ is the ambipolar diffusion coefficient and $\alpha$ the recombination coefficient.

There is some uncertainty over the values of $\alpha$ and $D_a$ that are appropriate for a plasma of this type, but using the value for $\alpha$ calculated from the empirical relation derived by Desai and Corcoran (69) for an argon plasma, for the conditions used for continuum sampling at 10 mm, and a value of $D_a$ from Ref. 59 a value of 2.28 mm is found for $\lambda_R$. Also from (59)

$$\lambda_e = 4 \sqrt{Z} \lambda$$

where $\lambda$ is the atomic mean free path. Thus
\[ \lambda_e = 5.09 \times 10^{-3} \text{ mm} \]

and therefore
\[
\frac{n_e^*}{n_{eb}} = \frac{\lambda_e}{\lambda_R} = \frac{4 \pi \lambda}{\lambda_R} = 4.96 \times 10^{-3}
\]

This leads to a value of
\[ (\phi_\infty - \phi_b)_{amb} = 3.43 \text{ V} \]

Thus the total floating potential between plasma and sampling cone is
\[ (\phi_\infty - \phi_b)_{amb} + \phi_0 = 7.78 \text{ V} \]

This value is clearly well below the plasma potential found experimentally from ion energy of approximately 25 V. This is much closer to the values obtained in low pressure plasmas of about 40 V (7).

An additional potential source is thus needed to explain the ion energy values experienced and it is suggested that this is the DC potential produced by rectification of capacitively coupled RF currents from the work coil to the plasma column by the non-linear current-voltage characteristic of the Debye sheath. This characteristic which can normally only be plotted with another electrode in the plasma (67), becomes involved because an RF return path exists through the capacity between coil and plasma and in alternate half cycles the current flow due to electron or ion motion is different. The plasma is not therefore truly floating and the net current flow to the cone is not zero as previously assumed. The mechanism of such a source of plasma potential is discussed by Butler and Kino (71). Application of their treatment to the ICP has not been attempted but it is evident that potentials of the right order are possible.

The effect of these sources of plasma-cone potential difference may now be considered in relation to the very different ion energies experienced in the two sampling modes.

In boundary layer sampling the Debye sheath thickness is approximately 0.1 \text{ \mu m}, very much smaller than the sampling aperture diameter. The sheath will not therefore bridge the aperture but merely cover the edges.
The momentum boundary layer thickness was calculated as 0.6mm and it has just been shown that $\lambda_R$, the effective thickness of the ambipolar diffusion layer is approximately 2.3mm. The influence of the flow through the sampling aperture extends upstream of the aperture by up to 2 diameters (53) so that the gas sample may be considered to come from a point 0.14 mm ($D_o = 0.07$ mm) in front of the aperture. Here the plasma within the boundary layer will certainly be at least at the Debye potential of 4.35 V. The boundary layer represents a stagnant region isolated from the bulk plasma flow (49) so that the potential distribution from the edge of the Debye sheath to the plasma will conform to the undisturbed ambipolar diffusion potential distribution (68). This may be shown to give a value for $\phi(y) - \phi_p$ at the distance $y = 0.14$ mm from the cone of only about 0.1 V, to be added to the sheath potential. Even if this is multiplied by about 6 to allow for the assumed rectified RF potential it still makes the potential at the sampling point only about 5 V.

The ions entering the aperture thus appear to originate from a positive potential of about 5 V in boundary layer sampling. Even though the treatment is very approximate it can be seen that contributions from the total floating plasma potential to the ion energy are very small in boundary layer sampling and the Debye potential sets the ion energy. In effect the sampling point may be seen to be screened from the bulk plasma potential by the boundary region of ambipolar diffusion.

In continuum sampling, however, the situation is quite different because of the very strong gas flow into the large aperture ($D_o = 0.4$ mm) which breaks down the boundary layer ($2D_o > \delta$). In fact at the normal central channel gas flows used for continuum sampling the gas inflow to the aperture is $7.21 \times 10^7 \ D_o^2 \ Pa \cdot m^3 \cdot sec^{-1}$, which for a 0.4 mm aperture is the equivalent of 0.11 $l \cdot sec^{-1}$. The total central channel flow in the plasma, however, is only 0.22 $l \cdot sec^{-1}$ at 7500 K, so it is clear that the sample extracted through the aperture is just half of the total sample flow. In the absence of the boundary layer in front of the aperture the conducting plasma is brought right up to the sampling cone surface and in fact was found to reach as far as the skimmer (Chapter 4.4.4) so that the normal ambipolar diffusion potential distribution is completely destroyed by the strong flow. The source of the extracted ions is thus at the full plasma potential and the ion energies found in continuum sampling reflect...
this. The Debye sheath remains intact, however, but follows the surface round into the expansion stage. Under continuum flow conditions the full plasma potential therefore probably appears across the Debye sheath. The much higher electric fields in the immediate vicinity of the aperture contribute to the formation of the pinch discharge although clearly the pressure gradient also plays a part.
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