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Improvements in Methods and Apparatus Relating to Inductively Coupled Plasma Atomic Fluorescence Spectrometry

by

Tariq Mehmud Durrani

A doctoral thesis
submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy of the Loughborough University of Technology
August, 1990

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Dedicated

"To my Parents"
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CERTIFICATE OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this thesis, that the original work is my own except as specified in acknowledgements or in footnotes, and that neither the thesis nor the original work contained therein has been submitted to this or any other institution for a higher degree.

Date 2-8-79

Tariq Mehmud Durrani
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Publication of Results

The work described in this thesis has been published in a number of Primary Scientific Journals and presented in Conferences etc., which are listed below:

Publications


Presentations


Abstract

This thesis describes a study of the technique and development of a system known as ASIA (Atomiser, Source, Inductively Coupled Plasmas (ICPs) in Atomic fluorescence spectrometry).

Copper, nickel and lead boosted-discharge hollow-cathode lamps (BDHCLs), have been compared with the ICP, as excitation sources. A detailed study of the spectra of nickel and lead was performed. No evidence was found for the differences in the radiances between the two sources when the copper lamp was overrun. Although the lamps gave rise to lower blank standard deviation values, the detection limits were worse with the lamp source compared to ICP source.

The modified Optica CF4 monochromator originally used, has been replaced by a Bentham Instruments computer controlled monochromator with better light gathering power. The optical arrangement for gathering the fluorescent radiation has also been re-designed. The performance of the modified system has been studied, based on detection limits (DLs), for a number of elements. In general, an improvement of 2 to 3 times in DLs is achieved. Further, improvements in the detection limits for molybdenum and tungsten have been achieved with the development of an on-line preconcentration procedure using a miniature column of Amberlite (IRA-93) anion-exchange resin.

A heated spray chamber desolvation system has been evaluated as a sample introduction device for atomiser and source plasmas but, unfortunately the results obtained with the device were unsatisfactory. Problems included periodic instability of the plasmas and salt deposition on the inner walls of the spray chamber when high concentration solutions were aspirated. Also, a brief study of the feasibility of an aerosol modulation device has been performed.

Finally, an interference study has been made to investigate the interference effects of high concentrations of interferent elements on a number of analyte elements. Spectral scans were obtained to visualise any possible interference effect. No spectral interference effect was observed on any of the analyte elements due to the interferent elements studied.
Introduction and aims

The Inductively coupled plasma has been shown to be an excellent source for emission spectrometry (ICP-AES), because of the intense atom and ionic line radiations produced for many elements. This is a result of a combined effect of high temperature and relatively long residence time leading to a high degree of volatilization and atomisation which results in freedom from physical and chemical interferences. Also high sensitivities and wide dynamic ranges are achieved. However, in spite of these advantages ICP-AES suffers from spectral interferences. The emission spectra are rich in lines because of the high temperature of the ICP and even a high resolution monochromator does not enable all the analytically useful lines to be used. The use of this device (ICP) has recently been extended to atomic fluorescence spectrometry and has been demonstrated to be both a useful excitation source and atomisation cell for AFS. The use of argon gas for plasma formation and as a carrier gas provides a chemically inert environment that possesses a small quenching cross section for the excited species, particularly desirable for the atomisation cell. The use of ICP as an
atomisation cell also minimizes particle scattering, which is a common problem associated with flames. A detailed review of the literature and theory on the Inductively coupled plasma-Atomic fluorescence spectrometry (ICP-AFS) is given in Chapter 1.

The application of the ICP as an excitation and atomisation source has been studied with an instrument arrangement that has been named ASIA. Previous studies with the system have demonstrated the usefulness of ICP both as excitation source and atomisation cell. The detection limits obtained for a number of elements are almost comparable to those obtained by ICP-AES except for refractory elements for which detection limits are about 10 to 20 times worse. The details of the system and preliminary experiments performed with the system are described in Chapter 2.

The present work aimed at improvements in signal collection, processing and optical arrangement and sample introduction into the plasmas to improve the analytical sensitivity of the system.

To ascertain, whether or not a high-powered ICP was a better excitation source than the BDHCLs which are the most commonly used excitation sources in atomic fluorescence spectrometry, a study was made. The performance of the BDHCLs was evaluated and compared with the ICP, before proceeding further with the development of the ASIA system. The results of the study are described in Chapter 3.

In order to improve the sensitivity of the system for the refractory elements an effort was made to increase the production of free atoms in the atomiser ICP using a number of methods. This was followed by the development of a method for the preconcentration of refractory elements prior to their determination by the system. The details of the study are given in Chapter 4.

The light collection optics were planned to be re-arranged in two steps. In the first step the distance between the atomiser plasma and the monochromator entrance slits has been reduced by using a single lens to collect the radiation from the atomiser plasma rather than two lenses used originally. In the next step, in order to simplify the optical arrangement between the two plasmas, an investigation was made of the possibility of replacing the optical chopper by aerosol modulation device. These modifications to the present set-up of the system, including the replacement of Optica CF4
monochromator by a Bentham Instruments computer controlled monochromator with better light gathering power, more appropriate blaze and throughput characteristics, are described in Chapter 5 and 6.

Chapter 6 also describes the experimental programme and the results obtained of a performance study of a desolvation system on the atomiser and the source plasmas. The aim of this study was to allow using low concentration solutions for the source plasma whereas, its utilization for the atomiser plasma was aimed to improve the sensitivity of the system.

Furthermore, to test the susceptibility of this technique to interferences, a study was made of a number of interferents that cause an interference effect on determinations in emission and is described in Chapter 7.

The conclusions and recommendations for future work are described in Chapter 8.
Chapter 1

Basic concepts in and growth of Inductively Coupled Plasma-Atomic Fluorescence Spectrometry

1.1. Atomic fluorescence spectrometry: Theory

Atomic fluorescence is an emission phenomenon which relies upon radiational excitation, rather than thermal excitation. It is based upon the absorption of radiation of a certain wavelength from a suitable source by an atomic vapour to produce excited atoms and the measurement of the radiation emitted when a fraction of these atoms lose their energy by a radiational process or processes called atomic fluorescence. Both the absorption and the measured emission processes occur at wavelengths which are characteristic of the atomic species present.
The intensity of fluorescence is measured in a direction perpendicular to the exciting beam and is dependent on a number of parameters according to the equation\(^1\) given below:

\[
I_f = I_o \frac{L}{l} \Phi f_s \frac{\Omega_f}{4\pi}
\]

The terms in the equation are defined as;

- \(I_o = \) integrated radiant power (per unit area) absorbed from the source - units of ergs sec\(^{-1}\) cm\(^{-2}\).

- \(\Phi = \) fluorescence power efficiency (ratio of radiant fluorescence power to radiant power absorbed) and is identical to the fluorescence quantum efficiency, \(\Phi\) (quantum efficiency of the fluorescence transition is the fraction of absorbed photons per unit time which is re-emitted as fluorescence radiation per unit time.), if only resonance absorption-fluorescence transition is considered as in this case.

- \(f_s = \) dimensionless self-absorption factor accounting for the decrease in fluorescence due to self-absorption by similar atoms.

- \(\frac{\Omega_f}{4\pi} = \) fraction of fluorescence radiation measured by the spectrometer within the solid angle of observation, \(\Omega_f\), in steradians.

The intensity of atomic fluorescence is measured in the units ergs sec\(^{-1}\) cm\(^{-2}\). In the above equation it is assumed that:

(i) Only a single, isolated resonance line is being studied.

(ii) The absorption and fluorescence lines are broadened only by Doppler and Lorentz broadening.

(iii) The atom source has a uniform temperature and atom concentration of absorbers in the volume increment of importance at the height of observation and is in thermal equilibrium.

(iv) The fluorescence region being studied is uniformly illuminated by the light...
source.
(v) The fluorescence over the entire atom cell (cell length L in the excitation
direction and length L in the emission (measurement) direction) and in the
direction of the detector is imaged on to the monochromator entrance slit.

1.2 Mechanism of atomic fluorescence

In atomic fluorescence an atom is radiationally excited, and radiation is emitted when
a fraction of these excited atoms undergoes radiational de-activation. The principal
types of atomic fluorescence effects which may be observed\(^2\) are detailed below:

![Diagram of atomic fluorescence](image)

Fig. 1.1 Types of resonance fluorescence: (A); Resonance fluorescence originating from the ground state of atom. (B); Resonance
fluorescence originating from a metastable state.
Note: 0 - Ground state of an atom, 1, 2 - Excited electronic states of an atom. Solid lines represent a radiational process and dashed
lines represent a non-radiational process.

1.2.1. Resonance fluorescence

Resonance fluorescence occurs when the fluorescent wavelength is the same as the
excitation wavelength. This is probably the most widely used form of fluorescence in
atomic fluorescence spectrometry and invariably concerns the transitions between the
ground state and the first excited state (see Fig 1.1). Some elements may have an
appreciable population of atoms in low-lying metastable energy levels which can be
thermally populated and exhibit resonance fluorescence. For example indium, gallium, lead, tin, etc. In such a case emitted fluorescence is of lower intensity than for the more abundant ground state atoms and is known as "excited state resonance fluorescence". Resonance fluorescence originating from the ground state is generally of higher intensity than that originating from metastable states, which depends upon the population of these states. Resonance fluorescence originating from the ground-state atoms is often accompanied by non-resonance fluorescence having the same excitation level.

1.2.2 Non-resonance fluorescence

Non-resonance fluorescence occurs when the excitation wavelength and wavelength of emitted fluorescence are different. There are two main types here, direct-line fluorescence and stepwise-line fluorescence are detailed as follows:

![Diagram of Direct-line Fluorescence](Image)

Fig. 1.2 Direct-line fluorescence transitions originating from the ground state of an atom (A) and from a metastable state (B). (See footnote in Fig. 1.1 and also - represents electronic excited state of an atom.)

1.2.2.1 Direct-line fluorescence

In the direct-line fluorescence an atom is radiatively excited (usually from the ground state) to a higher electronic state and then undergoes direct radiational transition to a metastable state above the ground state (see Fig. 1.2). For example, direct-line
fluorescence occurs in the case of lead when atoms are excited by 283.31 nm line and fluoresce at 405.78 and 722.9 nm lines. Similar examples are the excitation of thallium, indium, and gallium ground state atoms by absorptions at 377.5, 410.2 and 403.3 nm followed by emission at 535.0, 451.1, and 417.2 nm, respectively.

1.2.2.2 Stepwise-line fluorescence

In stepwise-line fluorescence the upper levels of the exciting and emitted fluorescence are different. Two cases can be distinguished here. i.e., normal stepwise-line fluorescence and thermally assisted stepwise-line fluorescence. These types of fluorescence are illustrated in Fig. 1.3.

![Diagram of Stepwise-line Fluorescence](image)

Fig. 1.3 Types of stepwise-line fluorescence: (A) normal stepwise-line fluorescence; (B) thermally-assisted stepwise-line fluorescence. (See footnote in Fig. 1.1 and 1.2)

In the case of normal stepwise-line fluorescence, the excited atoms lose part of their energy by collisional de-activation and then come to the original state (usually ground state) by radiational de-activation. A typical example of such fluorescence is the emission of the sodium 589.0 nm line after the excitation of sodium atoms by the sodium resonance lines at 330.2 and 330.3 nm.

In thermally assisted stepwise-line fluorescence the radiationally excited atom is further excited (thermally due to temperature in the atom cell) to a higher electronic state and then undergoes radiational de-activation to a metastable state. For example,
Bismuth excitation at 206.2 nm could result in thermally assisted stepwise-line fluorescence at both 293.8 nm and 262.8 nm lines. This type of fluorescence is of low intensity.

1.2.2.3 Anti-stokes fluorescence

This is a less common type of non resonance fluorescence and is known as thermally assisted anti-stokes fluorescence, in which the emitted wavelength is shorter than the excitation wavelength. This occurs when atoms populated near, but above the ground state undergo a radiation transition to the ground state or when ground state atoms are excited radiationally to a certain electronic state, subsequently raised to slightly higher electronic state by absorbing thermal energy and are finally radiationally de-activated to the ground state (see Fig. 1.4) Anti-stokes fluorescence is always accompanied by resonance fluorescence.

All types of non resonance, particularly direct-line fluorescence, can be analytically useful. Sometimes, as in the case of lead, it offers the advantage that scattering of the excitation radiation can be eliminated by the use of a filtering device.

---

Fig. 1.4 Types of thermally-assisted anti-stokes fluorescence: (A) is a special case of direct-line fluorescence and (B) is a special case stepwise-line fluorescence. (See footnote in Fig. 1.1 and 1.2)
1.2.3 Sensitised fluorescence

This occurs when a sample atom (acceptor) emits radiation after collisional activation by a foreign atom (donor) that was excited previously by an external source. The process can be represented as follows:

\[ A + h\nu \leftrightarrow A^* \]
\[ A^* + M \leftrightarrow A + M^* + \Delta \]
\[ M^* \leftrightarrow M + h\nu \]

where \( A \) is the foreign atom and \( M \) is the sample atom and \( \Delta \) represents thermal loss. This type of fluorescence requires a higher concentration of foreign atoms like that produced by non-flame sources like plasmas.

1.3 Quenching of fluorescence

The de-excitation processes by which quenching of excited metal atoms may occur are summarized as follows:

(i). Quenching by collisions with free atoms:

\[ A^* + B \leftrightarrow A + B^* \]

This type of quenching is the transfer of kinetic energy between the valence electron of the excited atom (\( A^* \)) and the rare gas atom (\( B \)) and is extremely inefficient owing to the great difference in mass of the colliding species.

(ii). Quenching by collisions with free electrons:

\[ A^* + e^- \leftrightarrow A + e^-^* \]

In the view of much smaller mass and higher velocity of the quenching electrons (\( e^- \)), this process should be more efficient than (i) above. This type of quenching becomes significant if plasma cells are used as atom cells in AFS which contain far higher electron population than the flames used in the early days of fluorescence technique.
(iii). Mixing of excited states by collisions with free atoms:

\[ A^* + B \leftrightarrow A' + B \]

This process involves the conversion, as a result of a collision, of one excited state of an atom \( A^* \) to another \( A' \) (rather than to the ground state as in quenching). It has been widely observed for the doublets of alkali metals where the energies of the excited states are relatively close.

(iv) Quenching by collisions with molecules:

\[ A^* + BC \leftrightarrow A + BC^* \]

This is by far the most important process for consideration of quenching in AFS applications where flames are used as atom cells. The ability of many of the simple molecules found in flame gases to quench efficiently the excited atoms is generally attributed to the ease with which the electronic energy of the atoms is converted to vibrational energy within the molecule.

1.4 Inductively coupled plasma

An inductively coupled plasma is a partially ionized gas formed in a flow of a suitable gas (such as argon), or a mixture of gases, by transferring energy from a radiofrequency field (typically 1-15 kW at 27-50 MHz) by means of an induction coil.

1.4.1 Inductively coupled plasma: Configuration and formation

The ICP torch configuration is shown in Fig. 1.5. It consists of two concentric quartz tubes, the inner tube (plasma tube) stopping below the induction coil and the outer tube (coolant tube). The plasma is formed above the inner tube and within the outer tube and its location is largely determined by the position of the induction coil. The induction coil is positioned around the tip of the outer quartz tube. A third tube called the "injector tube" is inserted into the inner tube to inject an aerosol through the plasma after it has formed.
To operate the plasma torch, argon gas stream flowing into the inner tube is "seeded" with electrons either by tesla coil or by introducing an isolated conductor such as graphite rod. Interaction of these electrons with the gas causes ionization of the gas. The charge carriers are constrained in circular paths, which run inside the quartz tube forming eddy currents. The accelerated electrons (and ions) meet resistance to their flow and thus produce ohmic heating by collisions with each other and neutral gas atoms. The whole process results in the spontaneous formation of plasma and the plasma formed in this way attains a gas temperature in the 9,000-10,000 K range, in the region of maximum eddy current. The temperature distribution inside the ICP with an injector flow passing through is shown in Fig. 1.6. A second stream of gas (coolant) is made to flow around the plasma stream, isolating the plasma from the walls of the tube. The sample, together with the carrier gas (injector), can now easily be blown into the plasma through the injector tube. In this process, a tunnel is formed in the plasma
and the tail-flame developed. The excited analyte atoms and ions pass through this narrow tail-flame and observations are made in the tail-flame. Since the temperature in the plasma is very high and because the tail-flame is optically thin which results in less self absorption, the tail-flame becomes an excellent spectroscopic source, giving a high degree of atomisation and ionization.

Originally, the gas flows in the various tubes of the plasma torch namely outer tube (coolant), inner tube (plasma) and injector tube, have been named as coolant gas flow, plasma gas flow and injector gas flow rates, respectively. When argon gas is used for both the coolant and plasma tubes, it was found that an ICP could be sustained with the coolant gas flow only. Therefore, a change in terminology was proposed: naming "coolant gas" as "plasma gas" and "plasma gas" as "auxiliary gas". However, in this work for the source plasma, the original terminology is still valid. Therefore, to avoid any confusion, in this thesis the original terminology is maintained.

![Diagram of Temperature Measurement above the Coil Region](Ref. 4)
1.4.2 Inductively coupled plasma: Appearance

The appearance of an ICP is that of an intensely luminous, non-transparent core and a flame-like, less luminous tail. The plasma core fills the space inside the coil and usually extends a few millimetres below and above the coil, having a spheroidal shape in which the lower boundary is flattened. It emits intense continuum, consisting of the spectrum of hydrogen and neutral argon, and a number of band spectra of the elements introduced as aerosols.

The second region of the ICP lies above the coil where the core becomes conical and is a slightly transparent zone. The third region is the tail-flame, which is hardly visible when pure water is nebulised and is of great analytical importance because observations are made of this region.

Fig. 1.7 Diagrammatic representation of various zones in an ICP (Ref. 5).

Koirtyohann et al.\textsuperscript{5} proposed names for different zones in an argon plasma. A schematic representation of these zones are shown in Fig. 1.7. They suggested that the important
parameter "observation height" could be measured from the top of the initial radiation zone, instead of from the top of the induction coil as is generally practised. But, their suggestion has not been generally adopted.

1.5 Inductively coupled plasma: Historical

The first known experiments on the use of ICP were conducted by Babat\textsuperscript{6,7} in the early 1940's. Babat used a radiofrequency (r.f) generator at powers up to 100 kW and at 1 to 100 MHz frequencies that enabled him to sustain a plasma discharge in air at low pressure and then he raised the pressure up to one atmosphere. Babat successfully employed a quartz tube to contain a low pressure plasma. However, with the atmospheric pressure plasmas at high powers, the quartz tube often melted and the plasma was extinguished. A need was evident from Babat's results for thermal isolation.

![Fig. 1.8 A plasma torch of Reed's early torch. (Ref. 8).](image-url)
of the plasma from the quartz tube. Babat also observed that the greater the frequency of the oscillator, the lower is the power required to stabilise the plasma, when operating ICP at atmospheric pressure.

Fig. 1.9 Schematic diagram of Reed’s torch arranged for crystal growth. (Ref. 9).

In the early 1960’s, Reed continued Babat’s work and solved the problem of thermal isolation of the plasma by introducing the argon gas tangentially into the tube. Such a plasma with tangential gas introduction is termed a vortex stabilised plasma. Reed operated the ICP in a quartz tube of 25 mm internal diameter at 4 MHz and power transfer to the plasma ranging from 1.6 kW to 3.1 kW. A schematic diagram of the ICP torch is illustrated in Fig. 1.8. Reed found argon the simplest gas in which to start and operate the discharge. In addition, the ICP was operated at higher power levels
chapter 1

with pure oxygen and argon mixtures containing as much as 20% hydrogen or 60% helium or air. In a subsequent paper, Reed\(^9\) described a plasma tube geometry which he used for crystal growing and is shown in Fig. 1.9. He mentioned its applications in welding, chemical synthesis, and spray coating. A water cooled copper injector tube was inserted into the discharge to ensure powder introduction into the high temperature discharge. Reed emphasised that powders injected in the discharge would sometimes vaporize completely. This suggested that the ICP discharge could be useful as a spectroscopic light source.

The application of the ICP to analytical spectroscopy was pioneered independently by two groups. One was Greenfield and his colleagues\(^{10}\) at Albright and Wilson, Oldbury, England and the other Fassel and co-workers\(^{11}\) at the Ames Laboratory, USAEC, at Ames, U.S.A. Both groups had recognized that Reed's "plasma torch" offered, in principle, unique potential as a high-temperature atomisation-excitation source, free of contamination from electrode vapours. These groups described their equipment, the characteristics and appearance of the plasma, and tabulated observed emission detection limits for several elements in solution. Greenfield et al.\(^{10,12}\) had initially recognized the necessity to form a plasma discharge with an axial pathway through its centre into which sample aerosol could pass. Initially the torch featured a tulip-shaped inner tube, but this was replaced with a straight cylindrical tube for ease of construction. Figure 1.10 shows the combined nebulizer-plasma tube arrangement which is a patented ICP torch commonly known as Greenfield torch. In this torch, a third concentric quartz tube was used, through which sample aerosol was blown into the plasma forming a central channel through the hot plasma. This arrangement gave superior analytical performance and was universally adopted.

The Greenfield torch uses gas flow-rates of 12 to 40 l min.\(^{-1}\) of argon as plasma gas and 20 to 70 l min.\(^{-1}\) of air/nitrogen as coolant gas. The plasma formed in the torch can withstand the injection of large quantities of air or hydrogen, and is capable of accepting a higher volume of solution or slurries than other plasmas.
Wendt and Fassel,\textsuperscript{11} on the other hand, used the ICP without a tangential flow in order to give greater stability to the discharge and injected aerosol carrier gas which diffused into the plasma and flowed around it. (See Fig. 1.11 (a)). Similarly, the arrangement used by Veillon and Margoshes\textsuperscript{13} at that time did not permit formation of a central
channel under their operating conditions until 1968, when Dickinson recognized the concept of Reed and Greenfield and configured the ICP arrangement in such a way that a toroidal instead of an ellipsoid "teardrop" discharge was formed. Later, Dickinson and Fassel reported the use of ultrasonic nebulisation and a desolvation system combined with a toroidal plasma. The detection limits values achieved were superior to any ICP values published before.

Later, Fassel and his co-workers further developed the torch which received the final form shown in Fig. 1.11 (b) and is often referred to as the "Fassel/Scott torch". Compared with the Greenfield torch, the Fassel torch uses lower gas flows (about 1 l min\(^{-1}\) for plasma and 10 l min\(^{-1}\) for coolant.) The economy of the gas usage is an advantage. However, a drawback is its lack of tolerance to the injection of air or hydrogen.
Since the modification to the ICP torch by Greenfield et al, Wendt and Fassel, and Dickinson and Fassel, the ICP torch has remained substantially unchanged. However, some minor variations on the basic design have been proposed, but all these designs have common features that they are open to the atmosphere, essentially at atmospheric pressure. An exception to these is a reduced pressure torch designed by Seliskar and Warner. The torch described by them which is shown in Fig. 1.12, is a single plasma chamber arrangement rather than of conventional three tube arrangement. A stable plasma was formed at power levels as low as 5 W and plasma-gas flows from 1 l min⁻¹ to several hundred ml min⁻¹. Plasmas were sustained in a range of gases (argon, helium, neon, hydrogen and nitrogen).

They employed this reduced-pressure torch successfully for hydrogen isotope analysis and achieved at least two orders of magnitude lower detection limits than those achievable by conventional mass spectrometry.
The use of low-power all argon plasmas has been accepted for marketing and economic reasons because a smaller, less expensive high frequency generator is needed and running costs are lower. The research into the direction of attempts to reduce the power input or gas flows or both is continuously appearing in the literature.\textsuperscript{19-21}

The extreme versatility of the ICP as an excellent atom and ion excitation cell has extended the applications of ICP to other techniques like atomic absorption, atomic fluorescence and mass spectrometry. Montaser and Fassel\textsuperscript{22} demonstrated the use of ICP in AFS using a conventional Fassel/Scott type torch with extended outer tube to prevent air entrainment and dilution of atomic vapour. Later, Demers and Allemand\textsuperscript{23} explored an extended tube ICP as atomiser for AFS using pulsed hollow-cathode lamps as excitation sources. This work led to the development of a commercial instrument. The torch design used in the Baird instrument is shown in Fig. 1.13. Further details on the application of ICP in AFS are given in Section 1.6. Gray et al.\textsuperscript{24,25} and Houk et al.\textsuperscript{26,27} explored the feasibility of ICP as an ion source in mass spectrometry. This study led to the introduction of commercial ICP-mass spectrometers.\textsuperscript{28,29}

During the past twenty years, numerous reviews have appeared in the literature\textsuperscript{30,31} and a number of books have been published which give comprehensive details on the principles, theory and applications of Inductively coupled plasma atomic emission spectrometry (ICP-AES), Inductively coupled plasma atomic fluorescence spectrometry (ICP-AFS), and Inductively coupled plasma mass spectrometry (ICP-MS). These books include, A handbook of ICP-spectrometry,\textsuperscript{32} Application of plasma emission spectrochemistry,\textsuperscript{33} Development in atomic plasma spectrochemical analysis,\textsuperscript{34} Inductively coupled plasma emission spectroscopy Part 1 and Part 2,\textsuperscript{35} Inductively coupled plasmas in analytical atomic spectrometry,\textsuperscript{36} and Introduction to inductively coupled plasma atomic emission spectrometry.\textsuperscript{37} Also, a monthly newsletter, edited by Barnes\textsuperscript{38} is published on the applications of inductively coupled plasmas.

An important conclusion arises from the literature that ICP development is not yet finished although, it is expected that a stage will be reached in the near future when both the strengths and weaknesses of the ICP have been fully assessed.
1.6 Atomic fluorescence spectrometry: Historical

The practical analytical potential of AFS was first demonstrated by Winefordner\textsuperscript{39,40} in the United States and West\textsuperscript{41} in England, although fluorescence emission from flames had been observed as early as 1923.\textsuperscript{42} Several reviews on the analytical technique have been published to date.\textsuperscript{43-45}

During the early development of AFS, flames were used as atom cells and AFS measurements were carried out on commercial AAS/AES instruments which were modified easily by the addition of an excitation source and its power supply and changes in entrance optics. The only commercial AFS instrument\textsuperscript{46} available at that time was a six-channel Technicon AFS (Model AFS-6) introduced by Technicon Instruments Corporation, Tarrytown, N.Y., U.S.A. A schematic diagram of the instrument is shown in Fig. 1.14. The instrument includes a pulsed hollow cathode lamp, rotating interference filter wheel, a Cassegrain mirror system, a flame cell, and logic circuitry to measure the fluorescence signal of each element when a proper interference filter is in place.
While ICP has been used primarily as a source for atomic emission spectrometry, a number of studies concerning the use of ICP for AFS have been carried out. The first use of ICP as an excitation source in AFS was reported by Hussain and Nickless\textsuperscript{47} in 1969. But poor detection limits obtained at that time, probably resulted in its absence from further use in AFS, until 1976, when Montaser and Fassel\textsuperscript{22} demonstrated the use of ICP as an atomisation cell in AFS. They obtained low detection limits and long dynamic ranges with freedom from scattering and matrix interference. Since then a growing number of papers have been published, using ICP in AFS.

Three approaches have been reported to the use of ICP in atomic fluorescence spectroscopic systems. The first technique is the application of an ICP as an excitation source for fluorescence in a flame atom cell.\textsuperscript{48-50} The second adapts the use of the ICP as an atomisation or ionization cell for fluorescence spectrometry for which an intense excitation source, for example, an electrodeless discharge lamp (EDL),\textsuperscript{22} a HCL,\textsuperscript{23,51-60} or a laser\textsuperscript{61-73} are required. The third approach is use of ICP both as an excitation source and atomisation cell in AFS.\textsuperscript{74-89}
1.6.1 Hollow-cathode lamp excited ICP-AFS systems

Initial studies on a hollow-cathode lamp excited ICP-AFS system were carried out in 1981 by Demers and Allemand. They evaluated the system by studying the detection limits of thirty two diverse elements and compared their results with those from flame AAS and ICP-AES. The encouraging results obtained prompted the introduction by Baird corporation of a commercial atomic fluorescence system for simultaneous multielement analysis called Plasma/AFS. A schematic diagram of the AFS system is shown in Fig. 1.15. The system employs an ICP as an atomisation cell and a pulsed hollow-cathode lamp for excitation. The pulsing of the HCLs is controlled by a microcomputer. This system has been shown to retain to a very high degree the advantages of ICP-AES systems, with the capability of determining up to 12 elements simultaneously using self-contained interchangeable modules. A number of reports have been published describing its application to different water samples, geological samples, precious metals, electroplating solutions, petroleum and petroleum
products. Mercury determinations\textsuperscript{57} have been carried out with slight modifications in the system, by using the cold vapour technique. This has resulted in superior limits of detection for the element.

Further, developments to such a system have been studied by Masamba et al.,\textsuperscript{60} utilizing pulsing of HCLs at high currents and using a Baird ICP torch and element module. They reported detection limits using the pulsed system to be better than those obtained by the Baird HCL-ICP-AFS system and attributed this to an increase in the intensity of atom lines and ionic lines originating from the HCLs.

1.6.2 Laser excited ICP-AFS systems

One of the major problems in the early stages of AFS, was the unavailability of a high intensity primary excitation source. It was in 1971, when Frasser and Winefordner\textsuperscript{61} introduced the use of laser as an excitation source in flame-AFS. This was followed by the introduction of lasers in ICP-AFS by Pollard et al.\textsuperscript{62} in 1979. They used a continuous-wave argon ion pumped dye laser to excite atomic fluorescence from the atoms in an ICP. Unfortunately, they obtained poorer detection limits for a number of elements compared to ICP-AES. However, they suggested that the use of lasers in ICP-AFS could be a practical tool in the diagnostic studies (spatial temperatures and densities) of the plasmas. Since then a number of reports using pulsed and continuous wave dye lasers (N\textsubscript{2}-pumped dye laser, flash lamp pumped dye laser, excimer (XeCl) pumped pulsed dye laser) as primary excitation sources, with ICP atomisation have been published.

Epstein et al.\textsuperscript{63} utilized a flash-lamp pumped dye laser as an excitation source in ICP-AFS. They also obtained disappointing results and attributed this to the increase in background intensity due to the ICP which they considered offsets the improvement achieved in the quantum efficiency and restricted volume of analyte in the plasma compared to flames. Uchida et al.\textsuperscript{64} studied the characteristics of several kinds of ionic fluorescence from yttrium in the ICP and vertical distribution of atomic and ionic fluorescence for calcium and yttrium along the central axis of the plasma using a N\textsubscript{2}-pumped dye laser. They also studied the detection limits for a number of elements in fluorescence and compared directly with those from emission. They found the
detection limits to be inferior to those from emission. In a subsequent paper, they reported time resolved fluorescence measurement in ICP with a N₂-pumped dye laser to evaluate the lifetimes of an excited atomic and ionic level. This parameter in turn allows calculation of the overall quantum efficiency of the excited level. They showed that in most cases, the overall quantum efficiency, given by the ratio between the measured lifetime and the calculated radiative lifetimes, ranges between 0.7 to 1.0 for the sodium lines.

From these early disappointing results, it was concluded that, in practice, the technique of laser induced atomic fluorescence does not represent as significant an improvement over the other analytical techniques as was theoretically predicted and emphasized in the literature. However, it gained firm reputation as one of the most attractive tools for diagnostic studies.

Omenetto and coworkers evaluated the analytical characteristic of excimer (XeCl) pumped pulsed laser as an excitation source in ICP-AFS and have shown that a laser source and an ICP for fluorescence can yield very low detection limits. This demonstrates that laser excited atomic fluorescence spectrometry (LEAFS) in argon ICP is an extremely powerful analytical technique. Shortly afterwards, Huang et al. using a similar type of laser as an excitation source for ICP-AFS reported detection limits for a number of elements including refractory elements that were superior to those obtained by flame atomic absorption spectrometry and similar to those obtained by ICP-AES.

Tremblay et al. have used laser excited ionic fluorescence (LEIFS) in an ICP in order to minimize the spectral interference from the other rare earth elements in the mixture. As a result of narrow spectral band-width dye laser excitation excellent freedom of spectral freedom were achieved. They explored the usefulness of adding a second laser to the experimental system in order to further improve the selectivity of the technique and detection limits.

The author believes that the use of lasers minimizes some of the severe interference problems which occur in ICP-AES. However, the relatively high cost of the laser excitation system and the restriction of the technique to single-element detection
system will surely limit the use of lasers in ICP-AFS systems to special situations where other excitation sources in ICP-AFS systems are lacking in some figures of merit.

1.6.3 ICP excited flame/ICP AFS Systems

The spectral characteristics of the emission from the ICP source, such as high intensity, excellent short term stability, narrow line-width, and freedom from self-reversal, make it an ideal radiation source for the excitation of atomic fluorescence in flames.

Winefordner and coworkers\textsuperscript{48-50} investigated the performance of ICP as an excitation source for flame atomic fluorescence spectrometry and examined ICP emission profiles by using the resonance monochromator method. In this method, a low concentration of analyte is aspirated into the atom cell (in this case flame) and increasing concentrations of the analyte are aspirated into the ICP excitation source, allowing limiting characteristics of the ICP emission profiles to be inferred.

The use of two plasmas, one as a source of excitation and the other as an atom cell in the instrument, was first postulated for atomic absorption spectrometry by Greenfield and coworkers\textsuperscript{74} in 1968. Using his own idea, Greenfield\textsuperscript{75} assembled an AFS system in 1981. He used a high powered ICP as an excitation source, induced in a Greenfield torch and a low powered ICP as an atom cell, induced in a Baird torch.

Winefordner’s group\textsuperscript{76} at the Florida University, U.S.A., also assembled a similar type of AFS system using two low powered ICPs. Preliminary results reported by Winefordner and coworkers, were disappointing. But later,\textsuperscript{77} they obtained low detection limits for a number of elements, by modifying the optical system and the use of radiofrequency filters in their ICP-ICP-AFS system. In their AFS system they operated the source ICP induced in a conventional Fassel/Scott type torch, at 2 kW power and aspirating 20 g l\textsuperscript{-1} solutions. The atomiser ICP was induced in an extended sleeve torch (Baird), operated from 500-700 W power for all elements except refractory elements. For refractory elements they used 1.0 kW power in the atomiser plasma.

In a subsequent publication,\textsuperscript{78} the Winefordner group reported further work on the ICP-ICP-AFS system. They evaluated detection limits for a number of elements particularly for refractory elements and reported detection limits for most of the
elements similar to those obtained by ICP-AES and HCL-ICP-AFS systems. They reported linear dynamic ranges up to $5 \times 10^7$. They also studied the plasma emission background and spectral interference effects and found these effects minimal compared to ICP-AES. This they attributed to the spectral selectivity of the fluorescence technique. An important feature of this experimental set-up (dual ICP-AFS system), is the analysis of high concentration solutions without unnecessary dilutions by using the atomiser plasma as a resonance monochromator.

Greenfield and Thomsen\textsuperscript{79} evaluated the performance of their ICP-ICP-AFS system and reported detection limits for a number of elements. They obtained detection limits both in fluorescence and emission modes and compared them directly. They found the detection limits for non-refractory elements to be better in fluorescence mode than the emission mode while, for refractory elements the converse was true. In a subsequent publication,\textsuperscript{80} they introduced carbon-containing species like methane, propane, ethanol, etc. into the atomiser plasma for the determination of refractory elements and reported detection limit for tungsten a factor of two better by using ethanolic solution instead of adding hydrocarbon gases. Greenfield et al.\textsuperscript{81} also studied atomic fluorescence transitions of lead in detail and investigated interelement effects. They found the resonance lines of lead to be free from any interference from iron and chromium. Later,\textsuperscript{82} in an another paper they reported a study on interference effects of phosphate, aluminium, sodium, and potassium on the atomic fluorescence signal of calcium atomic and ionic lines. They observed interference effects which they attributed to refractory compound formation, ionisation suppression and fluorescence quenching. However, they suggested that these effects could be minimised by re-optimisation of the plasma operating conditions.

From the point of view of analytical spectroscopist, one would think of working with two plasmas in the same instrument would take longer time to optimise the operating conditions for sample analysis, compared to an ICP-AES instrument. But, with the ASIA system it is has been shown that using an alternating variable search a similar period of time is required for optimising the operating parameters as utilized by any ICP-AES system.\textsuperscript{83,84}
Studies on the improvements in the ASIA system are continuing and appear regularly in the literature, as will be described in this thesis in the following chapters.

This survey of the history of ICP-AFS shows the pace with which AFS instrumentation has developed in the last fifteen years. The development of an excitation source (ICP and lasers), a more efficient atom source (ICP) and non-dispersive system can successfully be joined to provide a fairly compact fluorescence instrument with adequate sensitivity, precision and accuracy for a large number of analytical problems.

1.7 Analytical Figures of Merit of ICP-AFS

1.7.1 Detection limits

In analytical determination the total intensity measured consists of intensity from the analyte atoms plus the intensity originating from other sources in the plasma. To obtain a net response from the analyte atoms alone, it is necessary to estimate the background response and subtract its value from the total. At the concentration level when analyte atoms are very low, and similar in magnitude to the uncertainty in the background signal, the presence of analyte atoms cannot be definitely established. Nevertheless, a decision can be made by using the criterion agreed upon by the IUPAC.

The detection limit is defined by IUPAC as the concentration that produces a net signal intensity equivalent to three times the standard deviation of the background signal. The number of measurements that have been recommended are at least twenty and are considered sufficient for attaining reasonable accuracy. Several researchers have also recommended at least twenty measurements. Boumans calculates that ten times the standard deviation of the background must be used if the precision is fixed at ten percent, and a factor of twenty times the standard deviation of the background if the precision is fixed at five percent.

It is clear from the definition of detection limit that detection limit of an analyte can be lowered either by increasing the sensitivity of the analyte or by reduction of background. The sensitivity can only be increased by increasing the rate at which...
analyte is injected into the plasma. This can be effected by a variety of methods such as using a more efficient nebuliser or utilizing the existing nebuliser more effectively, nebulizing a preconcentrated solution, and injecting hydrides or other volatile species.

The detection limit is often quoted as a measure for the comparison of methods and instruments and, as a result, some importance is attached to this quantity. However, it is of little value when trace concentrations of analyte are determined in real samples, as these are unrealistically low for practical analysis. In ICP-AES, the practical determination is normally taken as being at least five times higher than the detection limit, and many analysts have used a factor of ten. Greenfield\textsuperscript{96} suggested that detection limit should be measured in real samples or in matrices such as 10\% sodium chloride, 10\% calcium carbonate, rather than determined in pure aqueous solutions. In this way he believes that an account of nebulisation interferences, ionization interferences, and problems of stray light and possible spectral interference can result in considerably higher detection limits. Boumans\textsuperscript{95} has suggested that in ICP-AES it is necessary to determine detection limits for each spectral line.

1.7.2 Numerical values of detection limits

The detection limits for easily ionisable and easily dissociated elements obtained using ICP-AFS, are comparable to or better than those for ICP-AES. For the refractory elements, detection limits are worse than those for ICP-AES because the atomisation efficiencies in a plasma generated in an extended torch are poor, and also, atomic lines, rather than ionic lines, are used. Several reports\textsuperscript{23,49,78,81} have given tables of detection limits achieved using the atomic fluorescence technique. Recently,\textsuperscript{97} a comprehensive collection of atomic fluorescence detection limits has been reported covering detection limits obtained from different experimental configurations. In Table 1.1 the best atomic fluorescence detection limits of representative elements are presented which have been obtained using ICP as a source of excitation or atomisation, or both.
Table 1.1 Limits of detection for various ICP-AFS systems.

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<td>NS</td>
<td>ICP</td>
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<td>100</td>
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<td>232.0</td>
<td>232.0</td>
<td>S/Air/Ac</td>
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<tr>
<td>Ni</td>
<td>NS</td>
<td>NS</td>
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<td>HCL</td>
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<tr>
<td>K</td>
<td>766.5</td>
<td>766.5</td>
<td>ICP</td>
<td>HCL</td>
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<td>ICP</td>
<td>ICP</td>
<td>100</td>
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<td>Si</td>
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<td>NS</td>
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<td>NS</td>
<td>ICP</td>
<td>HCL</td>
<td>0.2 *</td>
</tr>
<tr>
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<td>NS</td>
<td>ICP</td>
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<td>0.1</td>
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<td>S/Air/Ac</td>
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continued
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<tr>
<th>Element</th>
<th>wavelength</th>
<th>Atom cell</th>
<th>Exc. Source</th>
<th>DL, ng/ml</th>
<th>Ref.</th>
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<tr>
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<td>NS</td>
<td>ICP</td>
<td>HCL</td>
<td>35 *</td>
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<tr>
<td>Sn</td>
<td>300.9</td>
<td>317.5</td>
<td>ICP</td>
<td>PDL</td>
<td>3</td>
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<tr>
<td>Ti</td>
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<td>316.3</td>
<td>ICP</td>
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<td>1</td>
</tr>
<tr>
<td>Ti</td>
<td>NS</td>
<td>NS</td>
<td>ICP</td>
<td>HCL</td>
<td>30 *</td>
</tr>
<tr>
<td>W</td>
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<td>ICP</td>
<td>ICP</td>
<td>200 *</td>
</tr>
<tr>
<td>W</td>
<td>307.8</td>
<td>311.3</td>
<td>ICP</td>
<td>ICP</td>
<td>900</td>
</tr>
<tr>
<td>V</td>
<td>609.0</td>
<td>609.0</td>
<td>ICP</td>
<td>CWDL</td>
<td>5000</td>
</tr>
<tr>
<td>V</td>
<td>NS</td>
<td>NS</td>
<td>ICP</td>
<td>HCL</td>
<td>25 *</td>
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<tr>
<td>V</td>
<td>309.3</td>
<td>309.3</td>
<td>ICP</td>
<td>ICP</td>
<td>40</td>
</tr>
<tr>
<td>Zn</td>
<td>NS</td>
<td>NS</td>
<td>ICP</td>
<td>HCL</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>213.9</td>
<td>ICP</td>
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<td>2</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>213.9</td>
<td>N-S/Air/Ac</td>
<td>ICP</td>
<td>0.5</td>
</tr>
<tr>
<td>Zr</td>
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<td>256.9</td>
<td>ICP</td>
<td>PDL</td>
<td>3</td>
</tr>
<tr>
<td>Zr</td>
<td>310.7</td>
<td>256.9</td>
<td>ICP</td>
<td>HCL</td>
<td>3</td>
</tr>
<tr>
<td>Zr</td>
<td>339.2</td>
<td>339.2</td>
<td>ICP</td>
<td>ICP</td>
<td>10</td>
</tr>
</tbody>
</table>

Exc. - Excitation wavelength, nm; Fluo. - Fluorescence wavelength, nm
NS - not specified; * - Ultrasonic nebulisation and/or desolvation.
Atom cell: Flames are specified as; sheath gas/oxidant/fuel
Ac - acetylene; S - separated flame; N - nitrogen; DL - detection limit; ICP - inductively coupled plasma; PDL - pulsed dye laser; HCL - hollow cathode lamp; CWDL - continuous wave dye laser; HgDI - mercury discharge lamp.

1.7.3 Spectral Selectivity

The virtual absence of spectral interference in atomic fluorescence spectrometry is a well known fact to analytical spectroscopists. The utilization of ICP atom cell in AFS results in remarkable freedom from chemical interference due to the efficient atomizing and ionizing capabilities of the ICP for virtually all elements.
Possible interference effects in ICP based AFS systems are discussed in Chapter 7 on interference studies. In general, vaporization-atomization interferences are minimal in ICP atom cells, compared to flames.

1.7.4 Linearity of Calibration Curves

The calibration curves of analyte concentration versus signal intensity are linear in

<table>
<thead>
<tr>
<th>Element</th>
<th>System</th>
<th>Linear dynamic range / linearity of the curve</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>PDL-ICP-AFS</td>
<td>&gt;10[^5] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>Au</td>
<td>PDL-ICP-AFS</td>
<td>&gt;10[^5] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>Ba</td>
<td>ICP-ICP-AFS</td>
<td>* 5000 μg ml[^-1]</td>
<td>78</td>
</tr>
<tr>
<td>Ca</td>
<td>HCL-ICP-AFS</td>
<td>5 x 10[^5] orders of magnitude</td>
<td>23</td>
</tr>
<tr>
<td>Cu</td>
<td>ICP-ICP-AFS</td>
<td>1000 g ml (* 3000)</td>
<td>78</td>
</tr>
<tr>
<td>Ca</td>
<td>ICP-ICP-AFS</td>
<td>* 3000 μg ml[^-1]</td>
<td>78</td>
</tr>
<tr>
<td>Cr</td>
<td>ICP-ICP-AFS</td>
<td>* 5000 μg ml[^-1]</td>
<td>78</td>
</tr>
<tr>
<td>Fe</td>
<td>ICP-ICP-AFS</td>
<td>100 μg ml[^-1]</td>
<td>56</td>
</tr>
<tr>
<td>Ir</td>
<td>PDL-ICP-AFS</td>
<td>up to 1000 μg ml[^-1]</td>
<td>70</td>
</tr>
<tr>
<td>Hf</td>
<td>PDL-ICP-AFS</td>
<td>10[^6] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>K</td>
<td>HCL-ICP-AFS</td>
<td>about 75 μg ml[^-1]</td>
<td>56</td>
</tr>
<tr>
<td>Mg</td>
<td>HCL-ICP-AFS</td>
<td>1 x 10[^5] orders of magnitude</td>
<td>23</td>
</tr>
<tr>
<td>Mg</td>
<td>ICP-ICP-AFS</td>
<td>* 10,000 μg ml[^-1]</td>
<td>78</td>
</tr>
<tr>
<td>Mn</td>
<td>ICP-ICP-AFS</td>
<td>6 x 10[^5] orders of magnitude</td>
<td>23</td>
</tr>
<tr>
<td>Mo</td>
<td>PDL-ICP-AFS</td>
<td>10[^6] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>Na</td>
<td>HCL-ICP-AFS</td>
<td>2.5 x 10[^6] orders of magnitude</td>
<td>23</td>
</tr>
<tr>
<td>Na</td>
<td>ICP-ICP-AFS</td>
<td>* 2000 μg ml[^-1]</td>
<td>78</td>
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<tr>
<td>Ni</td>
<td>HCL-ICP-AFS</td>
<td>8 x 10[^4] orders of magnitude</td>
<td>23</td>
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<td>Nb</td>
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<td>70</td>
</tr>
<tr>
<td>Pb</td>
<td>ICP-ICP-AFS</td>
<td>over 3000 μg ml[^-1]</td>
<td>81</td>
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<tr>
<td>Pd</td>
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<td>70</td>
</tr>
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<td>Pt</td>
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<td>&gt;10[^6] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>Ru</td>
<td>PDL-ICP-AFS</td>
<td>10[^6] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>Ta</td>
<td>PDL-ICP-AFS</td>
<td>10[^6] orders of magnitude</td>
<td>70</td>
</tr>
<tr>
<td>Zn</td>
<td>HCL-ICP-AFS</td>
<td>5 x 10[^4] orders of magnitude</td>
<td>23</td>
</tr>
<tr>
<td>Zn</td>
<td>ICP-ICP-AFS</td>
<td>slightly less than 10[^5]</td>
<td>49</td>
</tr>
<tr>
<td>Zn</td>
<td>ICP-ICP-AFS</td>
<td>* 5000 μg ml[^-1]</td>
<td>78</td>
</tr>
<tr>
<td>Zr</td>
<td>PDL-ICP-AFS</td>
<td>&gt;10[^5] orders of magnitude</td>
<td>70</td>
</tr>
</tbody>
</table>

* determined in the resonance mode of operation.

(See footnotes in Table 1.1.)
atomic fluorescence spectrometry with ICP over concentration ranges spanning four to seven orders of magnitude. This range is comparable with ICP-AES. A list of linear dynamic ranges reported in literature for a number of elements is given in Table 1.2.

1.8 Noise considerations

A fundamental knowledge of the noise characteristics of an ICP based instrument is important as it affects the instrument performance. A tutorial review and discussion of the noise and signal to noise ratio in analytical spectroscopy has been given by Alkemade et al.105

Walden et al.106 in their study on different types of noises experienced in ICP, have reported three major types of noise:

White noise
Low frequency noise
High frequency proportional noise

White noise is a type of noise that has a constant amplitude at all frequencies and as such forms the baseline for measurements of other noise components above this level. This type of noise is due to random variations in the analytical system.

Low frequency noise is usually referred to as 1/f noise. The frequency below which 1/f noise becomes important depends on the noise source and the signal level and can vary from less than 1 Hz to frequencies over 1000 Hz. The major source of this noise involves random drift of light sources, analyte production, and detection.

High frequency proportional noise occurs at given frequencies throughout the range of the spectrum. Walden et al.106 observed that this type of noise increased with the concentration of the analyte and r.f power and decreased proportionally with increasing injector gas flow-rate. High frequency proportional noise may be avoided through careful choice of the modulation frequency. This can be easily achieved by trying several modulation frequencies and picking the one giving the best signal to noise ratio.
Montaser and Fassel\textsuperscript{22} in their study using ICP-AFS system suggested that the flicker noise (1/f) effect could be minimised by taking measurements at low r.f power and distance well above the load coil. The baseline shift due to ICP background noise level (a d.c signal) can be reduced or even eliminated by using an a.c coupled detection electronics.\textsuperscript{53}

Snook and coworkers,\textsuperscript{107-110} attempted to reduce noise in the ICP-AES by employing an extended outer tube laminar flow ICP torch (LFT) instead of commonly used tangential flow ICP torch (TFT). They used a series of 21 holes (2 mm diameter) arranged circumferentially around the torch base through which the coolant gas flow was introduced into the outer most tube of the torch. They claimed that the principal source of noise i.e., the random noise in the plasma, was removed by the laminar flow and reported signal to noise ratios at least an order of magnitude higher in the LFT than in the TFT. As a result, they achieved an improvement in detection limits by at least an order of magnitude.

The sensitivity and blank noise level depend on the length of time over which the stabilized signal from the ICP is integrated. The sensitivity is proportional to the integration time, but the standard deviation of the blank noise should vary as the square root of the integration time, given that the noise is random and has a "white" spectrum. Under these conditions detection limits should vary with the square root of the integration time.

When ICP is employed in AFS, radiofrequency can influence the electronic system and may strongly interfere with the operation of the lock-in amplifier, if the entire system is not properly grounded. Montaser and Fassel\textsuperscript{21} employed standard r.f filters on all electronic devices and connected the r.f generator to a r.f ground consisting of a long (3.65 meter) steel pipe inserted in a hole drilled in the laboratory floor. A recent study on reducing r.f interference effect on spectrometer outputs, have been described by Kennedy.\textsuperscript{111} He used an aluminium screen wire frame (floor to ceiling) and placed between the spectrometer and readout system to stop r.f interfering with the equipment electronics. This resulted in effective reduction in r.f effects.
Instrumentation and Preliminary Experiments

2.1 ASIA system.

The instrumentation used in this study has been named "ASIA". As the acronym implies, ASIA is a system consisting of two plasmas, one used as a source plasma to provide the excitation radiation for atomic fluorescence. While, the other plasma is the atomiser plasma and is used to provide atoms/ions of the element of interest. The system can be used in both atomic fluorescence and atomic emission modes. A schematic diagram of the arrangement of experimental components is given in Fig. 2.1. The details of the system are as follows:
Fig. 2.1 Schematic diagram of the experimental arrangement of the ASIA system.
2.1.1. Source Plasma.

The source plasma is powered by a Radyne RD150 high frequency generator with 15 kW nominal output at 7 MHz frequency. The generator is a free running type, having an efficiency of power transfer of about 50%. The source plasma is contained in a large Greenfield torch, a diagrammatic representation of which is given in Chapter 1, Fig. 1.10. The plasma operates on argon gas, with air as a coolant provided by a compressor at a minimum pressure of 20 psi. The torch is positioned centrally in a two and a half turn water-cooled copper coil, in such a way that the plasma (inner) tube is positioned 1/8th inch below the lowest turn of the coil.

2.1.2. Atomiser Plasma.

The atomiser plasma is powered by a Radyne SC15 high frequency generator with 2.5 kW output at 36 MHz frequency. This generator is also a free running type, having an efficiency of power transfer of about 50%. The atomiser plasma is contained in a long-sleeve (Baird) torch, a diagrammatic representation of which is given in Chapter 1, Fig. 1.13. The torch is positioned centrally in a one and a half turn water-cooled copper coil. The plasma operates at low power, typically 350-750 W and uses argon gas as coolant and injector gas. The plasma gas was not used because it was not necessary for the operation of plasma.

Both the torches were mounted on separate racking assemblies which allowed the movement of the torches independently of each other along a perpendicular axis, colinear with the optical axis. The racking assemblies along with the load coil and the torches were housed in separate aluminium boxes in order to prevent high frequency radiation from interfering with the nearby electronics and to reduce the stray light entering the monochromator. Also, the aluminium boxes were blackened internally to reduce radiation scatter. Each box was provided with holes at appropriate locations to allow the exit for the gases to the extraction system, to allow the source plasma radiation to excite atomic fluorescence from the atoms in the atomiser plasma and to permit the escape of the fluorescence radiation to the monochromator.
For the emission studies the source plasma was turned off, the long sleeve (Baird) torch was replaced by a conventional Fassel torch and the sample introduction system was changed as described in Section 2.1.3.

2.1.3. Sample introduction system.

The sample introduction systems with the ASIA system in both the fluorescence and the emission modes are described below separately.

2.1.3.1. Atomic Fluorescence study.

The sample delivery system for the source plasma consisted of a single channel peristaltic pump (Ismatec), de Galan nebuliser and a cyclone spray chamber. High concentration solutions upto 50% were pumped into the de Galan nebuliser. The de Galan nebuliser consisted of a teflon rod, with a V-groove cut across it’s diameter. At
the top of the groove appeared a capillary hole through which the solution flows and in the middle of the groove, from another capillary hole, issued argon gas to disrupt the solution flow causing the nebulisation process and the formation of an aerosol. The aerosol entered the conical spray chamber which was fabricated from a 500 ml conical flask. The conical spray chamber had an aerosol outlet at the top and an outlet for the large droplets at the bottom which were pumped back into the solution container (see Fig. 2.2).

Fig. 2.3 Sample introduction system for the atomiser plasma.

The sample delivery system for the atomiser plasma incorporated a peristaltic (8 channel Gilson Minipuls II) pump set and a GMK nebuliser and spray chamber. The sample solution was pumped into the GMK nebuliser. The nebuliser is illustrated in Fig. 2.3. It is a modern Babington-type nebuliser, in which the solution trickles along a "V"-shaped groove. A gas jet in the middle of the groove disrupts the flow of the solution and causes nebulisation. The spray impinges on an impact bead to form a fine
aerosol. The spray chamber had an outlet at the top for the aerosol exit into the plasma and another outlet at the bottom to drain the large droplets into a drain collecting reservoir.

2.1.3.2. Atomic Emission study.

The sample introduction system for the plasma formed in the Fassel torch consisted of a Meinhard nebuliser and a double pass (Scott type) spray chamber. The sample solution was pumped into the Meinhard nebuliser by a peristaltic pump or fed pneumatically. The Meinhard nebuliser is a concentric design as shown in Fig. 2.4, in which the reduced pressure resulting from a fast-moving gas jet causes solution to be
drawn into the gas jet and to be broken into droplets of various sizes. The aerosol entered into a double pass spray chamber having two outlets one for the aerosol exit to the ICP torch and the other a drain for the large particles (see Fig. 2.4).

2.1.4. Optical System.

The optical arrangement of the ASIA system is shown in Fig. 2.5. Radiation from the source plasma was collected by a spherical fused quartz double convex lens, 5.08 cm in diameter and focussed on the aperture of the chopper blade forming a 1:1 image of the tail-flame of the plasma. The image formed at the chopper blade was then focussed by a second lens similar to the first one, on the tail flame of the atomiser plasma and reduced five times. This second image had a breadth 3 mm and height 10 mm forming the atom cell in the plasma. The fluorescence radiation from the atom cell was then collected at a 90° angle by two similar lenses as before and a 1:1 image of the cell was focussed onto the entrance slits of the monochromator.

For the operation of the ASIA system in the emission mode the optical arrangements remained unchanged except the chopper position, because a single plasma (Radyne SC15) was used. The chopper was positioned centrally between the lenses L3 and L4 in a way that a 1:1 image of the plasma tail-flame was formed on the aperture of the chopper blade (see Fig. 2.5). All the four lenses and the chopper were mounted on an optical rail and aligned with the optical axis using a He/Ne laser.

2.1.5. Monochromator.

The monochromator used in the ASIA system included an entrance and an exit slit, a focussing mirror, lenses and a diffraction grating. It was an Optica, CF4 monochromator with a single channel detection system and a focal length of 0.75 m having an aperture ratio of f/14. It consisted of Czerny-Turner mount optical arrangement incorporating a 600 lines/mm diffraction grating, blazed at 300 nm giving a reciprocal linear dispersion of 1.6 nm/mm. The slit-width could be varied within the range 20 micrometer to 3.6 mm, giving maximum spectral bandpass of 5.76 nm.
L1, L2, L3 and L4: fused silica lenses, \( f = 5.08 \text{cm} \) and \( d = 5.08 \text{cm} \).

C1 and C2: chopper positions in fluorescence and emission, respectively.

\[
\begin{align*}
u1 &= 2f = 10.16 \text{cm}, & u2 &= 30.48 \text{cm}, & v2 &= 6.1 \text{cm}, & u3 &= v3 = 2f = 10.16 \text{cm} \\
u4 &= v4 = 2f = 10.16 \text{cm}
\end{align*}
\]

Fig. 2.5 Optical design of the ASIA system.
2.1.6 Detector.

The detector used in the system was a bi-alkali photomultiplier tube (EMI 9789QB) covering a wide spectral range between 200 nm to 650 nm, giving maximum sensitivity around 400 nm wavelength (see Fig. 2.6). It was a 13 stage tube with a quartz window. A maximum gain rating of $10^8$ could be achieved from the tube. The photomultiplier tube was kept ON continuously during the study in order to stabilise the dark current. The high voltage to the photomultiplier was supplied by a power supply (Applied Photo Physics Ltd.).

![Graph showing radiant energy spectral coverage of PMT (9789 QB).]
2.1.7 Light Chopper

The light chopper was an EG & G, Brookdeal Model 9479 consisting of a chopper with 30 blades, capable of chopping at frequencies between 5 Hz to 1000 Hz, in steps of 1 Hz each. A chopping frequency of 997 Hz was used throughout the study.

2.1.8 Signal Processing system.

The signal processing system included current amplifier, Lock-in Amplifier, a computer, a printer and a chart recorder. The current amplifier, Brookdeal Model 5002, is a current sensitive amplifier and is incorporated in a single unit with the Lock-in Amplifier Brookdeal Model 9503. The current amplifier receives the signal from the photomultiplier and amplifies the signal before sending it to the Lock-in Amplifier. The Lock-in Amplifier also receives the reference signal from the light chopper and demodulates the amplified signal from the current amplifier before sending it to the computer.

The computer system consisted of an Apple Ile 128 K RAM with a dual drive, a monochrome monitor and a canon PW 1080A 9 pin dot matrix printer. The computer was interfaced to the amplifier and a computer program written by Thomsen and modified by Malcolm was used to integrate the signal received, displaying the signal intensities in millivolt (mV) units on the monitor screen and the printer simultaneously. A chart recorder (Brain Gould BS-271) was used to record fluorescence and emission spectra when required.

2.2 Operating Procedure.

The procedure adopted for the operation of the ASIA system is described as follows:

**Atomiser plasma initiation**

1: Turn ON the power supply to the SC15 H.F. generator, cooling water and the argon gas supplies.
2: Release the argon gas flows into the torch (injector and the coolant flows) for about two minutes
3: Turn the wheel of the generator fully anti-clockwise and press the red
button on the front panel to turn ON the r.f.
4: Release the coolant flow-meter tap to give an argon flow of 11 l min⁻¹ and now press the tesla coil button.
5: As soon as the plasma is formed turn down the radio-frequency power to 500 watts and release the injector gas flow into the torch.

**Source plasma initiation**

1: Turn ON the power supply to the RD150 H.F generator, cooling water, argon gases and the air compressor for coolant flow.
2: Release the argon gas flows into the torch (injector and the coolant flows) for about two minutes.
3: Switch ON the tesla coil and release the plasma flow-meter tap to give an argon flow of 12 l min⁻¹.
4: Press the r.f ON button and slowly increase the power by turning the power knob clockwise until 4.5 kW, then press the tesla coil button.
5: As soon as the plasma is formed increase the plasma gas flow to at least 20 l min⁻¹ and release the coolant and the injector gas flows. To put off the plasmas simply press the STOP buttons of the respective generators and turn off the gases and cooling water flows after approximately five minutes.

For the emission studies follow the same procedure as described for atomiser plasma initiation and release plasma gas flow of about 2.0 l min⁻¹ after the plasma is formed.

**Operation of the electronics**

1: Turn ON the chopper, Lock-in Amplifier, and load the computer program.
2: Open the monochromator slits to the required width.
3: Adjust the sensitivity controls on the current amplifier to obtain one third full scale output on the display meter with the reference controls set to 0 or 90 on the Lock-in Amplifier.
4: Adjust the OFFSET control as necessary. Now use the reference controls to obtain a zero output on the display meter and switch in 90 or -90 to give
2.3 Preliminary Experiments.

Preliminary experiments were performed to get familiarised with the use of the system. Nickel was chosen as the element to be studied.

2.3.1 Optimisation procedure.

The experimental variables optimised for the nickel element included the spectrometer slit-width, gas flow rates for both the plasmas and solution flow rates for the atomiser plasma. The technique used for the optimisation was an alternating variable search in which a cyclic univariate search was carried out. This method has been found to be much quicker than the simplex method of optimisation with this system. In this method each variable was changed in steps keeping the other variables fixed until a maximum signal for that variable was obtained. This procedure was repeated with each variable until no increase in signal intensity was noted. Three cycles were needed to obtain the optimum conditions.

2.3.2 Detection limit.

The detection limit for an element is calculated by the following equation:

\[
\text{Detection limit} = \frac{C \times (3 \times SD)}{S - B}
\]

where \( C \) is the concentration of the standard solution used; \( SD \) is the standard deviation of the blank solution (de-ionized water); \( S \) is the signal intensity of the standard solution used; and \( B \) is the signal intensity of the blank solution. An integration time of 10 seconds was used for each measurement.

2.4. Results and Discussion

To obtain analytical data for nickel by the ASIA system, a variety of parameters, such as the viewing height above the coil of the plasmas, the injector gas flow-rate, the
plasma gas flow-rate (for source plasma only), coolant gas flowrate (for atomiser plasma only), the r.f power in the plasmas, and the solution flow-rate into the atomiser plasma, were optimised.

It has been shown with this system before, that maximum fluorescence signal was obtained with a negligible increase in background noise when a maximum slit-width of 3.6 mm (5.76 nm band-width) was used for atomic fluorescence measurements of a number of elements, including nickel. This is due to the fact that a higher band-width allows an increase of fluorescence flux because of the contribution from neighbouring lines. Therefore, the maximum slit-width was used for these measurements.

![Graph showing fluorescence intensity vs. flowrate](image)

*Fig. 2.7 Atomic fluorescence signal intensity of nickel as a function of injector gas flow-rate in the atomiser plasma, at $\lambda 231.1-232.5$ nm wavelength. (Note: * - amplifier output): All other operating parameters used were the optimal.*
2.4.1 Atomiser plasma parameters

2.4.1.1 Influence of the injector gas flow-rate on the atomic fluorescence signal intensity

The effect of injector gas flow-rate on the atomic fluorescence signal of nickel is shown in Fig. 2.7. It can be seen that the signal intensity increases with the gas flow-rate up to \(2.8 \cdot 1 \text{ min}^{-1}\) after which a drop in the signal intensity was noted. As a result, injector gas flow-rate of \(2.8 \cdot 1 \text{ min}^{-1}\) was chosen as the optimal.

![Graph showing the relationship between flowrate and fluorescence intensity](image)

*Fig. 2.8 Atomic fluorescence signal intensity of nickel as a function of coolant gas flow-rate in the atomiser plasma, at \( \lambda = 231.1 \text{-} 232.5 \text{ nm wavelength}\). (See footnote in Fig. 2.7). Note: All other operating parameters used were the optimal.*
2.4.1.2 Influence of the coolant gas flow-rate on the atomic fluorescence signal intensity.

The variation of the atomic fluorescence signal as a function of the coolant gas flow-rate is shown in Fig. 2.8. The fluorescence signal intensity increased as the flow-rate was increased up to 12.0 l min\(^{-1}\) after which a drop in the signal was observed, presumably due to the dilution of the atomic vapour in the atom cell.

2.4.1.3 Influence of viewing height above the coil on the fluorescence signal intensity

The effect of the viewing height above the coil on the atomic fluorescence signal of nickel is shown in Fig. 2.9. The fluorescence signal intensity increased as the viewing height above the coil was increased from 8 cm to 10 cm, after which a drop in the signal was observed.

**Figure 2.9** Atomic fluorescence signal intensity of nickel as a function of viewing height above the coil of the atomiser plasma, at \(\lambda 231.1-232.5 \text{ nm wavelength. (See footnote in Fig. 2.7)}\). Note: All other operating parameters used were the optimal.
nickel is shown in Fig. 2.9. It was noticed that the maximum signal intensity was obtained at a height of 10.3 cm above the coil, below which a very sharp decrease in signal intensity was noted. This could possibly be due to a decrease in atom population because of increased temperature. The small decrease in the atomic fluorescence signal intensity above 10.3 cm height in the plasma probably results from the diffusion of atoms out of the irradiated volume in the plasma tail-flame or increased fluorescence quenching.

Fig. 2.10 Atomic fluorescence signal intensity of nickel as a function of power in the atomiser plasma, at 223.1-232.5 nm wavelength. (See footnote in Fig. 2.7). Note: All other operating parameters used were the optimal.
2.4.1.4 Influence of r.f. power in the plasma on the atomic fluorescence signal intensity.

The nickel atomic fluorescence-r.f. power in the atomiser plasma profile is shown in Fig. 2.10. It can be seen that increasing the power above 0.52 kW showed a decrease in the fluorescence signal intensity, probably due to a shift of the equilibrium between atoms and ions towards ions, thus causing a decrease in the atom population in the atom cell.

2.4.1.5 Influence of solution flow-rate into the plasma

The effect of the solution flow-rate on the atomic fluorescence signal intensity of nickel

![Graph showing the relationship between flow rate and nickel fluorescence intensity.](image-url)
is shown in Fig. 2.11. It was noticed that the signal intensity increased with the increase of solution flow-rate up to 4 ml min\(^{-1}\) after which a small drop in the signal intensity was noted. This is probably due to an increase in large droplet formation. These droplets eventually end up in the drain.

2.4.2 Source plasma parameters

2.4.2.1 Influence of injector gas flow-rate on the atomic fluorescence signal intensity

Figure 2.12 shows the behaviour of the fluorescence signal intensity of nickel as a function of injector gas flow-rate in the source plasma, at 231.1-232.5 nm wavelength. (See footnote in Fig. 2.7). Note: All other operating parameters used were the optimal.
function of injector gas flow-rate. It can be seen that the signal intensity increases rapidly as the gas flow-rate is increased up to 3.0 \text{ l min}^{-1} and then a drop is noticed on further increase in gas flow-rate. Therefore, injector gas flow-rate of 3.0 \text{ l min}^{-1} was chosen as the optimal.

2.4.2.2 Influence of plasma gas flow-rate on the atomic fluorescence signal intensity

The effect of plasma gas flow-rate on the atomic fluorescence signal intensity is shown in Fig. 2.13. It was noticed that plasma gas flow-rate up to 26 \text{ l min}^{-1} showed rapid increase in signal intensity and above which the increase in signal intensity was not very significant. However, a flow-rate of 30 \text{ l min}^{-1} was chosen as the optimal.

![Graph showing atomic fluorescence signal intensity vs. flowrate](image-url)

**Fig. 2.13** Atomic fluorescence signal intensity of nickel as a function of gas flow-rate in the source plasma, at \lambda 231.1-232.5 \text{ nm wavelength. (See footnote in Fig. 2.7). Note: All other operating parameters used were the optimal.)
2.4.2.3 Influence of viewing height above the coil on the atomic fluorescence signal intensity

Figure 2.14 shows the influence of viewing height in the plasma on the atomic fluorescence signal intensity of nickel. It can be seen that a significant decrease in signal intensity is noticed above 2 cm viewing height above the coil in the plasma, presumably due to the diffusion of atoms/ions in the plasma tail-flame.

Fig. 2.14 Atomic fluorescence intensity of nickel as a function of viewing height above the coil of the source plasma, at Σ231.1-232.5 nm wavelength. (See footnote in Fig. 2.7). Note: All other operating parameters used were the optimal.
2.4.2.4 Influence of r.f. power in the plasma on the atomic fluorescence signal intensity

The variation in atomic fluorescence signal as a function of power in the source plasma is shown in Fig. 2.15. The atomic fluorescence signal intensity increased linearly as the power was increased up to 6.5 kW, after which the increase in signal intensity was not linear.

![Graph showing the relationship between power and fluorescence intensity for nickel.](image)

Fig. 2.15 Atomic fluorescence signal intensity of nickel as a function of power in the source plasma, at Σ231.1-232.5 nm wavelength. (See footnote in Fig. 2.7). Note: All other operating parameters used were the optimal.

2.4.2.5 Excitation curve of growth for nickel

The concentration of nickel to be used for introduction into the source plasma was optimised. An excitation curve of growth was constructed by aspirating increasingly concentrated solutions of nickel into the source plasma while aspirating a fixed
concentration of nickel solution into the source plasma (See in Fig. 2.16). It was observed that the fluorescence signal intensity increased linearly as the concentration of nickel was increased until 20% concentration, after which the increase in signal intensity was not linear probably due to self-absorption occurring in the source plasma.

![Excitation curve of growth for nickel.](Fig. 2.16)

**2.4.3 Analytical performance**

The performance of the instrument was studied by the construction of a calibration curve and the measurement of detection limit for nickel. The calibration curve was constructed by aspirating increasing concentrations of nickel solutions into the atomiser plasma while aspirating 20% nickel solution into the source plasma at the optimum
Chapter 2

Fig. 2.17 Calibration curve for nickel at 231.1-232.5 nm wavelength while aspirating 20% nickel solution into the source plasma. (See footnote in Fig. 2.7)

operating conditions for nickel determinations. The calibration curve obtained is shown in Fig. 2.17 and was found to be linear. This was followed by the determination of detection limit for nickel which was found to be 29 ng ml⁻¹.
Chapter 3

A Comparison of Boosted Discharge Hollow-Cathode Lamps and ICP as Excitation Sources in AFS

3.1. Introduction.

In atomic fluorescence spectrometry (AFS) the intensity of the fluorescence signal and, therefore, the sensitivity increases with the source radiance. Consequently, much research has been directed towards developing sources of radiation with a high radiance, good stability and relatively low cost and simplicity in operation. Hollow-cathode lamps (HCLs) are most frequently used source of excitation in AFS. In conventional HCL an efficient use of the discharge is made which localizes within
the cylindrical cavity. This geometry allow relatively small currents to produce significant sputter atomisation of the cathode material, as well as the excitation and ionization of the sputtered atoms in the discharge.

Inductively coupled plasma has been established as an intense source for emission spectrometry. In the search for intense light sources for excitation purposes in atomic fluorescence spectrometry, attention has been drawn towards the ICP. A number of studies have been reported in the literature on the use of ICP as an excitation source and have been discussed in detail in Section 1.6.

A comparison study of a high-powered inductively coupled plasma and BDHCLs as excitation sources was carried out to ascertain whether or not ICP was a better excitation source than recently developed BDHCLs. The performance data obtained from the study is presented here.

3.2. Hollow-cathode lamps as excitation sources: A short review.

Hollow-cathode lamps (HCLs) have a history extending over thirty years, during which time it has become well established as a line source and has offered particular advantages for analytical studies. Hollow-cathode lamps have been employed primarily as a line source for atomic absorption spectrometry (AAS). However, alongside their use in AAS, these have been extensively used for atomic fluorescence spectrometry.60,113-119

Larkins113 tested a large number of HCLs as excitation sources for use in atomic fluorescence using a simple non-dispersive instrument. He found that the detection limits obtained were not very impressive. All the early attempts using standard hollow-cathode lamps as excitation sources in AFS were not completely successful in attaining better detection limits than atomic absorption spectrometry owing to the very low output intensities.

Pulsed excitation techniques in which HCLs are operated in the pulsed mode, have shown to give considerable improvement in signal to noise ratio. In addition to this pulsed technique has shown to exhibit rapid warm up and longer life times. Dawson and Ellis114 have shown that large current pulses when passed through the HCL produces a peak radiance that is up to several hundred times greater than that obtained.
in direct current (dc) mode. The lamps were operated with current pulse of 300-600 mA and a pulse width of only 15-40 μsec. Prugger et al. have applied pulse technique for simultaneous determinations of a number of elements by atomic fluorescence spectrometry. They obtained an increased total flux of lamp radiation by a factor of 20 for the resonance lines of aluminium, barium, and calcium.

Also, pulsed HCLs have been used by Dagnall et al., as line sources in a commercial atomic fluorescence spectrometer for simultaneous multielement analysis and have reported satisfactory performance for most of the elements studied. Recently, Masamba et al., have demonstrated that pulsing technique could be used to achieve ionic line intensities from standard HCLs which could be used to generate ionic fluorescence from the ions in an ICP. However, ionic fluorescence results showed poorer limits of detection, compared to atomic fluorescence owing to insufficient ionic line intensities from the standard hollow-cathode lamps.

Sullivan and Walsh designed a new HCl which used two discharges. In this design one discharge was used to produce atomic vapour by cathode sputtering and a secondary discharge caused increased excitation of the sputtered atomic vapour. The construction of the lamp is shown in Fig. 3.1. Essentially these lamps were designed for use with atomic absorption spectrometry. However, such type of HCLs have been used to excite atomic fluorescence from metal atoms. These high intensity lamps (HIHCLs) have proved to be excellent excitation sources, exhibiting high output intensity and good stability. Later Sullivan designed a new boosted-output spectral lamp with interchangeable cathode that required only a small quantity of pure metal. This new design enabled the lamp to be used with cathodes of relatively volatile elements such as arsenic and selenium, without the element being deposited on the exit window. He investigated the performance of arsenic, selenium, cadmium, lead, and antimony lamps in AFS and reported better detection limits for these elements than those from the earlier design.
Lowe\textsuperscript{118}, also developed a boosted-output hollow-cathode lamp primarily for the use as an excitation source for AFS. It is a modified version of Sullivan-Walsh type of high intensity hollow-cathode lamp. A schematic diagram of the lamp is shown in Fig. 3.2. The performance of these lamps was measured and compared with standard and high intensity lamps. The results indicated that considerably greater intensity resonance line were emitted by the new Lowe design lamps than those of Sullivan and Walsh type high intensity lamps. Larkins\textsuperscript{113} also, carried out a comparison study between standard HCLs, high intensity Sullivan-Walsh type HCLs and high intensity Lowe type HCLs. Detection limits for 24 elements were studied. The high intensity Lowe type HCLs produced better detection limits by a factor of 6 to 400 for most of the elements, than those obtained by standard HCLs.
3.3. Boosted discharge Hollow-cathode lamps (Photron) with an auxiliary discharge.

A schematic diagram of the boosted discharge hollow-cathode lamp (BDHCL) is shown in Fig.3.3. In general, hollow cathode-lamp has a body made of Pyrex and an end window of quartz. The body contains an anode mounted behind a cylindrical cathode. The lamp is evacuated and filled with an ultrapure monoatomic gas (to avoid molecular continuum spectra), usually neon, occasionally argon, to a few torr. In case of Photron BDHCL the lamp is filled with neon gas. In practice a voltage is applied between the anode and cathode and a primary discharge occurs between the electrodes. The filler gas is ionized by the anode forming positive ions and electrons. The positive ions are attracted by the negative cathode and accelerated under the influence of the charge. Upon reaching the cathode they impinge on the metal surface, dislodging or
"sputtering" excited metal atoms into the space inside the cathode. The excited metal atoms emit radiation which is used as a light source. In addition to the normal sputtering discharge, a secondary boost discharge occurs in the photron BDHCLS. The secondary discharge is struck between an efficient electron emitter and the anodes that pass through the primary atom cloud as shown in Fig. 3.3. This discharge ensures that most of the atoms in the cathode region are excited. Therefore, a few ground state atoms are left within the cavity to cause self absorption, allowing operation of BDHCL at higher currents than the normal hollow-cathode lamp resulting in high light output. The use of high efficiency electron emitter permits operation of the secondary discharge at comparatively low voltage so that doppler broadening is minimised.

Fig. 3.3 Schematic diagram of Photron BDHCL.
3.4. Experimental.

3.4.1. Apparatus.

The ASIA system used for this study was the same as described in Chapter 2. A primary current power supply (Varian-Techtron, Australia, Type MLS 1A) was used to provide primary current to the lamps. A boosted lamp power supply (Photron P8000, Photron (PTY) Ltd., Melbourne, Australia, available from Starna Ltd., Chadwell Heath, Essex, U.K.) was used to provide boost current to the lamps. The hollow-cathode lamps used for the experiments were "Super Lamp" boosted-discharge lamps (Photron, Australia).

The lamp position and the optics were aligned with the aid of a He/Ne laser.

A signal generator (Advance H4 audio-generator) was used to provide a square wave modulation of primary current for the lamps. (The optical chopper on the ASIA instrument was not used with the lamps).

A neutral density filter was placed at the entrance slit of the monochromator for some experiments to prevent overloading of the photomultiplier tube.

3.4.2. Chemicals.

All the chemicals used in this work were of analytical reagent grade. Stock solutions (BDH chemicals) containing 1000 \( \mu g \) \( mL^{-1} \) of each element were used. High concentration solutions for the source plasma were prepared from nitrate salts of the respective elements. Dilutions were made in de-ionized water.

3.4.3. Operating conditions.

3.4.3.1. Plasma operating conditions.

All optimisations were carried out using the alternating variable search (AVS) method described in detail in Section 2.3.1. The optimised operating conditions for the atomiser plasma in conjunction with the BDHCL are shown in Table 3.1. The optimised operating conditions for the source and atomiser plasmas are shown in Table 3.3.
Fig. 3.4. Schematic diagram of the experimental arrangement used for measurements.
Table 3.1. Atomiser plasma operating conditions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Height above the coil (mm)</th>
<th>Power (kW)</th>
<th>Coolant gas 1 min⁻¹</th>
<th>Injector gas 1 min⁻¹</th>
<th>Solution ml min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>10.5</td>
<td>0.45</td>
<td>12.0</td>
<td>2.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni</td>
<td>10.3</td>
<td>0.52</td>
<td>12.0</td>
<td>2.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Pb</td>
<td>10.1</td>
<td>0.42</td>
<td>10.1</td>
<td>2.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

3.4.3.2. Lamp operating conditions.

All the lamps were aligned on the optical axis at positions 1 and 2 as shown in Fig. 3.4. Experimental variables for the lamps were optimised for each experiment to give maximum atomic fluorescence signal. The highest signal for each element was obtained, initially, by running the lamps at the maximum operating primary currents recommended by the manufacturer and adjusting the boost current to obtain maximum response. The results obtained are shown in Figs. 3.5, 3.6, and 3.7 for lead, nickel and copper, respectively. The initial operating conditions are shown in Table 3.2.

Table 3.2. Lamp operating conditions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Primary current (mA)</th>
<th>Boost current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>15</td>
<td>37.5</td>
</tr>
<tr>
<td>Ni</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>25</td>
</tr>
</tbody>
</table>

In a another experiment to operate copper lamp at higher currents. The lamp primary current was varied in steps of 5 mA and the boost current optimised for maximum signal, while aspirating 1.0 μg ml⁻¹ copper solution into the atomiser plasma. The results obtained are shown in Fig. 3.8. The maximum spectral band-width of the
monochromator was used as this maximised the radiant flux and also permitted a contribution to the fluorescence signal from other lines in the 5.76 nm effective band-pass.

Table 3.3. ASIA operating Conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Copper atomiser plasma</th>
<th>Copper source plasma</th>
<th>Lead atomiser plasma</th>
<th>Lead source plasma</th>
<th>Nickel atomiser plasma</th>
<th>Nickel source plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height above the coil (cm)</td>
<td>10.5</td>
<td>2.0</td>
<td>10.1</td>
<td>2.3</td>
<td>10.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Power in the plasma (kW)</td>
<td>0.45</td>
<td>7.3</td>
<td>0.42</td>
<td>6.5</td>
<td>0.52</td>
<td>7.3</td>
</tr>
<tr>
<td>Injector gas flow-rate 1 min⁻¹</td>
<td>2.6 Ar</td>
<td>4.0 Ar</td>
<td>2.6 Ar</td>
<td>3.5 Ar</td>
<td>2.8 Ar</td>
<td>3.0 Ar</td>
</tr>
<tr>
<td>Plasma gas flow-rate 1 min⁻¹</td>
<td>-</td>
<td>30 Ar</td>
<td>-</td>
<td>30 Ar</td>
<td>-</td>
<td>30 Ar</td>
</tr>
<tr>
<td>Coolant gas flow-rate 1 min⁻¹</td>
<td>12 Ar</td>
<td>30 Air</td>
<td>10.1 Ar</td>
<td>30 Air</td>
<td>12 Ar</td>
<td>30 Air</td>
</tr>
<tr>
<td>Liquid uptake rate ml min⁻¹</td>
<td>2.0</td>
<td>3.0</td>
<td>2.5</td>
<td>3.0</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Monochromator slit-width, mm</td>
<td></td>
<td>-3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The lead and copper lamps were tested for their intensity and compared with an ordinary HCL. It was noticed that about ten times higher signal was obtained with the BDHCL.

3.4.4. Modus operandi.

It was appreciated from the outset that simply replacing the plasma torch on the high powered generator, used as a source in the ASIA, by a BDHCL (position 1. Fig.3.4.) was unlikely to yield good detection limits for the elements, since the size of the image from the BDHCL would form a very small fluorescence cell in the atomiser plasma. Nevertheless, it was thought best to confirm this prediction.
Having confirmed this belief, the BDHCL was next placed in the position 2 as in Fig.3.4, where the beam from the lamp would just fill the diameter of the atomiser tail-flame and detection limit were determined. Even so, the size of the irradiated area in the atomiser tail-flame was still much smaller than that irradiated when the high powered ICP was used as a source (3 mm diameter circle compared with a 3 x 10 mm rectangle i.e. 7 sq mm versus 30 sq mm). So, an experiment was conducted where a 3 mm aperture was placed to the atomiser tail-flame thus reducing the area irradiated by the source plasma in an attempt to form an estimate of the respective irradiation per unit area.

![Diagram](image)

**Legend**
- **primary current 4mA**
- **primary current 6mA**
- **primary current 8mA**
- **primary current 10mA**

*Fig. 3.5 Effect of boost current on atomic fluorescence signal of lead at different primary currents using lamp in position 2. (See footnote Fig. 2.7).*

-70-
3.4.5. Analytical studies of lead.

3.4.5.1. Lead spectra.

To choose the most sensitive line and to compare the relative intensities of the fluorescence radiation at various wavelength, fluorescence spectra were obtained with both ICP and BDHCL light sources.

In scanning the fluorescence spectrum with ICP light source, a 1.0 μg ml⁻¹ solution of lead was aspirated into the atomiser plasma, while aspirating 20% lead solution into the source plasma. The spectrum obtained is shown in Fig. 3.9. A fluorescence spectrum with BDHCL as light source was obtained, by aspirating 50.0 μg ml⁻¹ solution into the atomiser plasma under optimum conditions, using lamp at position 2 and is shown in Fig. 3.10.

3.4.5.2. Calibration curves.

Separate calibration curves for lead were obtained using lamp at position 1 and 2. Lead solutions ranging from 5.0 to 50.0 μg ml⁻¹ and 5.0 to 100.0 μg ml⁻¹ were sprayed into the atomiser plasma for lamp position 2 and 1, respectively. The results obtained are shown in Fig. 3.11 (A) and (B). Measurements were made at 405 nm wavelength and monochromator slit width of 3.6 mm was used.

3.4.5.3. Detection limit.

With BDHCL as an excitation source detection limits were obtained by aspirating 5.0 μg ml⁻¹ and 50.0 μg ml⁻¹ lead solutions into the atomiser plasma, at lamp position 2 and 1, respectively, at optimum operating conditions. Fluorescence radiation was collected at 405 nm wavelength. At least five, ten second integrations were made for the detection limit determined.
3.4.6. Analytical studies of nickel.

3.4.6.1. Nickel spectra.

To choose the most sensitive fluorescence line and to evaluate the relative intensities of the fluorescence radiation at various wavelengths, fluorescence spectra were obtained using ICP and HCL light sources.

In scanning the fluorescence spectrum with ICP as a light source, 5.0 µg ml⁻¹ nickel solution was aspirated into the atomiser plasma, while aspirating 20% nickel solution into the source plasma under the optimum operating conditions. The spectrum obtained is shown in Fig. 3.12. A fluorescence spectrum with BDHCL as a light source was obtained, by aspirating 50.0 µg ml⁻¹ nickel solution into the atomiser plasma, using lamp at position 2 under the optimum operating conditions and is shown in Fig. 3.13.
3.4.6.2. Calibration curves.

Calibration curves were constructed for nickel using BDHCL at position 1 and 2, separately. A series of nickel solutions were prepared ranging from 1.0 to 10.0 µg ml\(^{-1}\) and 10.0 to 100 µg ml\(^{-1}\) for lamp position 2 and 1, respectively. These solutions were aspirated into the atomiser plasma and measurements were made at wavelengths \(\Sigma 231.1-232.5\) and \(\Sigma 351.5-352.4\) nm with ICP and BDHCL as excitation sources, respectively, under optimum operating conditions. The results obtained are shown in Fig. 3.11 (A) and (B).
3.4.6.3. Detection limit.

The detection limits were obtained for nickel using BDHCL at position 1 and 2. Nickel solutions containing 1.0 and 10.0 µg ml\(^{-1}\) were aspirated into the atomiser plasma for lamp position 2 and 1, respectively. Measurements were made at wavelengths Σ231.1-232.5 nm and Σ351.5-352.4 nm. At least five, 10 second integrations were made for each detection limit determined.

![Graph showing the effect of boost current on atomic fluorescence signal of copper at different primary currents using lamp in position 2.](image-url)
Fig. 3.9 Atomic fluorescence spectrum for lead using the ICP as a source of excitation while aspirating 1 ppm and 20% lead solutions into the atomiser and source plasmas respectively.
3.4.7. Analytical studies of copper.

3.4.7.1. Calibration curves.

To obtain a calibration curve for copper using ICP as a source of excitation, increasing concentrations of copper solutions up to 1.0 \( \mu \text{g ml}^{-1} \) were aspirated into the atomiser plasma while, aspirating 20% copper solution into the source plasma. The results obtained are plotted as concentration against fluorescence intensity and are shown in Fig. 14.

A curve of growth for copper was obtained using BDHCL at position 2, operated at manufacturers operating conditions and increasing concentrations of copper solutions up to 5000 \( \mu \text{g ml}^{-1} \) were aspirated into the atomiser plasma. A neutral density filter was used to reduce the radiant flux entering the monochromator at high concentrations of copper and signal was corrected by a calculated factor. The results obtained are plotted as concentration against fluorescence intensity and are shown in Fig. 3.15.

Another calibration curve was constructed using copper BDHCL at position 2, operated at twice the manufacturers operating conditions, as an excitation source. Increasing concentrations of copper solutions up to 1.0 \( \mu \text{g ml}^{-1} \) were aspirated into the atomiser plasma and measurements were made.

In an another experiment the ASIA instrument was run under optimum conditions with 20% copper solution being aspirated into the source plasma and increasing concentrations of copper solutions up to 1.0 \( \mu \text{g ml}^{-1} \) were aspirated into the atomiser plasma. An iris diaphragm was placed close to the atomiser plasma so that the area of the atomiser tail-flame being irradiated matched that which would be irradiated by a copper BDHCL. The iris diaphragm was aligned with the optical axis using a He/Ne laser. A plot of concentration against fluorescence intensity is shown in Fig. 3.14.

Measurements for all these experiments were made at wavelengths \( \Sigma 324.8-327.4 \) nm.
Fig. 3.10 Atomic fluorescence spectrum for lead using the lamp as a source of excitation while aspirating 50 ppm lead solution into the atomiser plasma.
3.4.7.2. Detection limit.

With BDHCL as an excitation source detection limits were obtained by aspirating 0.2 and 3.0 \( \mu \text{g \ ml}^{-1} \) copper solutions were aspirated into the atomiser plasma, at lamp position 2 and 1, respectively. With ICP as an excitation source detection limit was obtained by aspirating 0.020 \( \mu \text{g \ ml}^{-1} \) copper solution into the atomiser plasma and a 20\% copper solution was aspirated into the source plasma.

Detection limits with ICP as an excitation source and using the iris diaphragm as discussed in Section 3.4.7.1, was also investigated. Copper solution containing 0.1 \( \mu \text{g \ ml}^{-1} \) was aspirated into the atomiser plasma while, aspirating 20\% copper solution into the source plasma. The results are shown in Table 3.4 and 3.5. At least three, ten seconds integrations were made for each detection limit determined.

3.5. Results and discussions.

3.5.1. Atomic fluorescence of lead.

Lead was chosen as the first element to be studied. Following a wavelength scan it was found that a much stronger signal was obtained at 405.78 nm (direct line fluorescence) compared with other lines such as 283.3 nm and 363.96 nm (see Fig.3.10). Similar observations have been made by Sychra and Matousek. When irradiation is by the source plasma in ASIA, all lead lines are involved and the most sensitive region in fluorescence is \( \Sigma 280.2-287.3 \) nm. This is evident from the spectrum as shown in Fig.3.9. It is interesting to note that Demers used 364 nm wavelength for excitation with conventional HCLs in the commercial HCL-ICP-AFS instrument.\(^9\)

3.5.2. Atomic fluorescence of nickel.

A wavelength scan of the fluorescence produced with the nickel BDHCL as source showed that maximum intensity occurred at \( \Sigma 351.5-352.4 \) nm (Fig. 3.13), Whereas in ASIA the maximum fluorescence occurred over \( \Sigma 231.1 \) to 232.5 nm (Fig. 3.11).

Again, detection limit were determined at the appropriate wavelength and these are shown in Tables 3.4 and 3.5.
3.5.3. Atomic fluorescence of copper.

The resonance lines of copper at $324.8$ to $327.4$ nm were found to be the most sensitive in fluorescence for the BDHCL as source and in ASIA, and the detection limits at the two lamp positions and in ASIA were determined and are shown in Table 3.4. The results of the curve of growth experiment show that the curve reached a peak at 1000 $\mu$g ml$^{-1}$ copper (see Fig. 3.15) after which the fluorescence signal drops possibly due to self absorption and the fluorescence quenching in the atom cell. The detection limits determined are shown in Table 3.5 for the two lamp positions together with the ASIA results.

---

![Calibration curve](image)

Fig. 3.11 Calibration curves for Ni and Pb using: (A) Pb and Ni BDHCLs in position 1, (B) Pb BDHCL in position 2 and (C) Ni BDHCL in position 2. (See footnote in Fig. 2.7.)

---
Fig. 3.12. Atomic fluorescence spectrum for nickel using the ICP as a source of excitation while aspirating 5 ppm and 20% nickel solutions into the atomiser and source plasmas respectively.
Table 3.4. Signal and Noise results for various modes of operation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (μg ml⁻¹)</th>
<th>Mode*</th>
<th>Mean signal (mV)</th>
<th>SD (mV)</th>
<th>RSD (%)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.00</td>
<td>L1</td>
<td>0.09</td>
<td>0.060</td>
<td>66</td>
<td>10</td>
</tr>
<tr>
<td>Pb</td>
<td>50.00</td>
<td>L1</td>
<td>1.41</td>
<td>0.092</td>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td>Pb</td>
<td>0.00</td>
<td>L2</td>
<td>0.13</td>
<td>0.070</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>Pb</td>
<td>5.00</td>
<td>L2</td>
<td>2.92</td>
<td>0.122</td>
<td>4.2</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
<td>0.00</td>
<td>L1</td>
<td>0.09</td>
<td>0.050</td>
<td>53</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>20.00</td>
<td>L1</td>
<td>1.25</td>
<td>0.070</td>
<td>5.6</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>0.00</td>
<td>L2</td>
<td>0.20</td>
<td>0.070</td>
<td>36</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>1.00</td>
<td>L2</td>
<td>2.16</td>
<td>0.087</td>
<td>4.0</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>L1</td>
<td>1.84</td>
<td>0.097</td>
<td>5.3</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>3.00</td>
<td>L1</td>
<td>4.91</td>
<td>0.142</td>
<td>2.9</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>L2</td>
<td>6.54</td>
<td>0.186</td>
<td>2.8</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.10</td>
<td>L2</td>
<td>10.64</td>
<td>0.248</td>
<td>2.3</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>L2-OR</td>
<td>6.62</td>
<td>0.220</td>
<td>3.3</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
<td>L2-OR</td>
<td>12.96</td>
<td>0.253</td>
<td>1.9</td>
<td>3</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>A</td>
<td>10.45</td>
<td>0.260</td>
<td>2.5</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02</td>
<td>A</td>
<td>17.11</td>
<td>0.758</td>
<td>4.4</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>A-ST</td>
<td>7.55</td>
<td>0.250</td>
<td>3.3</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.10</td>
<td>A-ST</td>
<td>16.11</td>
<td>0.340</td>
<td>2.1</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 3.13 Atomic fluorescence spectrum for nickel using the lamp as a source of excitation while aspirating 50 ppm nickel solution into the atomiser plasma.
In the experiment with the copper lamp to operate it at higher primary currents, up to 30 mA, the lamp was covered with a blackened metal case which was wrapped with a black damp cloth to avoid overheating the lamp envelope. The results (Fig. 3.8) showed that copper fluorescence signal increased as the primary current of the lamp increased. However, this increase was small above 25 mA primary current. This effect may have been due to the reason that at high currents the atom cloud might have been slightly removed from the optical axis. The calibration curve constructed with the new lamp operating conditions was obtained and shown in Fig 3.14. A detection limit of 0.0052 μg ml⁻¹ was obtained at these new operating conditions, as shown in Table 3.5,

---

**Legend**

- ASIA; normal operation
- ASIA; 3 mm aperture
- HCL; normal operation
- HCL; high pri-current

---

*Fig. 3.14 Calibration graphs for copper using ICP as excitation source with and without 3 mm aperture and using a copper BDHCL as excitation source at normal and higher than recommended currents. (See footnote in Fig 2.7).*

based on the signal produced when aspirating 0.05 μg ml⁻¹ copper solution into the atomiser plasma.
As can be seen from Table 3.5 and 3.6 the detection limits are better with the ICP source than with the BDHCL sources even when the BDHCL source is located in the position in which maximum radiant power in the image in the atomiser plasma is produced (position 2). The results for copper suggest that this is due to the increased fluorescence signal sensitivity with the ICP source which more than offsets the BDHCL advantage of lower noise. As the monochromator can measure fluorescence from a cell in the atomiser tail-flame irradiated by a 3 mm x 10mm image of the source plasma, it may be that the better performance of the plasma light source is due to its greater area rather than a greater intrinsic radiance. This possibility is suggested by the fact that very similar sensitivities and detection limits are obtained for the BDHCL and the plasma source when the image of the later is stopped down to a circle of approximately 3 mm diameter. When the BDHCL is over-run the sensitivity and detection limits are better than those obtained for the stopped down plasma source.

To determine whether the BDHCL has a greater radiance than the ICP it was necessary to examine the effect of different positions of the sources and the lens between the chopper position and the atomiser plasma. Based on the area of the lens, \( A \) (2027 mm\(^2\)) and the distance from intermediate image to the lens \( S_1 \), the solid angle gathered may be calculated \( \frac{A}{S_1^2} \). The effect of moving a source from position 1 to position 2 in terms of the radiant power in the image, in the tail-flame of the atomiser plasma, would be to increase this power by a factor of 9. However, when the fluorescence sensitivities are compared for the BDHCL source in position 1 and 2, the sensitivity advantage of position 2 varies from a factor of 21 to 40, though the detection limit advantage remains constant at around 20, for the three elements in this study. This suggests that additional factors contribute to the disadvantage of position 1, such as absorption of light by the lenses and absorption in the fluorescence cell due to the reduced image produced when the source is in this position. This additional factor could be between 2.3 (for lead) and 4.4 (for copper).
Table 3.5. Sensitivities, Noise, and Detection Limits.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength, nm</th>
<th>Mode</th>
<th>Sensitivity, mV/µg ml⁻¹</th>
<th>SD of Blank, mV</th>
<th>DL µg ml⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Σ401.9-405.8</td>
<td>L1</td>
<td>2.64 x 10⁻⁵</td>
<td>0.06</td>
<td>6,800</td>
</tr>
<tr>
<td>Pb</td>
<td>Σ401.9-405.8</td>
<td>L2</td>
<td>5.58 x 10⁻⁴</td>
<td>0.07</td>
<td>380</td>
</tr>
<tr>
<td>Pb</td>
<td>Σ280.2-287.3</td>
<td>A</td>
<td></td>
<td></td>
<td>80*</td>
</tr>
<tr>
<td>Ni</td>
<td>Σ351.5-352.4</td>
<td>L1</td>
<td>5.76 x 10⁻⁵</td>
<td>0.05</td>
<td>2,600</td>
</tr>
<tr>
<td>Ni</td>
<td>Σ351.5-352.4</td>
<td>L2</td>
<td>1.96 x 10⁻³</td>
<td>0.07</td>
<td>110</td>
</tr>
<tr>
<td>Ni</td>
<td>Σ231.1-232.5</td>
<td>A</td>
<td></td>
<td></td>
<td>21*</td>
</tr>
<tr>
<td>Cu</td>
<td>Σ324.8-327.4</td>
<td>L1</td>
<td>1.02 x 10⁻³</td>
<td>0.10</td>
<td>290</td>
</tr>
<tr>
<td>Cu</td>
<td>Σ324.8-327.4</td>
<td>L2</td>
<td>4.10 x 10⁻²</td>
<td>0.19</td>
<td>14</td>
</tr>
<tr>
<td>Cu</td>
<td>Σ324.8-327.4</td>
<td>L2-OR</td>
<td>1.27 x 10⁻¹</td>
<td>0.22</td>
<td>5.2</td>
</tr>
<tr>
<td>Cu</td>
<td>Σ324.8-327.4</td>
<td>A</td>
<td>3.33 x 10⁻¹</td>
<td>0.26</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu</td>
<td>Σ324.8-327.4</td>
<td>A-St</td>
<td>8.56 x 10⁻²</td>
<td>0.25</td>
<td>8.8</td>
</tr>
</tbody>
</table>

* Values from reference 81; DL, Detection limit.

The validity of the calculation of the image radiant power may be assessed by a calculation of the effect of the stop introduced to give a plasma source image of 3 mm diameter. Without the stop the image is 3 mm x 10 mm and thus the size of the intermediate image, at the chopper, is 15 x 50 mm and the area viewed by the lens is thus 750 mm². In the presence of the stop, the circular 3 mm diameter image is equivalent to an intermediate image of 15 mm diameter (area 177 mm²). The reduction
in power in the image in the plasma tail-flame due to the stop is thus a factor of 4.2. This is in good agreement with the experimental ratios of fluorescence sensitivities of 3.9 (see Table 3.6).

Table 3.6. Sensitivity and Detection Limit Ratios.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sensitivity Mode</th>
<th>Ratio</th>
<th>Detection Limit Mode</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>L2/L1</td>
<td>21</td>
<td>L1/L2</td>
<td>20</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>-</td>
<td>L2/A</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni</td>
<td>L2/L1</td>
<td>34</td>
<td>L1/L2</td>
<td>24</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>L2/A</td>
<td>5.2</td>
</tr>
<tr>
<td>Cu</td>
<td>L2/L1</td>
<td>40</td>
<td>L1/L2</td>
<td>21</td>
</tr>
<tr>
<td>Cu</td>
<td>L2-OR/L2</td>
<td>3.1</td>
<td>L2/L2-OR</td>
<td>2.7</td>
</tr>
<tr>
<td>Cu</td>
<td>A/L1</td>
<td>330</td>
<td>L1/A</td>
<td>126</td>
</tr>
<tr>
<td>Cu</td>
<td>A/L2</td>
<td>8.1</td>
<td>L2/A</td>
<td>6.1</td>
</tr>
<tr>
<td>Cu</td>
<td>A-ST/L1</td>
<td>84</td>
<td>L1/A-ST</td>
<td>33</td>
</tr>
<tr>
<td>Cu</td>
<td>A-ST/L2</td>
<td>2.1</td>
<td>L2/A-ST</td>
<td>1.6</td>
</tr>
<tr>
<td>Cu</td>
<td>L2-OR/A-ST</td>
<td>1.5</td>
<td>A-ST/L2-OR</td>
<td>1.7</td>
</tr>
<tr>
<td>Cu</td>
<td>A/L2-OR</td>
<td>2.6</td>
<td>A-ST/A</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu</td>
<td>A/A-ST</td>
<td>3.9</td>
<td></td>
<td>3.8</td>
</tr>
</tbody>
</table>
It may be calculated that if the sources had equal radiance, the ratio of the copper fluorescence sensitivities for the ICP source to that for the BDHCL in position 2 would be 12. Taking into account the additional factor of 4.4 calculated for copper, it would be expected that the ratio would be 2.7. This is very close to the value of 2.6 measured (see Table 3.6) and therefore suggests that there is no significant difference between the radiance of the ICP source and the BDHCL source run at higher currents. For the operation of the BDHCL at the over-run operating currents the radiance would appear to be increased by a factor of 3.1.
Analytical Studies of Refractory Elements

4.1 Introduction.

The determination of refractory elements by atomic spectrometric techniques is more difficult than the non refractory elements, particularly at the trace levels. This is believed to be due to the formation of refractory oxides of these elements in the atom cell. Refractory elements such as aluminium, barium, beryllium, calcium, chromium, strontium and ytterbium are grouped together to form moderately strong oxides. Whereas, elements such as boron, silicon, titanium, vanadium, tungsten, zirconium, etc. are grouped into strong oxide forming elements.
The analytical performance of AFS technique is comparable to other atomic spectroscopic techniques, except for refractory elements. Refractory elements such as tungsten exhibit low sensitivity by this technique due to the formation of refractory oxides as described earlier. The use of carbon-containing species has been recommended for the reduction of oxides formed in the atomiser plasma. Carbon can be introduced by passing propane gas at low flowrates into the injector tube of the atomiser plasma, to produce a long tail plasma resembling a flame. Alternatively, organic solvents can be introduced into the atomiser plasma. This leads to an increase in sensitivity but, unfortunately, neither case provides sufficient sensitivity to enable achievement of detection limits comparable to those achievable by ICP-AES. Preconcentration of refractory elements prior to their nebulisation is an alternative for improving the sensitivity by this technique. A variety of preconcentration methods are available to enhance the sensitivity of such elements. These include solvent extraction, ion-exchange chelating resins, co-precipitation, electrodeposition, vapour generation, evaporation, polyurethane foams, and freeze drying.

The most widely used preconcentration method is based upon the formation of insoluble metal complexes followed by extraction into an immiscible organic solvent. Shindi and Khopkar have reported extraction of tungsten with mesityl oxide (4-methyl-3-pentene-2-one) in methylisobutylketone (MIBK) from solutions in 1.0 M hydrochloric acid. They successfully applied the method to the analysis of an alloy steel. Roy and Das have proposed a method for the determination of tungsten in rocks and minerals. The method involves chelate formation of tungsten with N-Benzoyl phenyl hydroxylamine (BPHA), followed by extraction in toluene and determination by atomic absorption spectrometry. Preconcentration of tungsten from steel samples and its extraction as thiocyanate complex has been reported by Musil and Dolezal. Tungsten as thiocyanate complex was extracted into MIBK in hydrochloric acid medium and determined by atomic absorption spectrometry. Solvent extraction techniques suffer from several limitations, however, possible emulsion formation, and increased sample manipulation makes difficult automation of the method.
Among the ion-exchange chelating resin, chelex-100 is perhaps the most commonly used. Riley and Taylor\textsuperscript{125} have investigated uptake of trace elements including refractory elements from both, distilled water and sea samples by chelating chelex-100. They reported 99-100\% recovery of most of the elements studied. Ion-exchange chelating resins have found widespread applicability and have proved to be an effective means of increasing the sensitivity of atomic spectrometric techniques as well as matrix removal. However, the conventional column mode of ion-exchange concentration procedure is tedious and incompatible with many industrial problems. Therefore, several successful attempts have been made to apply Flow Injection Analysis (FIA) as a means of preconcentration by ion-exchange to atomic spectrometric determinations with the aim of speeding up and simplifying the preconcentration procedure. This approach not only increases the speed of preconcentration process, but, could rival the sensitivity of electrothermal atomisation atomic absorption spectrometry. Olsen et al.\textsuperscript{126} first applied a miniature column of chelex-100 in an on-line FIA-FAAS and achieved 20-fold preconcentration of heavy metals from seawater. Later, many papers were published using ion-exchange columns in FIA systems. Hartenstein et al.\textsuperscript{127}, proposed a method utilizing a micro column of chelex-100 to increase the sensitivity for multielement determinations by ICP-AES. They reported 20 times lower detection limits for a number of elements than for conventional continuous aspiration sample introduction. Recently, Furuta et al.,\textsuperscript{128} have reported a preconcentration FIA system utilizing a microcolumn of activated alumina to preconcentrate molybdenum prior to determination by ICP-AES. They obtained detection limits better than those using continuous nebulisation technique by a factor of approximately 50. When they applied the method to sea water samples they observed a suppression effect for the sea water standards which was attributed to the presence of sulphates and phosphates in sea water. However, they overcame the effect by employing a standard addition method.

In this work efforts were made to determine refractory elements such as tungsten in aqueous solutions without the addition of carbon-containing species. Later, experiments were performed using ethanol as a reducing medium for the determination of tungsten and molybdenum in pure aqueous solutions. Also, development of a rapid
and simple on-line preconcentration procedure allowing concentration of refractory elements in a short period of time, was performed with an objective of preconcentrating a group of elements.

4.2 Experimental.

4.2.1 Apparatus.

The A S I A spectrometer used in this study is described in Chapter 2. During the course of this work modifications to the instrument have been made which are described in detail in Chapter 5. The Optica monochromator has been replaced with a Bentham Instruments computer controlled monochromator with better light gathering power. A single lens is used between the atomiser plasma and the monochromator entrance slits rather than the original two lenses. This allows greater collection of the fluorescence radiation from the atomiser plasma.

The preconcentration manifold (see Fig. 4.1) consisted of a Gilson miniplus 2 (8 channel) peristaltic pump, and Omnifit six port injection valve incorporating a laboratory made glass column (Fig. 4.2) containing the resin. Two different sizes of columns were used, one was 50 mm long having an internal diameter of 2.3 mm and the other 70 mm long with 4 mm inner diameter. A chelating resin, chelex-100, 200-400 mesh and an anion exchange resin, Amberlite IRA-93, 16-50 mesh, were tested for adsorption of refractory elements. All the connecting tubing consisted of 0.8 mm I.D PTFE. Solutions were pumped with appropriate size tygon tubing to obtain desired flowrates.

4.2.2 Column preparation.

The column was prepared by placing a porous polyvinylchloride (PVC) membrane at one end of the column and aspirating a water-slurry of the resin into the column until filled. Another PVC membrane was placed at the other end of the column and sealed to the plastic connectors using an epoxy resin. The column was placed in the injection loop of the valve so that the sample was loaded in one direction and eluted in the other. This prevented the resin from packing into one end of the column.
Fig. 4.1 Preconcentration manifold with injection valve and peristaltic pump. (a) Single-line manifold: A, sample mixed with buffer at variable flow-rate; B, eluant at variable flow-rate; W, waste; P, pump; V, valve; C, column. (b) Dual-line manifold: D, sample; E, buffer; F, eluant.

Fig. 4.2 Diagramatic representation of the micro-column.
4.2.3 Chemicals and Reagents.

All the reagents used in this study were of analytical reagent grade. Standard stock solutions of tungsten, molybdenum and vanadium were prepared from sodium tungstate (BDH chemicals), molybdenum oxide (BDH chemicals) and vanadium oxide (Aldrich chemicals), respectively. A stock solution of zirconium (995 µg ml⁻¹) from Aldrich chemicals was used. A series of standard solutions for each of the four elements were prepared by dilution of respective stock solution in de-ionized water.

For the source plasma a high concentration solution of tungsten (40% w/v) was prepared from dodeca tungstosilicic acid (Fisons chemicals) dissolved in cold de-ionized water. Whereas, the 20% w/v molybdenum solution was prepared by dissolving molybdenum oxide in the minimum amount of 35% ammonia. A stock solution of vanadium (1000 µg ml⁻¹) was prepared by dissolving the oxide salt in 10 ml of concentrated hydrochloric acid. Molybdenum oxide and vanadium oxide salts were dried at 110 °C for two hours before weighing. Low concentration solutions of molybdenum and tungsten were prepared by adding ethanolic 2.0 M ammonia slowly with constant shaking into an accurately measured volume of concentrated molybdenum solution. The ethanolic 2.0 M solutions were prepared freshly because solutions containing 80% or more ethanol tend to precipitate out after some time. The buffer solutions were prepared from ammonium acetate (BDH chemicals). The pH of these solutions was adjusted to appropriate pH by adding acetic acid/ammonia solution, whereas the pH of potassium chloride buffer solutions was adjusted by adding hydrochloric acid/ammonia solution.

4.2.4. Optimisation procedure.

A systematic study was carried out to determine the operating conditions of the instrument for the elements studied using an alternative variable search method, while monitoring the total fluorescence signal. In the case of emission experiments the figure of merit used was signal to background ratio. The emission lines selected for tungsten, molybdenum, zirconium and vanadium were 400.9 nm, 379.8 nm, 339.198 nm, 310.2 nm, respectively. For the fluorescence experiments the wavelengths selected for tungsten and molybdenum were 295.6 nm and 313.3 nm, respectively. The operating
conditions for tungsten and molybdenum in the fluorescence mode and for tungsten, molybdenum, zirconium, and vanadium in the emission mode of the instrument operation are shown in Table 4.1 and Table 4.2.

Table 4.1. Typical operating conditions using ASIA system in emission mode for Mo, V, W, and Zr.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>Coolant gas flow-rate, l min⁻¹</td>
<td>14-16</td>
</tr>
<tr>
<td>Plasma gas flow-rate, l min⁻¹</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Injector gas flow-rate, l min⁻¹</td>
<td>0.8-1.1</td>
</tr>
<tr>
<td>Height above the coil, cm</td>
<td>2.0-2.5</td>
</tr>
<tr>
<td>Slit-width, μm</td>
<td>50</td>
</tr>
<tr>
<td>Time constant, m sec.</td>
<td>300</td>
</tr>
</tbody>
</table>

4.2.5. Observations on the determination of tungsten in aqueous solutions.

It has been reported in the literature that for refractory elements particularly, tungsten carbon-containing species are necessary to produce an atomic fluorescence signal due to reasons described earlier. Nevertheless, it was thought necessary to confirm this prediction.
Table 4.2. Operating conditions for Mo and W in fluorescence mode with the ASIA system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Atomiser plasma</th>
<th>Source plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>molybdenum</td>
<td>molybdenum</td>
</tr>
<tr>
<td></td>
<td>tungsten</td>
<td>tungsten</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>0.58</td>
<td>7.3</td>
</tr>
<tr>
<td>Coolant gas, 1 min⁻¹</td>
<td>14 Ar</td>
<td>30 Air</td>
</tr>
<tr>
<td>Plasma gas, 1 min⁻¹</td>
<td>none</td>
<td>30 Ar</td>
</tr>
<tr>
<td>Injector gas, 1 min⁻¹</td>
<td>2.5 Ar</td>
<td>2.5 Ar</td>
</tr>
<tr>
<td>Height above the coil, cm</td>
<td>7.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Sample solution, ml min⁻¹</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Slit-width, mm</td>
<td>3.6 and 5.0*</td>
<td></td>
</tr>
</tbody>
</table>

* with the modified ASIA system.

Two alternative hypothesis are considered to be the likely reasons for not getting any fluorescence signal from the aqueous solutions; The first hypothesis is that relatively low temperature in the long-sleeve Baird torch compared to that achieved in the conventional Fassel torch was the possible reason for not producing enough atoms of the refractory elements. Therefore, in an attempt to check this possibility, the basic set-up of the ASIA spectrometer was slightly changed. The Baird torch from the atomiser plasma position was replaced with a conventional Fassel torch and positioned in the optical axis by means of a He/Ne laser. Tungsten was chosen as a test element. Several attempts were made using atomiser plasma powers upto 1.0 kW but, no success was obtained in producing an atomic fluorescence signal of tungsten. Tungsten concentrations upto 10,000 µg ml⁻¹ were aspirated into the atomiser plasma at the optimum operating conditions of the spectrometer. During this study it was noticed that the atomiser plasma was very turbulent. Glass wool was inserted into the coolant gas and the plasma gas tubes of the torch at the bottom in an attempt to obtain a laminar flow in the torch but, no success was achieved.
The second hypothesis is that the formation of stable oxides in the plasma could be due to oxygen entrainment from the surrounding air. To study this effect an argon gas shielding apparatus as shown in Fig. 4.3 was arranged. Experiments were performed using the shielding apparatus on the atomiser plasma, but, no fluorescence signal for tungsten was generated. These results indicate that the oxygen does not arise from the air entrainment from the surroundings of the atomiser plasma alone but could also be from the oxygen in the solution.
4.2.6. Observations on the effect of different organic solvents on the plasma (atomiser) stability.

The effect of a number of organic solvents was investigated on the stability of the atomiser plasma. The solvents included toluene, xylene, methlisobutylketone, chloroform, methanol, ethanol, propanol, n-hexane and 1-2,dichloroethane. A limiting aspiration rate of up to $0.5 \text{ ml/min}$ was obtained for these solvents. Above which it was difficult to sustain the plasma. However, when ethanol, propanol and methanol were diluted with water, the limiting aspiration rate was found to be approximately $3.0 \text{ ml/min}$. These solvents when aspirated into the plasma produced a noisy tail plume, yellow in colour. It was observed that carbon was deposited on the tip of the plasma injector tube after some time. The plasma was frequently extinguished when the aqueous solution was switched with all these organic solvents except when ethanol mixed with water was aspirated into the plasma. A drop in the power was noticed on introduction of organic solvent into the plasma. One possible explanation to this behaviour could be that the organic vapour absorb r.f. power in some way. The organic vapour does not pass entirely through the central channel but some fraction is believed to pass around the base of the plasma and possibly effect the energy transfer process in the plasma.

Several reports on the use of organic solvents for the determination by ICP have appeared. Boom and Browner have discussed plasma instability with alcohols. The limiting aspiration rate obtained for 100% methanol was found to be $0.1 \text{ ml/min}$, which they improved to $3.0 \text{ ml/min}$ when 25% dilution of methanol was made with water. Nisamaneepong et. al., have shown that frit nebuliser enhances the introduction of some organic solvents to the ICP compared to a concentric nebuliser. They observed that solutions of methanol (>30%) and acetonitrile could not be used with concentric nebuliser without extinguishing the plasma at $1 \text{ ml/min}$. The small droplet size and fine aerosol produced by the frit nebuliser was believed to have improved the tolerance of ICP for methanol and acetonitrile, in their study.
4.2.7. Determination of W and Mo in aqueous solutions using ethanol as a reducing environment.

4.2.7.1. Effect of ethanol on the atomic fluorescence signal of tungsten and molybdenum.

In order to study the effect of ethanol on the atomic fluorescence signal of tungsten an experiment was performed. Measurements were made by aspirating solutions containing increasing percentage of ethanol, into the atomiser plasma while, aspirating 40% (w/v) tungsten solution into the source plasma. Similarly, the effect of ethanol on the fluorescence signal of molybdenum was investigated, using 20% (w/v) molybdenum solution into the source plasma. A slit-width of 3.6 mm was used in both cases.

4.2.7.2. Calibration curves for tungsten and molybdenum.

To obtain calibration curves for tungsten and molybdenum, increasing concentrations of each solution were aspirated into the atomiser plasma while aspirating a fixed concentration of the respective element solution into the source plasma. Measurements were made using 3.6 mm slit-width.

4.2.7.3. Detection limit.

The detection limits were obtained for molybdenum and tungsten at wavelengths 313.3 nm and 295.6 nm, respectively. After the modifications to the instrument were made, detection limits for both the elements were repeated. Calculations were made according to the method described in Chapter 2. Ten consecutive measurements were made for each element in both cases.

4.2.7.4. Results and Discussions.

The effect of ethanol on the atomic fluorescence signal of tungsten and molybdenum is shown in Fig. 4.4. The results show that the fluorescence signal of tungsten increases as the percentage of the ethanol increases until the 75% limit is reached after which a rapid decrease in signal is noted. This drop in the fluorescence signal is probably due to quenching of the fluorescence signal by the carbon species. Subsequently 75%
ethanolic solutions were used for the determination of tungsten in aqueous solutions. Similarly, the results of the effect of ethanol on atomic fluorescence signal of molybdenum showed that 75% ethanolic solution produced a maximum signal.

![Graph](image)

Fig. 4.4 Effect of ethanol on atomic fluorescence signal of: (A) tungsten, (B) molybdenum, at 295.6 nm and 313.3 nm wavelengths, respectively. (See footnote in Fig. 2.7).

The plot (Fig. 4.5) acquired for the calibration curve for tungsten shows a linear increase of fluorescence signal intensity. A similar pattern is shown by the calibration curve for molybdenum as shown in Fig. 4.5. The correlation coefficient values of the calibration curve data for tungsten and molybdenum was found to be 0.98 and 0.99, respectively. These values are close to the theoretical values of 1.0.

The detection limits obtained are shown in Table 4.3. A comparison of the values obtained before and after the modifications to the instrument shows about 2-fold improvement in the detection limits.
4.2.8. Preconcentration studies using chelex-100 resin column.

To investigate the performance of chelex-100 for preconcentration of refractory elements a thorough study of the behaviour of the resin was performed. A number of parameters that affect the performance of the resin were studied. Tungsten was chosen as the test element. The instrument was operated in the emission mode for this study.

4.2.8.1. Procedure.

The manifold for these studies is shown in Fig. 4.1 (a). Buffered sample solutions were pumped at the desired flowrate and then passed onto the resin column. A preconcentration time of five minutes was used for all the experiments. The preconcentrated tungsten was eluted with a continuous stream of ammonia solution at optimal flowrate. Upon the completion of each measurement the column was preconditioned to the required pH by washing with 1.0 ml of de-ionized water and then passing buffer solution through the column for another one minute.

Fig. 4.5 Calibration graphs for tungsten and molybdenum aspirating 70% ethanolic solutions into the atomiser plasma while aspirating 40% and 20% solutions of tungsten and molybdenum into the source plasma, respectively. (See footnote in Fig. 2.7).
All tungsten determinations in this study were made using the monochromator slits of 50 µm.

4.2.8.2. Effect of pH.

The effect of pH for the retention of tungsten onto the resin was studied using a 70 mm long column having 4 mm I.D. A series of buffered sample solutions at different pHs were prepared each containing 5.0 µg ml⁻¹ of tungsten. Buffers used included: 0.1 M potassium chloride (pH 1-3) and 1.0 M ammonium acetate (pH 3.5-8.0). A flowrate of 1.0 ml min⁻¹ was used.

![Figure 4.6](image_url)

Fig. 4.6 Effect of varying pH on tungsten retention onto chelex-100 resin, at 400.9 nm wavelength in the emission mode using manifold as in Fig. 4.1 (a).

The column effluent was collected in small polypropylene cups and analysed to determine tungsten. The percentage of metal retained on the resin column was
calculated from the concentration of metal in the original sample and the concentration of metal in the effluent from the column. A plot of behaviour of chelex-100 resin for tungsten as a function of pH is given in Fig. 4.6.

4.2.8.3. Effect of buffer molarity.

To investigate the effect of buffer molarity a series of solutions containing a fixed concentration of tungsten and variable molarity of ammonium acetate buffer were prepared. A flowrate of 1.0 ml min^-1 was used. The percentage of metal retained on the column was calculated as describe in the previous section.

Fig. 4.7 Retention behaviour of chelex-100 resin column for tungsten at 400.9 nm wavelength in the emission mode using manifold as in Fig. 4.1 (a).
4.2.8.4. Resin capacity curve.

Resin capacity curve was prepared by pumping tungsten solution through the resin column at a flowrate of 1.0 ml min⁻¹. The column effluent was continuously monitored for the resin capacity and measurements were made at regular intervals. The resin capacity curve was constructed by plotting percentage retention against the tungsten concentration and is shown in Fig. 4.7.

![Graph showing resin capacity curve](image)

**Fig. 4.8** Effect of varying sample flow-rate on tungsten retention onto Chelex-100 resin column at 400.9 nm wavelength in the emission mode using manifold as in Fig. 4.1 (a).

4.2.8.5. Effect of flowrate.

To study the effect of sample flowrate on the retention of tungsten onto the resin column a 5.0 µg ml⁻¹ buffered sample solution was passed through the column at variable
flowrates. The column effluent was analysed for tungsten and the percentage retention was calculated as described in Section 4.2.8.2. A plot of percentage tungsten retention versus flowrate was constructed as shown in Fig. 4.8.

4.2.9. Preconcentration studies using IRA-93 anion exchange resin column.

4.2.9.1. Method development.

The effect of various parameters on the retention of a number of refractory elements onto the resin was studied. The parameters investigated included: buffer pH, sample flowrate, eluant flowrate, and eluant and buffer molarity. Measurements were made on-line for most of the parameters studied in the emission mode using the manifold as shown in Fig. 4.1 (a).

i). Effect of pH.

To investigate the effect of pH on the adsorption of refractory elements, a series of buffered solutions containing 5.0 µg ml$^{-1}$ of refractory element at various pH levels were prepared. The buffer used for pH 1.0-3.0 was 0.1 molar potassium chloride and for pH 3.5-8.0 was 1.0 molar ammonium acetate. A flowrate of 1.0 ml min$^{-1}$ was used. The procedure followed was the same as in Section 4.2.8.1. Effluent from the column was treated for the determination of the element. All the four elements, tungsten, molybdenum, zirconium and vanadium were studied individually.

ii). Effect of buffer molarity.

A series of different molarity buffer solutions were prepared, with molarity varying from 0.1 to 2.0. Each of these solutions contained 5.0 µg ml$^{-1}$ concentration of the element. A 0.1 molar KCl buffer was used for molybdenum, whereas for the other three elements 1.0 molar ammonium acetate buffer was used. A flowrate of 1.0 ml min$^{-1}$ was used and the rest of the procedure was same as described earlier in Section 4.2.8.1. A 7.0 cm long column was used for this experiment.
iii). Resin capacity curves.

The resin capacity curve was obtained by passing buffered metal solution at a flowrate of 1.0 ml min\(^{-1}\) through the column. Column effluent was monitored continuously. Effluent was collected at regular intervals and analysed to determine the element. All the four elements were studied separately. Again, a 7.0 cm long column was used for this experiment.

iv) Effect of sample flowrate.

To determine the effect of sample flowrate, buffer solutions containing 5.0 \(\mu\)g ml\(^{-1}\) were prepared. Flowrate varying between 1.0 to 10.0 ml min\(^{-1}\) were used to pump the solution through the column. Column effluent was analysed for the element. Each of the four elements was studied separately. The same procedure as described in Section 4.2.8.1 was followed.

v). Effect of eluant type and flowrate.

A number of eluants were investigated to elute the adsorbed metal species from the resin column. These include: sodium carbonate, hydrochloric acid, nitric acid and ammonia solution. Eluants of varying molar concentrations between 1.0 to 4.0 were used. Metal species from the column were eluted following the procedure described before in Section 4.2.8.1 using manifold (b) shown in Fig. 4.1. Determinations were made in the emission mode of the instrument.

Additional experiments were performed to study the effect of ethanolic ammonia solution for tungsten and molybdenum in the fluorescence mode of the instrument. Manifold (b) as in Fig. 4.1 was used in this case. Sample and buffer solutions were pumped at a flowrate of 1.0 ml min\(^{-1}\) in separate streams. The two streams were allowed to merge and pass through the column a combined flowrate of 2.0 ml min\(^{-1}\) for a period of five minutes. Adsorbed metal species were eluted with ethanolic ammonia solutions of varying strengths at optimal flowrates. Each of the two element was studied separately.
4.2.9.2. Method performance.

The performance of the method was studied by constructing calibration curves for molybdenum and tungsten. Standard solutions pumped at 7.0 ml min\(^{-1}\) were merged with a buffer flowing at 3.2 ml min\(^{-1}\) at the optimum pH. This solution was then passed through the column for five minutes. After the analyte was deposited on the resin column, elution was effected by switching the valve to allow a stream of 2.0 molar ammonia in 75% ethanol at the optimised flowrate, to pass through the column. The valve was then switched to the "load" position and the column was washed with blank for a period of 30 seconds to allow the column to reach the optimum pH. The procedure was repeated for the next solution.

4.3. Results and Discussions.

4.3.1. Preconcentration studies using chelex-100 resin column.

A thorough study of the behaviour of the resin is necessary to achieve maximum efficiency. The retention-pH profile for the metal ion gives insight into the behaviour of the resin and aid in the choice of operating pH. The pH of the sample is a major factor that influence the performance of the column. Figure 4.6 shows that pH 6.0 was suitable for maximum retention of the tungsten. This is in agreement with pH chosen by Riley and Taylor\(^{125}\). However, only up to 70% retention of tungsten could be achieved, in contrast to 100% retention achieved by them.

The effect of sample flowrate on the retention of tungsten is represented in Fig. 4.8. The results shows that the retention efficiency decreased as the flowrate was increased, suggesting that the contact time between the metal species and the chelating resin was critical. Thus, increasing the column size by lengthening the column will probably increase the contact time and alleviate the retention problems upto a certain degree, yet increased back pressure would be the limiting factor in increasing the column length. Already, during this experiment problems were encountered of increased back pressure causing the leakage of the solution from the joints in the flow systems. Higher flowrates yielded tighter packing of the resin which ultimately blocked the flow of the liquid.
The study of the effect of buffer strength showed that no significant change in the retention behaviour of the resin was found. Therefore, 0.25 M buffer strength was maintained throughout the rest of the performance study. The resin capacity curve is shown in Fig. 4.7. The efficiency of the resin uptake remained constant until 300 µg ml\(^{-1}\) concentration of tungsten, after which a small drop in the efficiency was noted. These results indicated that tungsten concentration up to 300 µg ml\(^{-1}\) could be easily tolerated.

The results from these studies with chelex-100 resin column were not encouraging. Problems of lower uptake of the metal species by the resin and the erratic blockages, leakages, and flowrate fluctuations caused by back-pressure changes led to the decision of abandoning further study with this resin.

4.3.2. Preconcentration studies using IRA-93 anion exchange resin column.

4.3.2.1. Method development.

Figure 4.9. shows that quantitative retention for tungsten was obtained at pH 5 and below, whereas for molybdenum the response was fairly sensitive to pH, as indicated by the sharp maximum at pH 2.0. For zirconium and vanadium the behaviour of the resin was quite different showing quantitative retention at and above pH 4.0 for both the elements. This dissimilarity in the behaviour of the resin can be attributed to the dissimilarity of the metal species formed in the solutions. These results shows that pH 2.0 was suitable for the preconcentration of tungsten and molybdenum. However, pH 4.5 was used for the preconcentration of tungsten because of the prolonged deterioration of the resin at pH 2.0.

The effect of different sample flowrates on the retention of metal species is shown in Fig. 4.10. The retention of metal species decreases as the flowrate increases above 1.0 ml min\(^{-1}\). This could possibly be due to the kinetic behaviour relating to retention efficiency and the time the sample is in contact with the resin. Several factors are of value when making projections concerning the dynamic behaviour of resins. These include the rate constant and the rate of interaction between the resin and the ions which is a time dependent factor.
Fig. 4.9 Effect of varying pH on metal retention using manifold (a)
Fig. 4.10 Effect of varying sample flow-rate on metal retention onto the IRA-93 resin column using manifold (a).
On the basis of the results obtained these elements could be divided into two groups, 1) tungsten and molybdenum, and 2) zirconium and vanadium. The retention of zirconium and vanadium falls quite rapidly as the flowrate of the sample is increased above 1.0 ml min\(^{-1}\). One possible reason for this behaviour of the resin could be the formation of unstable hydroxo complexes or polymerization. The elements of fourth and fifth group in the periodic table of elements like zirconium and vanadium, tend to hydrolyze, polymerize or precipitate even in fairly acidic solutions; hydrofluoric acid has been recommended for the formation of fluoro complexes which are more stable than the hydroxo complexes. However, hydrofluoric acid could not be used with this particular manifold system because the column was made of glass.

The results of the retention efficiency experiments are shown in Fig. 4.11. The retention of tungsten, molybdenum, zirconium, and vanadium falls after loading 3000 \(\mu g\).
700 µg, 550 µg, and 500 µg of these elements onto the resin column, respectively. The retention efficiency calculations were made using the equation as follows:

\[
\%E = \frac{C_s - C_w}{C_s} \times 100\%
\]

Where \(C_s\) is the concentration of the analyte in the sample being loaded on the column and \(C_w\) is the concentration of the analyte in the sample waste off the column.

![Figure 4.12](image)

**Fig. 4.12** Effect of ethanol on AP signal of tungsten in 2.0M ammonia at 295.6 nm wavelength while aspirating 40% tungsten solution into the source plasma. (See footnote in Fig. 2.7).

Four different types of eluants were investigated for eluting the retained metal species. It was noticed that nitric acid and hydrochloric acid at concentrations upto 4.0 molar were less effective than ammonia solutions in eluting retained metal species from the resin column. The use of sodium carbonate solution resulted in high blank value which excluded its further use. A 2.0 molar ammonia solution was found to be suitable in
eluting all the retained metal species for the measurements made in the emission mode. However, for atomic fluorescence measurements a 75% ethanolic 2.0 molar ammonia solution was found to be suitable (see Fig. 4.12). An advantage of using ethanolic ammonia solution compared to aqueous ammonia solution was less swelling of the resin column. This avoided any pressure build up in the flow manifold helping long-term operation of the column without any leakage.

4.3.2.2. Role of carbon-containing species.

As described earlier, special means are employed to maintain refractory elements as free atoms in the tail plasma plume for atomic fluorescence measurements. In this study ethanol was used to provide necessary reducing environment. The introduction of carbon-containing species results in decomposition of the species producing radicals like C, CH, CO. These radicals help in the dissociation of major molecular species MO and MOH, formed of the refractory element (M). The proposed mechanism of the dissociation of the oxide species is that carbon reacts with the gas phase metal oxide (MO) to produce CO and the free metal ion.

\[ MO + C \leftrightarrow M + CO \]

In addition to this another reaction that occurs involves the quenching of entrained air with carbon radicals, formed, by reacting with the free oxygen.

\[ C + O \leftrightarrow CO \]

This would result in indirect reduction of the formation of the metal oxide species in the atomiser plasma.

4.3.2.3. Method performance.

It was noticed from the study of the effect of various parameters on the method performance that only tungsten and molybdenum could be rapidly preconcentrated. The other two elements, zirconium and vanadium showed less than 5% retention onto the resin column at a sample flowrate of 8.0 ml min\(^{-1}\) and therefore, it was considered unnecessary to continue with these elements. Calibration graphs for tungsten and molybdenum are presented in Fig. 4.13. These show good linearity. The relative
standard deviations for tungsten at 10.0 μg ml\textsuperscript{-1} and 0.5 μg ml\textsuperscript{-1} concentrations were 1.17% and 4.28%, respectively, whereas for molybdenum at 1.0 μg ml\textsuperscript{-1} and 0.1 μg ml\textsuperscript{-1} concentrations were 2.45% and 5.24%, respectively. The limit of detection based on 3 standard deviations of five replicate measurements of 0.5 μg ml\textsuperscript{-1} tungsten and 0.1 μg ml\textsuperscript{-1} molybdenum concentrations was 65 ng ml\textsuperscript{-1} and 15 ng ml\textsuperscript{-1}, respectively.

Fig. 4.13 Calibration graphs for (A): tungsten and (B): molybdenum while aspirating 40% and 20% solutions of tungsten and molybdenum, respectively into the source plasma. (See footnote in Fig. 2.7).

After modifications to the instrument were made a calibration curve for molybdenum was constructed using the manifold (b) in Fig. 4.1. The results obtained are shown in Fig. 4.14. A detection limit of 8 ng ml\textsuperscript{-1} was obtained for a set of five replicate measurements of 50 ng ml\textsuperscript{-1} molybdenum solutions using the procedure described earlier. The precision at this concentration was 4.76%.
Table 4.3. A comparison of detection limits obtained with the ASIA system, ng ml\(^{-1}\).

<table>
<thead>
<tr>
<th>Element</th>
<th>Original ASIA system</th>
<th>Modified ASIA system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional nebulisation</td>
<td>Preconcentration</td>
</tr>
<tr>
<td>Mo</td>
<td>146</td>
<td>15</td>
</tr>
<tr>
<td>W</td>
<td>900</td>
<td>65</td>
</tr>
</tbody>
</table>

NM: not measured.
A comparison of the results obtained using the preconcentration method and conventional nebulisation is shown in Table 4.3. The result show that using the preconcentration method a ten fold improvement in detection limit is noted compared to the conventional nebulisation.
5.1. Introduction.

The development of AFS instrumentation has been governed by three major requirements: large signals (i.e. high sensitivity); high signal to noise levels (i.e. low detection limits and high precision); and simple and rapid processing of analytical samples. The first of these has been met by extensive development of the atom cells and excitation sources. For high signal to noise levels it is important to ensure that no emission signal received from the atom cell is amplified by the detector. This has resulted in wide spread use of modulated sources. High stability and large amplifications of the fluorescence signals are also the important factors in the
instrumental requirements for AFS. The monochromator used for AFS should give high light transmission. However, good resolution is of secondary importance because there are few lines in AFS compared to AES.

Atomic fluorescence systems have been studied in a tremendous variety of configurations. These systems have different optical arrangements and detection and measurements systems both in the elegance of their design and detail and in the quality of their instrumental components. The only AFS system currently available is the Baird AFS-2000, which is described in Section 1.6.1.

5.1.1. Entrance optics and Monochromator.

The various entrance optical arrangements used in AF investigations, as in the other spectrometric techniques have covered a wide range of refinement. Some systems used had no focussing arrangements in either the exciting or the fluorescence radiation collection. However, excellent results have been reported.\(^{40,141}\) Other experimental set-ups have included focusing lenses.

The role of the entrance optics is two-fold, to project an image of the excitation source into the atom cell so that the highest radiant flux is achieved in the area observed by the monochromator, and further, to project the excited radiation onto the entrance slit of the monochromator so that the image of the fluorescing atoms cover the whole slit height, and at the same time the whole solid angle of the collimator is filled. Some researchers,\(^{142,143}\) have suggested the use of an ellipsoidal reflector placed off-axis or behind the excitation light source to collect a much larger solid angle of light and thus improve the optical transfer of the excitation light. Epstein et.al.,\(^{49}\) observed improvements in analytical sensitivity by placing a reflecting mirror behind the atomiser (flame) in line with the excitation source (ICP) in their ICP-Flame-AFS system. On the other hand, Long and Winefordner,\(^{77}\) improved their ICP-ICP-AFS system by placing a 50 mm diameter concave spherical mirror behind the excitation source (i.e., ICP) along with other improvements in the optical system. They observed at least an order of magnitude improvement in detection limits compared to their previous setup.\(^{76}\)
In most analytical studies of AFS, small grating monochromators have been used, because resolution is not of primary importance. Most of these grating monochromators are Czerny-Turner mounts. Filters employed for the non-dispersive systems of atomic fluorescence spectrometry usually have high transmission in the ultraviolet and block the visible light. Shao et al. studied a HCL-flame-AFS system in which filters and monochromators were employed, separately and compared the results obtained. They found that the detection limits obtained with the monochromator module were poorer in most instances for the same elements than with the filter module. They attributed this to the smaller light-gathering capability of the monochromator.

5.1.2. Photodetectors and electronic measurement systems.

Various detectors could be used for the detection of signals in atomic fluorescence spectrometry, but photomultiplier tubes have been used without exception and have become widely established. Selection of a suitable photomultiplier tube generally involves a compromise based on spectral response and gain.

The two methods used commonly for the measurements of electrical signals in fluorescence spectrometry are: direct-current (d.c) measurement and alternating-current (a.c) measurement methods. The a.c method has been widely used because of a principle advantage of a.c systems over the d.c systems is to distinguish between thermal radiation and optically-excited radiation. In the a.c systems the radiation from the excitation source is modulated either electronically or by a mechanical chopper and the modulated signal from the photomultiplier tube is coupled to a lock-in amplifier. This enables in distinguishing between the thermal radiation and optically-excited radiation, by rejection of the dc signal (i.e., thermal radiation) from the atom cell. The use of boxcar integrator has also been reported recently in electronic measurements for laser excited ICP-AFS systems. In such systems the output from a pre-amplifier is fed to a gated integrator and a boxcar averager, which periodically samples the same portion of a signal for a fixed period of time and then averages the samples using a low-pass RC filter. The output is then displayed on the strip-chart recorder.
5.2. Chemicals.

All chemicals used were of analytical reagent grade. For the atomiser plasma standard solutions for copper, lead, nickel, calcium, barium, cobalt, zinc, and were prepared

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power in the plasma</td>
<td>0.35-0.75 kW (atomiser plasma)</td>
</tr>
<tr>
<td>Observation height above the coil</td>
<td>6.0-7.3 kW (source plasma)</td>
</tr>
<tr>
<td></td>
<td>7.2-14.0 cm (atomiser plasma)</td>
</tr>
<tr>
<td></td>
<td>1.5-3.5 cm (source plasma)</td>
</tr>
<tr>
<td>Plasma gas flow-rate for the atomiser plasma</td>
<td>none</td>
</tr>
<tr>
<td>Coolant gas flow-rate for the atomiser plasma</td>
<td>8.5-14.0 l min⁻¹ Ar</td>
</tr>
<tr>
<td>Injector gas flow-rate for the atomiser plasma</td>
<td>1.8-3.0 l min⁻¹ Ar</td>
</tr>
<tr>
<td>Plasma gas flow-rate for the source plasma</td>
<td>20-30 l min⁻¹ Ar</td>
</tr>
<tr>
<td>Coolant gas flow-rate for the source plasma</td>
<td>30 l min⁻¹ Air</td>
</tr>
<tr>
<td>Injector gas flow-rate for the source plasma</td>
<td>2.5-4.0 l min⁻¹ Ar</td>
</tr>
<tr>
<td>Sample solution aspiration rate</td>
<td>1.0-3.0 ml min⁻¹ (atomiser plasma)</td>
</tr>
<tr>
<td></td>
<td>3.0 ml min⁻¹ (source plasma)</td>
</tr>
<tr>
<td>Slit-width (bandpass)</td>
<td>5.0 mm (6.75 nm)</td>
</tr>
<tr>
<td>Slit height</td>
<td>16.6 mm</td>
</tr>
<tr>
<td>Chopper frequency</td>
<td>997 Hz</td>
</tr>
<tr>
<td>Time constant</td>
<td>1 second</td>
</tr>
<tr>
<td>Integration time</td>
<td>10 seconds</td>
</tr>
</tbody>
</table>
from 1000 μg ml⁻¹ stock solutions (BDH chemicals). The stock solutions (1000 μg ml⁻¹) for molybdenum and tungsten were prepared from molybdenum oxide and dodeca tungstosilicic acid, respectively. For source plasma high concentration solutions (20-50%) were prepared either from pure metal (99.9%) dissolved in appropriate spectrosol grade acid solution or from respective A.R grade salts as required.

5.3. Optimisation.

A systematic study was carried out to optimise various operating parameters of the plasmas and the monochromator entrance slits. An alternative variable search method was employed which is described in detail in Section 2.3.1. The typical operating conditions established for the determination of a number of elements are shown in Table 5.1.

5.4. Instrument modifications.

The modifications made to the ASIA system include the replacement of the modified Optica monochromator and the detection system with a Bentham computer controlled monochromator and Bentham detection system. The summary of these replacements is given in Table 5.2. A schematic diagram of the modified ASIA system is shown in Fig. 5.1.

The optical arrangement between the atomiser plasma and the monochromator entrance slits was also re-designed and is shown in Fig 5.2.

The modified system can be used in the emission mode by simply connecting the output from the pre-amplifier directly to the input of the Analog-to-Digital Converter and by-passing the Lock-in Amplifier.

5.4.1. Monochromator.

The Bentham monochromator body is made of a single aluminium casting with a rebated lid and is fitted with entrance and exit slits. The slit-widths are variable between 10 μm to 5 mm and have 20 mm height. The optical configuration is a symmetrical Czerny-Turner arrangement consisting of two collimating mirrors, two reflecting
Fig. 5.1. Schematic diagram of the modified ASIA system.
Fig 5.2. Modified optical design of the ASIA system.

L1, L2, L3 and L4: fused silica lenses
f=5.08cm and d=5.08cm.
C1 : chopper position in fluorescence
u1=v1=2f=10.16cm.  u2=30.48cm, v2=6.1cm
u3=8.16 v3=13.46
Chapter 5

mirrors and a diffraction grating having 2400 lines/mm, blazed at 250 nm and giving a reciprocal linear dispersion of 1.35 nm/mm with a maximum bandpass of 6.75 nm. It has a focal length of 300 mm and an aperture ratio of f/4.2. Also, below the floor of the monochromator is fitted a stepping motor for wavelength scanning. The monochromator was positioned on a stable optical table which was designed and constructed in the laboratory from angle iron. The monochromator entrance slit was aligned on the optical axis using a He/Ne laser.

![Graph](image)

Fig. 5.3 Radiant spectral coverage of 9558 QB PMT.

5.4.2. Stepping Motor Drive (SMD3B).

The SMD3B is a programmable stepping motor drive for use with the monochromator. The unit allows wavelength scanning completely controlled by the computer via an
IEEE/488 interface or manually from the front panel switches. The scan rate between 1 and 400 steps could be obtained, each step resulting in a wavelength change of 0.01 nm.

5.4.3. Power Amplifier (SMD2).

The SMD2 is a power amplifier which drives the stepping motor drive from the output of the SMD3B and is interfaced with the computer via IEEE/488 bus at SMD3B.

5.4.4. Photomultiplier Tube (PMT).

The photomultiplier tube is a "red sensitive" end window type, with 11 stages, S20 photocathode and a uv transmitting window (EMI 9558QB). The tube housing incorporates shielding against stray magnetic fields and radio frequency interference (RFI). It has maximum sensitivity around 400 nm wavelength and is kept ON continuously in order to stabilise the dark current. The radiant energy spectral coverage of the PMT is shown in Fig. 5.3. The spectral curve shows that maximum response from the PMT is obtained at a wavelength around 400 nm and covers almost all of the visible region.

5.4.5. 265 Current Pre-amplifier and 217 Bin (Power and Display unit).

The 265 current pre-amplifier is a current sensitive amplifier which features switched and IEEE/488 programmable sensitivity ranging from 1.0 μA to 1.0 A, dark current null and output switches. The unit receives the current signal from the PMT and amplifies the signal before sending it to the Lock-in Amplifier. The 217 Bin forms the power supply and the output display unit, which supplies power to the 265 current pre-amplifier and the Lock-in Amplifier and displays the integrated signal.

5.4.6. Lock-in Amplifier.

The amplifier features a reference channel, a fully frequency independent phase shifting facility, switched and continuously variable sensitivity, time constant control, large range a.c zero offset/zero check facilities and output switches. The amplifier receives
a reference signal from the chopper and an amplified a.c signal from the current pre-amplifier. The a.c signal modulated at the chopper frequency is demodulated by the Lock-in Amplifier and sent to the Analog-to-Digital Converter (ADC).

Table 5.2. List of modifications made to the original ASIA system.

<table>
<thead>
<tr>
<th>Component Description</th>
<th>Original set-up</th>
<th>Modified set-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochromator</td>
<td>Modified Optica, CF4</td>
<td>Monochromator Bentham Instruments, M300. computer controlled Stepping motor drive (Bentham, SMD 3B/IEEE) Power amplifier for SMD (Bentham, SMD2).</td>
</tr>
<tr>
<td>Photo multiplier tube</td>
<td>EMI 9789QB, 13 stage.</td>
<td>Photo multiplier tube EMI 9558QB, 11 stage.</td>
</tr>
<tr>
<td>Computer</td>
<td>Apple IIe, dual floppy drive with mono monitor.</td>
<td>Computer Opus II, IBM XT compatible, dual floppy drive with colour monitor.</td>
</tr>
<tr>
<td>Peripherals</td>
<td>Canon PW 1080A, 9 pin dot matrix printer.</td>
<td>Peripherals MP-165, 9 pin dot matrix printer and Hewlett Packard HP 7470A 2 pen plotter.</td>
</tr>
<tr>
<td>Current Amplifier</td>
<td>EG &amp; G, Model 5002.</td>
<td>Current Amplifier Bentham, Model 265HF (programmable) with display unit, Model 217.</td>
</tr>
</tbody>
</table>
5.4.7. 228 integrating ADC and IEEE/488 interface.

The unit is capable of executing conversions fast, the conversion time being 10 ms. It converts the signal to digital form and transfers it to the computer via an IEEE/488 interface.

5.4.8. Data processing.

The data processing is performed with the computer. The computer originally used, an Apple IIe 128K microcomputer, was replaced with an IBM compatible, Opus PCII 640K RAM with dual floppy drives. The computer system included the main unit, a colour monitor and a MP165 9 pin dot matrix printer. It was interfaced with the electronic system and the monochromator. A computer program provided by Bentham Instruments was used which was modified to take fluorescence signal measurements (see Appendix I).

5.4.9. Entrance optics.

The optical system originally used between the atomiser plasma and the monochromator consisted of two, 5.08 cm diameter, fused silica lenses (see Fig. 2.5). A 1:1 image of the part of the tail-flame was focussed onto the entrance slits of the monochromator in the original system. The new optical system consists of a single lens of 5.08 cm diameter which is used to focus the image of the atom cell (10x3 mm) in the atomiser plasma tail-flame onto the monochromator entrance slit. A study was performed to find the optimum magnification of the atom cell image to be focussed onto the monochromator entrance slit. Copper solution containing 1.0 ug ml⁻¹ was aspirated into the atomiser plasma while aspirating 20% copper solution into the source plasma at the optimum operating conditions for copper determination. The lens between the atomiser plasma and the monochromator and the monochromator itself were moved to get different magnification. Measurements of the copper solution were made at each setting of the monochromator and the lens. Each time the lens and monochromator were moved, optical alignment was checked with the help of a He/Ne laser and the position adjusted as necessary. It was found that the maximum fluorescence signal was obtained at magnification of 1:1.67 of the atom cell onto the monochromator entrance slit. This was in good agreement with the theoretical value.
of 1:1.67 obtained to completely fill the entrance slit of the monochromator. The height of the entrance slit was reduced to 16.7 mm to match it with the image size by placing a piece of blackened cardboard having a hole of size 5 x 16.7 mm, in front of the slit.

5.5. Operating procedure.

The procedure for the initiation of the two plasmas was the same as described in Section 2.2. However, the procedure for the operation of the electronic system and the monochromator was modified according to the requirements and is described below:

1. Insert Revised Bentham software floppy disk in drive A and the data floppy disk in drive B of the computer.

2. Switch ON the electronics and the computer. Allow ten minutes for the electronics to stabilise.

3. After the Bentham program is loaded enter date and operator name.

4. Using the "Measurement parameters" subroutine of the program from the main menu, enter the parameters as necessary.

5. Using the "Input" subroutine enter the start and end wavelengths for the wavelength scan.

6. Keeping the monochromator slits closed, press function key F5 to autozero the dark current of the photomultiplier.

7. Set the monochromator wavelength to the required position either, by pressing the F5 function key of the computer from the main menu and follow the instructions on the computer screen, or do manually with the switch.
located on the front panel of SMD3B, stepping motor drive. (Note. Before the manual operation press F10 function key of the computer.)

8. Open the monochromator entrance and exit slits to the required level.

9. Adjust the sensitivity controls on the 265 current pre-amplifier (if operated in the manual mode) and the 223 Lock-in Amplifier to obtain one third full scale output on the 217 Bin, display unit with the reference controls set to 0 or 90.

If the "O'load" indicator is illuminated increase the time constant setting. If the output rise time is excessively long, decrease the time constant.

Each time the sensitivity of the Lock-in Amplifier is changed, press the zero check switch and, if necessary adjust the offset control to bring the output to zero.

When meter indicates one third scale signal and the offset has been adjusted, use the reference controls to obtain a zero output on the meter. Switch in 90 or -90 as necessary to give a positive output on the meter. Now the lock-in is in phase with the applied signal and ready for use.

10. Press "F" key on the computer keyboard for taking the fluorescence measurements.
5.6. Noise considerations and Precision.

In order to determine the principle source of noise in AFS with this particular system, a noise study was carried out for copper at $\lambda$324.8-327.4 nm. This study enabled an estimate of the background noise and precision.

5.6.1. Evaluation of background noise on the atomic fluorescence signal intensity.

A series of experiments were carried out aspirating de-ionized water in the atomiser plasma and 20% copper solution into the source plasma at the optimum operating conditions for copper. The results obtained with each experiment are shown in Table 5.3. The following observations were made from this investigation:

i): A negligible signal was obtained when the monochromator entrance and exit slits were closed suggesting that the dark current due to thermionic emission from the PMT was effectively subtracted by the use of the autozero subroutine of the Bentham software.

ii): When the atomiser plasma was turned off and only the source plasma was in operation with 20% copper solution going into the plasma, about 74% value of the total blank signal was recorded. This indicated that reflection of the excitation source light off the surfaces including the lenses was contributing to the blank signal. Demers and Allemand,23 also observed similar behaviour with their AFS system. They obtained reflected light levels ranging from undetectable above the background noise to about 3 times the zinc detection limit signal.

iii): When both the plasmas were in operation and 20% copper solution was being aspirated into the source plasma while no de-ionized water was aspirated into the atomiser plasma, about 94% of the total blank signal value was obtained. This shows that 20% of the blank signal value (i.e., 94%-74%) was caused by turning the atomiser plasma r.f. ON. This could possibly be due to the r.f interference effect on the detection system.
Table 5.3. Background noise measurements with the modified ASIA system.

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>Slits shut/open**</th>
<th>mean signal intensity (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only atomiser plasma in operation and no solution going into the plasma.</td>
<td>shut</td>
<td>0.05</td>
</tr>
<tr>
<td>-ditto-</td>
<td>open</td>
<td>0.05</td>
</tr>
<tr>
<td>Only source plasma in operation and no solution going into the plasma.</td>
<td>shut</td>
<td>0.05</td>
</tr>
<tr>
<td>-ditto-</td>
<td>open</td>
<td>0.05</td>
</tr>
<tr>
<td>Only atomizer plasma in operation and de-ionized water going into the plasma.</td>
<td>open</td>
<td>0.05</td>
</tr>
<tr>
<td>-ditto-</td>
<td>shut</td>
<td>0.05</td>
</tr>
<tr>
<td>Only source plasma in operation and 20% Cu solution going into the plasma.</td>
<td>open</td>
<td>0.06</td>
</tr>
<tr>
<td>-ditto-</td>
<td>shut</td>
<td></td>
</tr>
<tr>
<td>Both plasmas in operation, 20% Cu solution going into the source plasma and de-ionized water into the atomiser plasma.</td>
<td>open</td>
<td>3.72 (3.86*)</td>
</tr>
<tr>
<td>Both plasmas in operation, 20% Cu solution going into the source plasma but, no solution going into the atomiser plasma.</td>
<td>open</td>
<td>5.14 (5.24*)</td>
</tr>
<tr>
<td></td>
<td>open</td>
<td>4.92*</td>
</tr>
</tbody>
</table>

* - These measurements were made using a 30 second integration time with the new atomiser plasma torch.  ** - 5 mm slit-width was used.

5.6.2. Effect of integration time on the noise.

To study the effect of integration time, an experiment was carried out aspirating de-ionized water into the atomiser plasma while 20 % copper solution was being aspirated into the source plasma, at the optimum operating conditions for copper. The
results obtained are shown in Fig. 5.4. The shape of the curve suggest that the noise on the signal is a combination of pink and white noise. In ICP-AES, the background is the flicker noise,\textsuperscript{49} which means that the magnitude of the noise remains constant with integration time. However, with this AFS system the results indicate that the magnitude of the noise decreases as the integration time is increased up to at least 50 seconds. This means that detection limits can be improved further by increasing the integration time of the measurements to about 50 seconds. Similar observations have been reported by Sanzolone and Meier\textsuperscript{50} for their Baird AFS system. They obtained an improvement of detection limits by a factor of about two when the integration time was increased from ten seconds to forty seconds.
5.7. Effect of slit-width on the atomic fluorescence signal.

To investigate the effect of slit-width on the atomic fluorescence signal of copper, an experiment was performed aspirating 1.0 μg ml⁻¹ solution into the atomiser plasma while aspirating 20% copper solution into the source plasma at the optimum operating conditions for copper determination. Measurements were made using various slit-widths. The results obtained are shown in Fig. 5.5 which reveal that a wide slit-width allows increase in radiant flux due to the contribution of fluorescence lines within the effective spectral band-width (6.75 nm).
5.8. Performance studies.

To study the performance of the modified system calibration curves were obtained for a number of elements. This was followed by the evaluation of detection limits.


Series of solutions ranging from $0.1 \, \mu g \, ml^{-1}$ to $100 \, \mu g \, ml^{-1}$ were prepared for copper, nickel, lead, barium, calcium, zinc, molybdenum, tungsten, chromium, and iron. Separate determinations were made for each element by aspirating these solutions into the atomiser plasma while aspirating a high concentration solution of the respective element into the source plasma, at the optimum operating conditions of the respective...
element. Plots of concentration against the observed fluorescence intensity were plotted and are shown in Fig 5.6 to Fig. 5.9. The results obtained show a linear response and each curve showing a correlation coefficient in the range 0.98-99.

![Graph](image)

Fig. 5.7 Calibration curves for: (A); copper and (B); calcium at 324.8-327.4 nm and 422.7 nm wavelengths, respectively. (See footnote in Fig. 4.14).

5.8.2. Detection limits.

The limit of detection for each element was investigated using the procedure described in Section 2.3.2. These detection limits were based on 3 standard deviations of the blank signal. The observed detection limits of a representative list of elements are summarized in Table 5.4.

All detectable lines of each element were examined and the line giving maximum fluorescence signal was utilized to calculate the detection limit. The detection limits
obtained with the modified ASIA system were at least 2 to 3.5 times better than those obtained with the original set-up, except for copper for which a 5 times improvement in detection limit was noted.

![Calibration curves for: (A) lead and (B) tungsten at 280.2-283.3 nm and 295.6 nm wavelengths, respectively.](footnote in Fig. 4.14)

In order to evaluate more closely the improvements of detection limit a comparison of these detection limits is made with the lowest values reported for HCL-ICP-AFS, ICP-AES, and AAS as shown in Table 5.5. It can be seen from the comparison table that for most of the elements detection limits with the modified ASIA are either equivalent or show moderate improvement over those reported for HCL-ICP-AFS and are better by about an order of magnitude for most of the elements than those for flame AAS. Whereas, in the case of a comparison with the detection limits reported for ICP-AES it was observed that the detection limits obtained with ASIA are comparable for nearly all the elements studied except for the refractory elements such as, tungsten and molybdenum. However, it should be noted that the detection limits reported for
ICP-AES are based on 2 standard deviations of the blank signal. The detection limits for tungsten and molybdenum were at least an order of magnitude worse than those reported for ICP-AES. This observation is not surprising because the temperature and chemical environment around the argon plasma is quite different in the long sleeve torch (Baird) than that in the short torch (Fassel) used in ICP-AES.

The detection limits for the refractory elements such as molybdenum, barium and chromium are better with the ASIA system than those reported for HCL-ICP-AFS. A possible explanation for this could be the inefficient excitation by the HCLs compared to the ICP excitation source. The HCLs output is primarily atomic resonance radiation and ionic transitions are inefficient to excite ionic fluorescence of elements such as barium (455.4 nm).

![Calibration curves for zinc and barium at 213.9 nm and 455.4 nm wavelengths, respectively.](image-url) (See footnote in Fig. 4.14.)
Table 5.4. Comparative detection limits obtained in fluorescence mode, ng ml\(^{-1}\).

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength, nm</th>
<th>Detection limits (3 SD)</th>
<th>Original ASIA set-up. (Ref. 89)</th>
<th>Modified ASIA set-up. (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(\Sigma 324.8-327.4)</td>
<td>2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>(\Sigma 357.9-360.5)</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>422.7</td>
<td>0.5</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>455</td>
<td>8</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>(\Sigma 248.3-249.1)</td>
<td>19</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>(\Sigma 231.1-232.5)</td>
<td>21</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>(\Sigma 280.2-283.3)</td>
<td>80</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>(\Sigma 313.3-317.0)</td>
<td>146</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>295.6</td>
<td>900</td>
<td>428</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>6</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.5. Comparative detection limits.

<table>
<thead>
<tr>
<th>Element</th>
<th>ASIA (this work)</th>
<th>Flame AAS (Ref. 151 &amp; 152**)</th>
<th>HCL-ICP-AFS (Ref. 53 &amp; 23*)</th>
<th>ICP-AES (Ref. 150)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>3.5</td>
<td>90</td>
<td>50*</td>
<td>0.87</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
<td>3</td>
<td>0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu</td>
<td>0.4</td>
<td>7</td>
<td>4</td>
<td>3.6</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>100</td>
<td>8</td>
<td>4.1</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>20</td>
<td>10</td>
<td>3.1</td>
</tr>
<tr>
<td>Ni</td>
<td>6</td>
<td>100</td>
<td>7</td>
<td>6.7</td>
</tr>
<tr>
<td>Pb</td>
<td>27</td>
<td>60</td>
<td>250</td>
<td>28</td>
</tr>
<tr>
<td>Mo</td>
<td>63</td>
<td>60</td>
<td>200</td>
<td>5.3</td>
</tr>
<tr>
<td>W</td>
<td>428</td>
<td>500**</td>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>3</td>
<td>0.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

It should be pointed out here that the detection limits are influenced by many experimental factors and that comparison of values measured by other workers employing different analytical techniques is possible only on a semiquantitative basis. Nevertheless, this comparison gives useful information, demonstrating that the ASIA system possesses to a high degree the characteristics required of a general purpose analytical instrument.
Chapter 6

Evaluation of a Desolvation System and a Modulation Device

6.1 Introduction

6.1.1 Aerosol desolvation

A wide variety of sample introduction devices are used for atomic spectrometric techniques. A review has been published which provides a comprehensive survey of sample introduction devices used for atomic spectrometry. Liquid sample introduction with pneumatic nebulisation is the most common approach used for plasma spectrometric determinations. It has been estimated that for ICP-AES 90% of the samples are introduced in the liquid form, 8% by electrothermal vaporisation, and 2% by other techniques, including the direct insertion and slurry nebulisation. Aerosols
provide the easiest means of introducing liquid samples into plasmas. The breakdown of the aerosol into an ICP proceeds in a number of steps; desolvation, that is evaporation of the solvent; evaporation of the dry aerosol particles; thermal dissociation of molecules; and finally the partial ionization of free atoms. A sufficiently high gas temperature, small particle size, and a long residence time are needed for adequate thermal evaporation and dissociation of aerosol particles.

Two methods have been used for nebulisation of liquid samples; pneumatic nebulisation and ultrasonic nebulisation.

Pneumatic nebulisation has been used in most practical analysis, because it is simple, does not require expensive equipment, and usually produces accurate and precise results. The main problem associated with this type of nebulisation is that the analyte transport efficiency into the plasma is quite low (~1%) despite all efforts to improve this value.

Ultrasonic nebulisation, on the other hand can produce a high number-density aerosol with small and uniform droplet size and an increased analyte transport efficiency (~10%). Usually a desolvation system is connected in order to remove excess solvent vapour before aerosol introduction into the plasma. In ultrasonic nebulisation the surface of the liquid is exposed to ultrasound generated with an oscillating piezo-electric crystal. Under proper conditions, a very fine dense aerosol is produced with a narrow droplet size distribution (1-5 μm). The size of the aerosol can be varied by changing the frequency of the ultrasound; the higher the frequency, the smaller the droplet size produced.

The ultrasonic technique is very effective for the improvement of sensitivity, normally resulting in a ten fold increase in sensitivity compared with pneumatic nebulisation. However, there are some disadvantages associated with ultrasonic nebulisation; such as, it is complicated, needs expensive equipment, has problems in handling solutions with high salt contents, unstable and needs long clean-up time. So far these problems have not been convincingly overcome to the extent that ultrasonic nebulisation could be accepted for routine analysis of real samples.
As described earlier, pneumatic nebulisation transfers ~1% of the analyte into the plasma. It is clear from this that there is a great potential for improvement in terms of delivery of aerosol to the plasma, by simply not rejecting ~99% of the analyte solution into the drain. Therefore, there is a need for developing a technique which could transfer virtually all of the solution nebulised, into the plasma. One way of achieving this is heating the aerosol chamber and desolvating the aerosol by connecting the outlet of the aerosol chamber to a reflux condenser prior to its introduction into the plasma. This approach has been studied previously\textsuperscript{155,156} with some success. Veillon and Margoshes\textsuperscript{155} have investigated a heated spray chamber sample introduction system for ICP and have reported an overall transport efficiency of 35% with the system. Greenfield and Smith\textsuperscript{156} have used a sample introduction system by which sample solutions in microlitre quantities were introduced into the plasma torch using a heated spray chamber. The device was applied successfully for the determination of trace elements in oil, organic compounds and blood. More recently, Uchida et al.\textsuperscript{157} have reported a desolvation device applied to a capacitively coupled microwave plasma and ICP. They estimated that 50% of the analyte (Mn) was transferred to the plasma with 50 and 16 times improvement in sensitivity by capacitively coupled plasma and ICP, respectively, compared to conventional pneumatic nebulisation.

In this chapter an evaluation of a desolvation system is described which was applied both, to the atomiser plasma and the source plasma.

6.1.2 Sample Modulation

In atomic spectroscopy dc to ac signal conversion is usually carried out with a mechanical chopper positioned between the optical source and the detector. Since the chopper modulates the total signal, the source background, source flicker and the atomic lines interfering with the analytical measurement are detected along with the analytical signal of interest by ac electronics.

An alternative approach that has been used to recover the actual analytical information of interest is sample modulation. In this method analyte is periodically introduced into
the source and is selectively detected using an ac-amplifier. The result is that source background stays at the dc levels and a considerable increase in the signal to noise ratio is realised.

Several modulation techniques and devices have been reported for selective analyte signal modulation. Bojovic and Anti-Jovanoic\textsuperscript{158} proposed a dual nebuliser system supplying alternately two aerosol streams to the flame. Modulation was accomplished by switching the sample aerosol stream and an auxiliary solvent aerosol stream by means of a rotating disc moving at a constant speed (See Fig. 6.1). They claimed almost complete suppression of the background with 10 fold improvement in detection limits. Later the same group\textsuperscript{159} described another device in which a rotating chopper/disc alternatively blocked the two aerosol streams. Sample modulation schemes\textsuperscript{160} have even employed sewing-machine mechanisms to dip the end of a sample inlet tube into and out of a reservoir of analyte solution. Patterson\textsuperscript{161} described a motor driven rotary
valve for the repeated (0.2 Hz) alternating introduction of sample and blank solution into an atomic absorption spectrometer. He applied the device successfully to low level determinations of boron in rock samples. Recently, Steele and Hieftje\textsuperscript{162} have described a novel modulation device to pulsing the aerosol in the spray chamber for flame emission spectroscopy and reported two fold improvement in detection limits (Fig. 6.2). Later\textsuperscript{163}, they applied the device for use in ICP-AES but, failed to get similar improvements in detection capability as with flame due to the modulation of background emission from the ICP along with the analyte signal.

![Fig. 6.2 Block diagram of sample modulation system.](image)

The possibility of the use of modulation of aerosol has been investigated with the aim of applying the modulation device to either of the two plasmas used in the ASIA instrument thus eliminating the use of a mechanical chopper to modulate the source plasma radiation and thereby reducing the distance between the two plasmas. The results of this study are reported here.
Fig. 6.3 Schematic diagram of various configurations of the desolvation apparatus used.
6.2 Experimental

6.2.1 Apparatus

6.2.1.1 Aerosol desolvation system

The experimental arrangement used is shown in Fig. 6.3. The desolvation unit was made of Pyrex glass and consisted of two parts; the spray chamber, and a condenser. The spray chamber used was 15 cm long and had an I.D of 5 cm. The spray chamber was closely wound with a heating cord (5 mm O.D., and 8 ft. long, Electrothermal Engg. Ltd. U.K.) and was enveloped with glass wool. The temperature of the heating cord was controlled by a laboratory built temperature controller. The spray chamber contained a pocket to hold a thermometer 0-360 °C. The drain of the spray chamber was connected to a water trap to maintain pressure inside the system. The condenser was 40 cm long and had bulbs to increase the aerosol residence time in the condenser. The drain of the condenser was also connected to a water trap. In Fig. 6.3 (a) and (b) the spray chamber was connected to the condenser by a 1 cm I.D flexible PVC tubing whereas, in Fig. 6.3 (c) the spray chamber was connected to the condenser by a T-shaped glass tube, the drain from which was connected to a water trap.

Fig. 6.4 Schematic diagram of the aerosol modulation device.
Some changes in the instrument optical arrangement were made to perform emission experiments. The lens L2 as in Fig. 5.2 was moved towards the chopper to bring 1:1 image of the source plasma onto the silver faced mirror placed at the atomiser plasma position. The silver faced mirror was positioned at a 45° angle to reflect emission light from the source plasma onto the entrance slits of the monochromator. The lens L3 was positioned to give a 1:1 magnification of the source plasma image of the radiation reflected from the mirror onto the monochromator entrance slits.

6.2.1.2 Aerosol Modulation Device

Experimental arrangement of the aerosol modulation device is shown in Fig. 6.4. The device was connected at one end to the spray chamber just above the aerosol exit, by means of 10 mm ID pvc flexible tubing and the other end was connected to the plasma injector tube with a similar size tubing. Aerosol was chopped by a slotted perspex disc connected to an electric motor by a mechanical linkage through a slotted wheel. The slotted wheel had an equivalent number of slots to the holes in the modulator unit. The motor speed was controlled by an electrical circuit that had a speed controller to regulate the speed. Modulation frequencies over the range 1-30 Hz could be obtained with the device. A schematic diagram of the motor controller circuit and electronic circuit to send a reference signal to the Lock-in Amplifier, is given in Fig. 6.5.

![Fig. 6.5 Schematic diagram of the electronic circuitry for the aerosol modulation device.](image-url)
6.2.2 Reagents and chemicals

Copper solutions above 1000 µg ml\(^{-1}\) concentrations were prepared from AR grade copper nitrate, dissolved in 5 M nitric acid. Whereas, solutions below 1000 µg ml\(^{-1}\) concentrations were prepared from 1000 µg ml\(^{-1}\) copper nitrate solution (BDH chemicals) and diluting with de-ionized water as necessary.

6.2.3. Aerosol desolvation system; Measurement procedure

6.2.3.1 Optimisation

A systematic study was carried out to determine the operating conditions for copper. For source plasma the parameters; power, coolant gas, plasma gas, injector gas, solution flow-rate and the observation height were optimised in a cyclic manner. Similarly all the parameters for the atomiser plasma including the monochromator slits were optimised. The heating temperature of the spray chamber was also optimised (See Fig. 6.6).

![Graph](image)

Fig. 6.6 Effect of temperature on the emission signal of copper at 324.8 nm wavelength, using a slit-width of 50 µm (See footnote in Fig. 4.14).
6.2.3.2 System efficiency.

The analyte transport efficiency \( E \) was measured indirectly. A known volume of 100 \( \mu g \) ml\(^{-1}\) and 2000 \( \mu g \) ml\(^{-1}\) copper solution was aspirated into the heated chamber at the optimum temperature (200 °C) and the condenser drain was collected, made up to the mark in a volumetric flask after diluting with de-ionized water and analysed. The analyte transport efficiency was calculated using the formula:

\[
E = \frac{C_A - C_B}{C_A} \times 100
\]

CA = Cu concentration in the sample aspirated.
CB = Cu concentration in the condenser drain.

Fig. 6.7 Emission curves of growth for copper at 324.8 nm wavelength: (a); using normal pneumatic nebulisation and (b); using heated spray chamber-desolvation system as in Fig. 6.3 (c).

The desolvation efficiency was also measured indirectly by aspirating a measured volume of de-ionized water into the heated spray chamber at the optimum conditions.
and collecting the condenser drain. The difference between the two volumes was taken as the amount of undesolvated aerosol, assuming that negligible amount of water was left in the condenser.

6.2.3.3 Desolvation system on the source plasma

Emission curves of growth for copper were obtained by aspirating increasing concentrations of copper solutions into the source plasma acting as an emission source. The plot (a) shown in Fig. 6.7, was obtained using the conventional pneumatic nebulisation without desolvation. Whereas, the plot (b) shown in Fig. 6.7, was obtained using the desolvation system as in Fig. 6.3 (c). The wavelength and the slit settings of the monochromator were 324.8 - 327.4 nm and 50 μm, respectively.

The performance of the system was evaluated by determining the detection limit for copper. A 1600 μg ml⁻¹ copper solution was aspirated into the source plasma using the desolvation system at the optimum conditions, while aspirating 1.0 to 10.0 μg ml⁻¹ copper solution into the atomiser plasma. The detection limit was calculated using the method described in Section 2.3.2.

6.2.3.4 Desolvation system on the atomiser plasma

A dual spray chamber system as shown in Fig. 6.3 (b), was evaluated in an attempt to reduce the noise on the analyte signal. The system performance was evaluated by determining the detection limit for copper, using the desolvation systems shown in Fig. 6.3 (c). A 20% copper solution was aspirated into the source plasma, while aspirating copper solutions (0.50 - 5.0 μg ml⁻¹), into the atomiser plasmas using the experimental set up as shown in Fig. 6.3 (c). Chart recordings were obtained with and without heating of the spray chamber, by aspirating de-ionized water into the atomiser plasma and 20% copper solution into the source plasma using the desolvation apparatus as shown in Fig. 6.3 (b). The slit settings of the monochromator for these experiments were 5 mm.
Table 6.1 Numerical values of the operating parameters of the instrument for copper.

(a): Emission mode.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source plasma</th>
<th>Atomiser plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>Coolant flow-rate (l min(^{-1}))</td>
<td>30 Air</td>
<td>-</td>
</tr>
<tr>
<td>Plasma gas flow-rate (l min(^{-1}))</td>
<td>30 Ar</td>
<td>-</td>
</tr>
<tr>
<td>Injector gas flow-rate (l min(^{-1}))</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td>Solution flow-rate (ml min(^{-1}))</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>Viewing height above the coil (cm)</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Slits (µm)</td>
<td>50</td>
<td>-</td>
</tr>
</tbody>
</table>

(b) Fluorescence mode.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source plasma</th>
<th>Atomiser plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>6.0 (7.3(^*))</td>
<td>0.453</td>
</tr>
<tr>
<td>Coolant flow-rate (l min(^{-1}))</td>
<td>30 Air</td>
<td>14</td>
</tr>
<tr>
<td>Plasma gas flow-rate (l min(^{-1}))</td>
<td>30 Ar</td>
<td>-</td>
</tr>
<tr>
<td>Injector gas flow-rate (l min(^{-1}))</td>
<td>1.8 (4.0(^*))</td>
<td>1.8 (2.8(^*))</td>
</tr>
<tr>
<td>Solution flow-rate (ml min(^{-1}))</td>
<td>2.4 (3.0(^*))</td>
<td>2.4 (2.5(^*))</td>
</tr>
<tr>
<td>Viewing height above the coil (cm)</td>
<td>2.5</td>
<td>10.0</td>
</tr>
<tr>
<td>Slits (mm)</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Temperature (C)</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) normal pneumatic nebulisation i.e., without desolvation.
6.2.4. Aerosol Modulation Device

Under the normal operation of the instrument, the chopper positioned between the source and the atomiser plasmas, is operated at 997 Hz. An experiment was performed to investigate the effect of reducing the chopper frequency by aspirating 1.0 μg ml\(^{-1}\) copper solution into the atomiser plasma while, aspirating 20% copper solution into the source plasma using the normal pneumatic nebulisation for the ASIA system.

To study the performance of the aerosol modulation device an experiment was carried out, aspirating 20% copper solution into the source plasma, while varying concentration copper solutions up to 100 μg ml\(^{-1}\) were introduced into the atomiser plasma.

6.3 Results and Discussion

6.3.1 Desolvation system: Optimisation and Emission curves of growth

The experimental variables optimised for copper, in both the fluorescence mode and emission mode are shown in Table 6.1. Figure 6.6 shows the effect of chamber temperature on the copper emission intensity. It was noticed that maximum S-B (signal minus background) was achieved at 120 °C. Above this temperature increase in S-B was small. However, 200 °C temperature was used to ensure complete evaporation of the water in the aerosol.

Emission curves of growth for copper were constructed using the configuration of the desolvation apparatus shown in Fig. 6.3 (c). The plots of these curves (See Fig. 6.7) shows that an increase of about 50 times of copper emission intensity is achieved when a desolvation system is used, compared to conventional nebulisation, on the source plasma. However, it was noticed that above 1600 μg ml\(^{-1}\) copper concentration emission intensity drops. A possible explanation for this behaviour could be the black copper oxide deposits observed on the inner walls of the heated spray chamber when high concentration copper solutions were aspirated.
6.3.2 Desolvation efficiency

The efficiency of the condenser in terms of its effectiveness in removing water from the aerosol was calculated. The efficiency experiment was performed at 200 °C, at which temperature all the water aspirated and nebulized was completely evaporated in the spray chamber. An aerosol was not observed at the exit of the condenser when de-ionized water was introduced into the system. More than 90% of the water nebulized was found in the drain. The analysis of the condenser drain when 100 μg ml⁻¹ copper solution was aspirated into the desolvation system showed ~29% copper in the drain whereas, when 2000 μg ml⁻¹ copper solution was aspirated ~36% of copper was found in the drain. One possible explanation for this behaviour could be that as the concentration of dry aerosol particles increases; the probability of the particles sticking to the walls of the condenser increases, which are then washed into the drain. This could also be one of the reasons of the drop of emission intensity above 1600 μg ml⁻¹ copper concentration (See Fig. 6.7).

![Diagram](image)

**Fig. 6.8 Experimental arrangement of the injector gas by-pass used for the desolvation apparatus.**

6.3.3 Signal stability

The plasma became unstable as the heating of the spray chamber was turned "ON" and frequently extinguished at temperatures above 50 °C. However, some stability was gained by by-passing the nebuliser gas as shown in Fig. 6.8. Initially to form a stable
plasma, the aerosol tube immediately above the condenser was clamped and the injector
gas was released through the by-pass. After a stable plasma was formed, the injector
gas flowing through the by-pass was gradually decreased with the help of a mass
flow-controller and at the same time the clamp was loosened to allow dry aerosol into
the plasma injector tube. The plasma stability was slightly gained, enough to take
some measurements. Presumably, instability of the plasma was caused by random
pressure pulses induced in the aerosol gas stream. These variations in the pressure of
the gas stream were confirmed by the observation of aerosol flow at the exit of the
condenser. Pressure fluctuations might be caused by the large aerosol droplets as they
hit the heated walls of the spray chamber. The plasma was observed to periodically
"bounce" and intensity measurements of acceptable reproducibility could not be made.

In an attempt to find the reason of high noise on the signal intensity a dual spray
chamber desolvation system was arranged as shown in Fig. 6.3 (b) for the atomiser
plasma. The double pass spray chamber before the heated spray chamber allowed only
fine aerosol droplet to enter the heating chamber and discarded large droplets into the
drain. The results obtained indicated decrease in the noise on the signal. Chart recorder
tracings were obtained for the de-ionized water, with and without heating of the spray
chamber. A comparison of these results show the extent of noise (See Fig. 6.9) even
after the removal of large aerosol droplets.

6.3.4 Performance of the desolvation system

The system performance was evaluated in terms of detection limits. A comparison of
copper detection limits obtained with and without the use of desolvation system is
given in Table 6.2. The results showed that detection limit for copper was worse with
the desolvation system on either the atomiser plasma or the source plasma, compared
to those obtained with the normal ASIA set up. The reproducibility of intensity
measurements expressed as the relative standard deviation in the total fluorescence
intensity was established to be in the range 0.57 - 0.83 % at concentration levels of 5.0
- 10.0 µg ml⁻¹. The standard deviations increased to ~9% at concentration levels ~10
times the detection limit.
6.3.5 Aerosol Modulation device

6.3.5.1 Measurement procedure, Results and Discussion

The investigation of the effect of reducing chopper frequency below 997 Hz showed a negligible effect on the fluorescence signal and the noise level until 5 Hz, at which frequency the noise on the copper fluorescence signal and the background was quite significant. At 100 Hz frequency it was impossible to lock the signal with the reference due to noise causing jitters in the display needle of the lock-in Amplifier unit. However, these results indicated that it would be possible to operate the modulation device between 10-30 Hz frequencies without any serious interference on the detection electronics.
Table 6.2 Analytical evaluation of various configurations of the desolvation apparatus used for copper in the fluorescence mode of the ASIA system.

<table>
<thead>
<tr>
<th>Desolvation apparatus as in</th>
<th>Concentration $\mu$g ml$^{-1}$</th>
<th>%RSD</th>
<th>Detection limit $\mu$g ml$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a): Desolvation system on the atomiser plasma.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fig. 6.3 (b)</td>
<td>0.50</td>
<td>3.75</td>
<td>55.9</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>Fig. 6.3 (c)</td>
<td>1.00</td>
<td>8.35</td>
<td>98.6</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>0.57</td>
<td>-</td>
</tr>
<tr>
<td>(b): Desolvation system on the source plasma.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fig. 6.3, (c)</td>
<td>1.00</td>
<td>8.79</td>
<td>103.09</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.83</td>
<td>-</td>
</tr>
<tr>
<td>(c): Conventional pneumatic nebulisation.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Normal ASIA set-up</td>
<td>0.005</td>
<td>3.62</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.14</td>
<td>-</td>
</tr>
</tbody>
</table>

The device was connected to the sample introduction system for source plasma and the chopper was removed. The performance study of the aerosol modulation device showed that no fluorescence signal was detectable until, 100 $\mu$g ml$^{-1}$ solution was introduced into the atomiser plasma, at which concentration a small noisy signal was obtained. Presumably, mixing of the aerosol was occurring after it was chopped by the disc moving at 20 Hz speed. Later, the device was applied to the atomiser plasma but no improvement in the fluorescence signal was noticed. A possible means of reducing the aerosol mixing after it is chopped, is to reduce the distance between the
device aerosol outlet and the plasma injector tube. Unfortunately, this could not be achieved with the present set up of the ASIA system. Therefore, further work on the device was abandoned.
7.1. Introduction.

In AFS as in all other spectrometric methods of analysis interference occurs as a result of a number of factors including scattering of primary source radiation, incomplete sample volatilisation which results in severe solute vaporisation interferences, stable compound formation, ionization and fluorescence quenching interference.

Early investigations\textsuperscript{164-165} on the analytical utility of AFS have been performed with H\textsubscript{2}-air or H\textsubscript{2}-O\textsubscript{2}-Ar combustion flame atomisers. These flames have been restricted to situations in which relatively volatile elements are contained in essentially matrix free solutions.\textsuperscript{166} High temperature N\textsubscript{2}O-C\textsubscript{2}H\textsubscript{2} flames have been utilized, but the high background emission from the flames and fluorescence quenching by combustion products have necessiated the use of ICP as atomisation cell.
Although ICP is not totally free from interferences, it can be considered as an atomisation cell with fewest possible interferences in AFS. The use of an inert atmosphere in the ICP and due to the small quenching cross-section of the argon used, fluorescence quenching are is at a minimum. The common interferences which have been cited in the literature published to date, are described as follows:

7.1.1. Physical Interferences.

The common types of physical interferences that have been experienced with AFS measurements are radiofrequency interference and background noise, scattering interference and to a lesser extent spectral interferences. The radiofrequency and background noise interferences have been described in detail in Section 1.8.

7.1.1.1. Light Scattering Interference and its correction.

ICP-AFS In particular with resonance transitions, light scattering has been found to be a significant interference as it results in reduced signal to noise ratio (SNR) degrading detection limits. Additional background signal resulting from this may be interpreted erroneously to high analyte concentrations.\(^{167}\) Scattering of excitation source radiation occurs due to the scattering by the non volatilized particles (matrix). It can also be due to mirror reflections. Haarsma et al.\(^{168}\) have reported large decreases in scatter signal for cadmium and zinc when perchloric acid was added to the scatter producing samples.

7.1.1.2. Spectral Interferences.

Atomic fluorescence spectrometry is said to be less susceptible to spectral interferences than ICP-AES, because fluorescence spectra contain fewer lines than spectra produced by collisional excitation (ICP-AES) and also due to the different quantum efficiencies of the elements which decreases spectral interference. Non-resonance fluorescence has been advocated for overcoming the spectral interferences.\(^{67}\) Kosinski et al.\(^{73}\) observed no spectral overlap of iron at 370.925 nm on the yttrium emission at 371.030 nm, when the monochromator entrance slit was increased (50 fold), in contrast to the emission spectra.
The spectral selectivity of ICP-AFS has been demonstrated by Demers and Allemand,23 In their study they observed that interference effect was significantly less compared to AAS measurements, except for nickel interference on antimony, where they found the two techniques to be comparable.

7.1.1.3. Transport Interferences.

This type of interference is associated with the production, transport, and desolvation of aerosol particles in the nebuliser-plasma system. Variations in the contents (acid or dissolved solids) from one solution to another can alter the efficiency of nebulisation. Nagashima and Tanaka169 reported interference due to sulphuric acid when analysing niobium-tantalum minerals by ICP-AES. They recommended matrix matching of calibration standards and sample solutions. Desolvation matrix effects due to the presence of phosphoric acid have been reported.170 The interference effect was eliminated by heating the spray chamber to 240 °C temperature. Greenfield et al.171 examined physical interferences when solutions in high acid concentration were nebulised into the ICP. They observed a decrease in signal intensity for a number of elements and attributed it to the aspiration and nebulisation system rather than to the plasma source.

7.1.2. Chemical and ionisation Interferences.

Chemical interferences caused by the species such as aluminium, phosphorus, sodium, potassium, and phosphate ions are small in ICP compared to flames because of high temperature, long residence time and inert atmosphere in the plasma. But still they can cause severe degradation of detection limits.

Monataser and Fassel,22 studied interference effects of a number of species such as aluminium, calcium, potassium, magnesium, phosphates, etc. and found about 10% depression in the AF signal of these elements when 10,000 fold excess of the interferents were present in the solution and attributed this to the chemical interferences effect occurring in the plasma. Demers and Allemand,23 in their investigation of interference effect of phosphate ions and aluminium on calcium and zinc observed a classical "Knee" effect on calcium fluorescence signal intensity at low r.f powers. However, the effect was eliminated using high r.f powers. On the other hand, they
found interference effect due to phosphate ions and aluminium on zinc to be of complicated behaviour, showing a depression in zinc fluorescence signal intensity at low r.f powers and observed slight enhancement in fluorescence signal of zinc at high r.f powers.

Winefordner and coworkers,4,5,6,17 have also investigated interference effects of potassium, aluminium, sodium, and potassium on the calcium atomic and ionic fluorescence signal.

Kosinski et al.,7 in their study of interference effects observed a decrease in atomic fluorescence signal intensity of calcium in the presence of aluminium at 0.75 kW power. They attributed this depression effect to refractory oxide formation and found to decrease gradually as the power in the torch was increased to 1.2 kW. In an another study of interference effects, Kosinski et al.,6 reported an enhancement in calcium ionic fluorescence at 394.4 nm with the addition of aluminium and sodium. They attributed this effect to the possible change of atom and ion distributions in the plasma. In addition to this, they also studied the effect of the presence of phosphorus on calcium ionic fluorescence and observed a slight suppression in calcium AF signal which they attributed to the increase in sample solution viscosity.

Krupa et al.,7 in their study found no depression or enhancement of calcium fluorescence signal in the presence of phosphate up to 50,000 μg ml⁻¹. However, in the presence of sodium they observed enhancement of atomic and depression of ionic calcium fluorescence. Huang et al.,17 investigated interference effect of potassium on calcium atomic fluorescence signal intensity using an extended sleeve torch. They observed a 4-fold increase in the fluorescence signal of calcium and a decrease of greater than 100-fold on the calcium ion line in the presence of 1000 μg ml⁻¹ of potassium.

Gilson and Horlick,17 investigated interference effects of sodium on atomic and ionic fluorescence signal for a variety of operating conditions. They observed a depression in calcium ionic fluorescence with the addition of sodium which they found to lessen as the power and the observation height above the coil was increased. They found the effect of injector gas flow-rate on the calcium ionic fluorescence in the presence of sodium to be spatially dependent at low flow-rates.
In general, it can be concluded that chemical interference effects do occur in ICP-AFS and could be minimised or eliminated by a careful choice of operating parameters such as power in the plasma, observation height above the coil, etc.

In the work to be described here, the results of a study carried out with the ASIA system to investigate the interference effect of high concentration of interferents on a number of elements, is presented. A comparison of the results obtained is made with those obtained from a commercial ICP emission spectrometer.

7.2. Chemicals.

Most of the solutions used in this study were provided by Albright and Wilson Ltd., Oldbury. Stock solutions of elements containing 1000 µg ml\(^{-1}\) concentration were made up in 'Spectrosol' acids using materials as follows:

- **Ca**: CaCO\(_3\) in 9% v/v HCl.
- **Ni**: Ni in 9% v/v HCl.
- **Mg**: Mg in 9% v/v HCl.
- **As**: As in 6% v/v HCl.
- **Sn**: Ammonium Chloro Stannate in 9% v/v HCl.
- **Cu**: CuO in 9% v/v HCl.
- **V**: V in 6% v/v HCl. MIBK - diluted in 5% v/v HCl.
- **Pb**: Standard stock solution, 1000 µg ml\(^{-1}\) in N HNO\(_3\) (BDH Chemicals).

Also, 20 µg ml\(^{-1}\) element solutions were made up in 5% v/v HCl 'Spectrosol' from 1000 µg ml\(^{-1}\) BDH stock solutions in the form of two groups of mixtures i.e., one mixture contained Cr, Ni, Mn, Co, Pb, V, Cu, Zn, and Cd and the other contained Ca, Mg, Al, Si, Na, Sr, B, Fe, and K.

To obtain atomic fluorescence signal for aluminium, all interfering solutions studied for aluminium including the 20 µg ml\(^{-1}\) Al solution, were made up in 80% ethanol.
7.3. Instrumentation.

The emission results were provided by Albright and Wilson Ltd. company which were obtained using a multielement, Baird PS-2 Spectrovac ICP emission spectrometer. The fluorescence results were obtained using the ASIA system which is described in detail in chapter 5.

7.4. Optimisation.

For studies with the ASIA system optimisation of operating conditions was carried out using an alternating variable search method. Typical operating conditions are given in Table 5.1 (chapter 5). The operating conditions with the Baird PS-2 Spectrovac instrument are shown in Table 7.1 and the emission measurement wavelengths for the elements studied are shown in Table 7.2.

7.5. Interference studies.

To investigate the possible interference effect of high concentration interferent element solutions and reagents on a number of elements, wavelength scans were obtained. The elements studied included, aluminium, calcium, cobalt, chromium, lead, magnesium, managanese, nickel and zinc whereas, the interferent solutions included, 1000 μg ml⁻¹ solutions of calcium, lead, arsenic, tin, copper, and vanadium, 1100 μg ml⁻¹ solution of nickel, 6% orthophosphoric acid, 0.1% and 1% solutions of methylisobutylketone. A 5% hydrochloric acid solution was used as a blank in this study.
Table 7.1 Operating conditions of Baird PS-2 Spectrovac instrument.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector gas flow-rate 1 min⁻¹</td>
<td>1.8</td>
</tr>
<tr>
<td>Coolant gas flow-rate 1 min⁻¹</td>
<td>30 Nitrogen</td>
</tr>
<tr>
<td>Plasma gas flow-rate 1 min⁻¹</td>
<td>3.8 Argon</td>
</tr>
<tr>
<td>Power kW</td>
<td>2.0</td>
</tr>
<tr>
<td>Viewing height, mm</td>
<td>12</td>
</tr>
<tr>
<td>Range of scan</td>
<td>± 1.07 A second order</td>
</tr>
<tr>
<td>Integration time, sec.</td>
<td>1.0</td>
</tr>
<tr>
<td>No. of points per scan</td>
<td>150</td>
</tr>
<tr>
<td>No. of integrations per point</td>
<td>1</td>
</tr>
</tbody>
</table>

The nebuliser used was Meinhard TR-30-A3.

Table 7.2 Wavelengths used in emission measurements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength, nm</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>396.15</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>205.55</td>
<td>2</td>
</tr>
<tr>
<td>Zn</td>
<td>213.86</td>
<td>2</td>
</tr>
<tr>
<td>Co</td>
<td>228.62</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>231.6</td>
<td>2</td>
</tr>
<tr>
<td>Mn</td>
<td>257.61</td>
<td>2</td>
</tr>
<tr>
<td>Mg</td>
<td>279.55</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>283.31</td>
<td>2</td>
</tr>
<tr>
<td>Ca</td>
<td>317.93</td>
<td>2</td>
</tr>
</tbody>
</table>
Each wavelength scan was obtained by aspirating an interferent solution into the atomiser plasma while aspirating a high concentration analyte element solution into the source plasma at the optimum operating conditions of the analyte element. Wavelength scans were obtained in steps of 0.1 nm.

Also measurements were made at fixed wavelengths for the interference studied. For all these measurements a variable slit-width in the range 5.0 mm to 0.3 mm was used.

7.6. Analysis of cupronickel alloy for zinc.

A calibration curve was obtained by aspirating a series of zinc solutions with increasing concentration, into the atomiser plasma while a fixed high concentration zinc solution was aspirated into the source plasma at the optimum operating conditions for zinc determinations. These solutions were matrix matched by adding required amount of concomitant elements into pure zinc solutions. Fluorescence measurements were made using 10 seconds integration time and a slit-width of 5.0 mm at 213.8 nm wavelength.

7.7. Results and discussions.

The high concentration solutions used for introduction into the source plasma have been optimised before, except for magnesium and manganese. To find optimum high concentration solutions for these two elements excitation curves of growth were obtained as usual by aspirating a fixed low concentration solution into the atomiser plasma while aspirating increasing concentration solutions into the source plasma. The results obtained are shown in Fig. 7.1 and Fig. 7.2. Solutions containing 20% manganese and 10% magnesium were found to give maximum atomic fluorescence signal.

7.7.1. Interference studies.

To aid in visualisation of the possible interference effect of the interferent solution on analyte elements spectral scans obtained are presented in Fig. 7.3 to Fig. 7.10, for the elements for which some interference effect was observed. No interference effect was noted on copper, chromium, cobalt and zinc due to the interferents studied. However, small values were recorded for the interferents investigated on these elements which
Fig. 7.1 Excitation curve of growth for Mg while aspirating a 20μg ml⁻¹ Mg solution into the atomiser plasma and aspirating increasing concentration Mg solutions into the source plasma, at 285.2 nm wavelength (See footnote in Fig. 4.14).

Fig. 7.2 Excitation curve of growth for Mn while aspirating a 20 μg ml⁻¹ Mn solution into the atomiser plasma and aspirating increasing concentration Mn solutions into the source plasma, at 279.5-280.1 nm wavelength (See footnote in Fig. 4.14).
could be due to a slightly increased baseline noise. In order to quantify the interference effect in concentration units, calculations were made. As an example the effect of calcium on aluminium:

5% hydrochloric acid signal : 0.832 nA
20 µg ml⁻¹ aluminium signal : 21.22 nA
1000 µg ml⁻¹ calcium signal : 0.949 nA

Apparent aluminium concentration from 1000 µg ml⁻¹ calcium : \(0.117/20.39 \times 20 = 0.114 \mu g ml^{-1}\).

The results obtained are summarised in Table 7.3.

The spectral scan of 1000 µg ml⁻¹ calcium to investigate the interference effect on aluminium using 5 mm slit-width showed a high interference effect (See Fig. 7.3). The fluorescence spectrum of the same interferent solution was repeated using a freshly prepared high concentration aluminium solution for the source plasma and the monochromator slits were reduced to 0.3 mm (see Fig. 7.4). The results obtained showed that the interference effect produced was presumably due to the spectral broadening interference which was reduced when narrow slits were used thus giving an improved resolution. This interference effect resulted in a false signal equivalent to an apparent concentration of 0.114 µg ml⁻¹ aluminium.

Fig. 7.5. show the study of interferents on lead using the maximum slit-width (5 mm) available with the system. It was found that 1000 µg ml⁻¹ magnesium solution produced a noisy signal between 280 to 286 nm wavelength. An apparent concentration of lead in 1000 µg ml⁻¹ magnesium was found to be 1.3 µg ml⁻¹. In an effort to define more clearly the nature of interference effect the wavelength scan was repeated using a narrow slit-width and it was found that the interference effect was reduced. This was again, attributed to the spectral broadening interference that produced a false signal equivalent to an apparent concentration of 1.17 µg ml⁻¹ of lead (see Fig. 7.6). Although, a small peak was observed at 285.2 nm wavelength, it was not included in the spectral bandpass chosen and therefore, not contributing to the interference effect.
Table 7.3 A comparison of interference study results.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Interferent</th>
<th>Apparent concentration due to interferent (μg ml(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Baird</td>
<td>ASIA</td>
</tr>
<tr>
<td>Al</td>
<td>1000 μg ml(^{-1}) Ca</td>
<td>3.992 (00.114)</td>
</tr>
<tr>
<td></td>
<td>0.1% MIBK</td>
<td>1.609 0.003</td>
</tr>
<tr>
<td></td>
<td>1.0% MIBK</td>
<td>11.658 0.015</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.049</td>
</tr>
<tr>
<td>Ca</td>
<td>1000 μg ml(^{-1}) Pb</td>
<td>- 0.14 0.006</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.019</td>
</tr>
<tr>
<td>Co</td>
<td>1100 μg ml(^{-1}) Ni</td>
<td>1.732 (0.007)</td>
</tr>
<tr>
<td></td>
<td>0.1% MIBK</td>
<td>0.090 (0.018)</td>
</tr>
<tr>
<td></td>
<td>1.0% MIBK</td>
<td>0.495 (0.025)</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- (0.041)</td>
</tr>
<tr>
<td>Cr</td>
<td>1100 μg ml(^{-1}) Ni</td>
<td>2.430 0.011</td>
</tr>
<tr>
<td></td>
<td>0.1% MIBK</td>
<td>0.390 0.011</td>
</tr>
<tr>
<td></td>
<td>1.0% MIBK</td>
<td>1.880 0.014</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.008</td>
</tr>
<tr>
<td>Mg</td>
<td>1000 μg ml(^{-1}) As</td>
<td>0.018 0.021</td>
</tr>
<tr>
<td></td>
<td>1000 μg ml(^{-1}) Sn</td>
<td>0.035 (0.049)</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.024</td>
</tr>
<tr>
<td>Mn</td>
<td>1000 μg ml(^{-1}) V</td>
<td>0.068 0.133 (0.007)</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.024</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1% MIBK</td>
<td>0.330 0.016</td>
</tr>
<tr>
<td></td>
<td>1.0% MIBK</td>
<td>0.950 0.017</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.010</td>
</tr>
<tr>
<td>Pb</td>
<td>1000 μg ml(^{-1}) Mg</td>
<td>8.300 1.3 (1.170)</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.008</td>
</tr>
<tr>
<td>Zn</td>
<td>1000 μg ml(^{-1}) Cu</td>
<td>4.40 0.015</td>
</tr>
<tr>
<td></td>
<td>1100 μg ml(^{-1}) Ni</td>
<td>4.96 0.003</td>
</tr>
<tr>
<td></td>
<td>6% H(_3)PO(_4)</td>
<td>- 0.003</td>
</tr>
</tbody>
</table>

The values in brackets are obtained using narrow slits.
This peak was later confirmed to be due to the contamination of the high concentration lead solution used for source plasma when the solution was analysed for the presence of magnesium.

Fig. 7.7 illustrates the interference effect of tin on magnesium, using a slit-width of 5.0 mm. The fluorescence spectrum obtained showed a signal value equivalent to an apparent concentration of 0.31 µg ml⁻¹ magnesium. To investigate the cause of this high signal value, spectral scans were repeated using a narrow slit-width (see Fig. 7.8). It was noted that the interference effect was substantially reduced. However, a small peak was found at 285 nm wavelength demonstrating that the interference effect in the previous experiment was not caused alone by the primary source light scattering but, probably due to spectral broadening interference. This resulted in an apparent concentration of 0.049 µg ml⁻¹ of magnesium.

The interference effect of vanadium on manganese was investigated using a 5.0 mm slit-width and the spectra obtained are shown in Fig. 7.9. It can be seen from the result that an apparent fluorescence signal equivalent to 0.133 µg ml⁻¹ of manganese is produced when vanadium solution is analysed for manganese. To evaluate further, spectral scans were repeated using a narrow slit-width (see Fig. 7.10) and it was found that the fluorescence signal produced was negligible indicating that a false fluorescence signal was produced probably due to spectral broadening interference which was eliminated using narrow slits.

It was observed from the interference study of 6% orthophosphoric acid on the analyte elements that no interference effect was noted. Also, no problem was noticed with the plasma when solutions containing high concentration of interferents were aspirated into the atomiser plasma. However, small salt deposits around the tip of the injector and the plasma tubes were noticed at the end of the study.

The emission spectral scans for the elements on which serious interference effect was noticed are shown in Fig. 7.11 to Fig. 7.13.
Fig. 7.3 (a) Wavelength scan in the range 380-410 nm while, aspirating 20 µg ml⁻¹ aluminium solution in 80% ethanol into the atomiser plasma and 6% aluminium solution into the source plasma, using 5.0 mm slits.
Fig. 7.3 (b) Wavelength scan in the range 380-410 nm while aspirating 1000 µg/ml calcium solution in 80% ethanol into the atomizer plasma and 6% aluminium solution into the source plasma, using 5.0 mm slits.
Fig. 7.4 (a) Wavelength scan in the range 380-410 nm while aspirating 20 µg ml⁻¹ aluminium solution in 80% ethanol into the atomiser plasma and 6% aluminium solution into the source plasma, using 0.3 mm slits.
Fig. 7.4 (b) Wavelength scan in the range 380-410 nm while aspirating 1000 μg ml⁻¹ calcium solution in 80% ethanol into the atomiser plasma and 6% aluminium solution into the source plasma, using 0.3 mm slits.
Fig. 7.5 (a) Wavelength scan in the range 260-320 nm while, aspirating 20 ug ml⁻¹ lead solution into the atomiser plasma and 20% lead solution into the source plasma, using 5 mm slits.
Fig. 7.5 (b) Wavelength scan in the range 260-310 nm while, aspirating 1000 ug ml⁻¹ magnesium solution into the atomiser plasma and 20% lead solution into the source plasma, using 5 mm slits.
Fig. 7.6 (a) Wavelength scan in the range 260-290 nm while aspirating 20 ug ml\(^{-1}\) lead solution into the atomiser plasma and 20% lead solution into the source plasma, using 0.5 mm slits.
Fig. 7.6 (b) Wavelength scan in the range 260-290 nm while, aspirating 1000 ug ml⁻¹ magnesium solution into the atomiser plasma and 20% lead solution into the source plasma, using 0.5 mm slits.
Fig. 7.7 (a) Wavelength scan in the range 270-300 nm while, aspirating 20 μg ml⁻¹ magnesium solution into the atomiser plasma and 10% magnesium solution into the source plasma, using 5 mm slits.
Fig. 7.7 (b) Wavelength scan in the range 270-300 nm while, aspirating 1000 ug ml\(^{-1}\) tin solution into the atomiser plasma and 10\% magnesium solution into the source plasma, using 5 mm slits.
Fig. 7.8 (a) Wavelength scan in the range 270-300 nm while, aspirating 20 μg ml⁻¹ magnesium solution into the atomiser plasma and 10% magnesium solution into the source plasma, using 0.3 mm slits.
Fig. 7.8 (b) Wavelength scan in the range 270-300 nm while, aspirating 1000 \( \mu g \) \( \text{ml}^{-1} \) tin solution into the atomiser plasma and 10% magnesium solution into the source plasma, using 0.3 mm slits.
Fig. 7.9 (a) Wavelength scan in the range 270-300 nm while, aspirating 20 µg ml⁻¹ manganese solution into the atomiser plasma and 20% manganese solution into the source plasma, using 5 mm slits.
Fig. 7.9 (b) Wavelength scan in the range 270-300 nm while, aspirating 1000 ug ml\(^{-1}\) vanadium solution into the atomiser plasma and 20% manganese solution into the source plasma, using 5 mm slits.
Fig. 7.10 (a) Wavelength scan in the range 270-300 nm while, aspirating 20 ug ml$^{-1}$ manganese solution into the atomiser plasma and 20% manganese solution into the source plasma, using 0.3 mm slits.
Fig. 7.10 (b) Wavelength scan in the range 270-300 nm while, aspirating 1000 \( \mu \text{g ml}^{-1} \) vanadium solution into the atomiser plasma and 20% manganese solution into the source plasma, using 0.3 mm slits.
Figure 7.11 shows a significant interference effect of magnesium on lead emission signal. The zinc 213.86 nm line suffers direct overlap from the copper 213.85 nm line and nickel 213.86 nm ion line. This results in apparent concentration of 4.4 and 4.96 \( \mu g \text{ ml}^{-1} \) of copper and nickel when pure copper and nickel solution are analysed at zinc line (See Fig. 7.12).

Figure 7.13, which includes spectral scans of MIBK, calcium, nickel, hydrochloric acid (blank) and aluminium solutions on the aluminium line, indicates the severity of interference particularly, due to 1% MIBK solution. This interference effect was attributed to the carbonyl emission from MIBK at 396.15 nm. It is interesting to note that in emission an organic solvent causes interference effect on aluminium whereas, in fluorescence an organic solvent is recommended to achieve better sensitivity of aluminium AF signal.
The results of the interference study in emission using the Baird emission spectrometer are presented in Table 7.3. A comparison of the results show that in emission interference effects are quite worse compared to those in fluorescence using the ASIA system where no spectral interference effect was noticed. However, in a few cases minor interference effect was observed due to increased baseline noise due to the interferent solutions. These fewer interferences in atomic fluorescence suggest superiority of the technique compared to emission.
7.7.2. Analysis of cupronickel alloy for zinc.

The determination of zinc traces in high purity copper is a difficult problem using ICP emission technique due to a direct spectral overlap by the zinc resonance line at 213.856 nm on the copper 213.853 nm non-resonance line. This interference has been reported even with the echelle spectrometer (spectral bandpass = 0.003 nm)\textsuperscript{174}. The determination of zinc in a BCS cupronickel alloy was carried out to investigate any effect of copper on zinc. The alloy contained about 66% copper, 33% nickel and impurities including 0.05\% (wt/wt) zinc. Matrix matched standards were employed to compensate for the addition of any possible scatter signal from the high matrix in alloy sample to the fluorescence signal of zinc. The result obtained showed zinc value of 0.053 ± 0.0005\% zinc (wt/wt), which is in good agreement with the certified value.
Conclusions and Suggestions for further work

8.1. Conclusions

The evaluation of the ASIA system has established after some improvements in the basic set up and other improvements, that the system would possess to a high degree the characteristics required of a general purpose analytical instrument.

A comparison study of the ICP and BDHCL as excitation sources in AFS showed that there was no significant difference between the ICP source and the BDHCL source run at higher than recommended currents. However, this does not imply that the two sources have similar excitation mechanisms. It is considered that a high-powered ICP
source would be in local thermodynamic equilibrium (LTE) whereas the BDHCL source would not. There are considerable differences in excitation mechanisms between the two sources for lead and nickel as shown in Figs. 3.9, 3.10, 3.12 and 3.13.

It was concluded that high-powered ICP is a better excitation source than BDHCL, if the figure of merit is detection limit. Nevertheless, BDHCLs are obviously useful sources and in some instances may prove to be more convenient than an ICP. Also the lamps do allow the possibility that existing owners of ICP-AES instruments may use the lamps to carry out atomic fluorescence experiments by easy, relatively cheap, retrofits.

Also, it was concluded that a significant improvement in the performance of the instrument could be obtained by increasing the power in the image of the ICP source formed in the atomiser tail-flame by bringing the two plasmas closer to each other.

A study on the determinations of refractory elements has shown that a reducing environment must be present in the atomiser plasma. This is accomplished by introducing small amounts of carbon-containing species such as propane or ethanol, into the sample introduction system. The addition of carbon-containing species results in improvement in analytical sensitivity and therefore improvements in detection limits are obtained. However, it was found difficult to sustain the plasma when pure organic solvents were introduced into the long-sleeve torch. This is believed to be due to the reason that organic vapours absorbs r.f power in the plasma.

An on-line preconcentration method development, utilizing a micro column of Amberlite IRA-93 anion-exchange resin has improved the detection limits of tungsten and molybdenum by about an order of magnitude. But, unfortunately different conditions were found to be necessary for different elements. As the main objective of preconcentrating a group of refractory elements was not achieved therefore, the method would only have limited application for ASIA work. However, the method could be of value if tungsten and/or molybdenum were to be determined by AFS. Also, the method could be applied to other refractory elements that form oxyanions, for example boron and chromium for which normal sensitivity is relatively low in AFS.
The analytical sensitivity of the system has been improved by the replacement of Optica monochromator with a more efficient Bentham monochromator and by the re-arrangement of the optical system between the monochromator slits and the atomiser plasma. The distance between the monochromator slits and the atomiser plasma has been reduced to half the original distance by removing lens (L4) and moving the lens (L3) closer to the atomiser plasma thus increasing the solid angle of radiation collection (see Figs 2.5 and 5.2). These changes in the original set up of the system resulted in improvement of detection limits of a number of elements by a factor of 2 to 3 times.

It was established from the study on the blank signal that major contribution in the blank signal was the stray light entering the monochromator due to the reflection of the primary excitation light off the surfaces including the lenses. Also, it was found that an increase in measurement time resulted in a decrease in the magnitude of the background noise. It was therefore concluded, that ‘white noise’ was the major type of noise at 997 Hz modulation frequency used in this work. Thus, improvements in detection limits can be achieved by increasing the sample measurement integration time.

In order to simplify the optical arrangement between the source plasma and the atomiser plasma a performance study of an aerosol modulation device was unsuccessful. The aerosol modulation device did not proved to be effective on either of the sample introduction systems. It appeared that after chopping the sample aerosol, mixing of the aerosol resulted in complete disappearance of the square wave signal needed from the source plasma or the atomiser plasma.

Also, an evaluation study of the aerosol desolvation system was unsuccessful. The signal stability became worse when conventional nebulisation was switched to the desolvation system. Pulsing of the plasma could not be stopped by applying different approaches and using different configurations of the desolvation system. Furthermore, problem of salt deposition on the inner walls of the heated spray chamber when high concentration solutions were aspirated into the source plasma, worsened the performance of the desolvation system. The decreased signal to noise ratio due to these problems resulted in detection limit worse than that obtained with the conventional nebulisation.
A comparison of interference study results with those from a commercial ICP-AES instrument has shown that in ASIA, spectral interference is almost non-existent. This is largely due to the simplicity of the atomic fluorescence spectra compared with emission spectra, where there are many lines. The simplicity of the fluorescence spectra is largely due to the fact that transitions originating from the ground state and lower energy levels is observed.

There was no evidence of spectral interference effect due to the high concentration interferent solutions on a number of analyte elements investigated. A small interference effect was noted in a few cases which was attributed to spectral broadening interference. Also, no interference effect was noted when MIBK was introduced into the plasma. Whereas, the emission spectra from a commercial ICP-AES instrument showed a broad peak in the wavelength region of interest for Al, Cr and Ni. This was assumed to be due to the carbonyl emission band.

In conclusion, it can be said that AFS technique with two plasmas, is an ideal adjunct to ICP-AES spectrometry, capable of solving specific analytical problems. Moreover, it is felt that the improvements in the detection limits obtained from this work with the ASIA system are sufficiently encouraging for the work to continue.

8.2. Suggestions for further work.

In this work areas have been found where further work appears to be both necessary and promising. Further work on the ASIA system could include:

1. The necessity of two high frequency generators in this system is a distinct disadvantage. It has been shown in this University,\textsuperscript{172} that two plasmas could be run with a single generator. This study is worthy of more investigation and if successful would result in reducing the cost of the equipment, thus making it more competitive with commercial ICP-AES instruments.

2. There is possibility of improving the detection power of the system by making some more refinements in the optical arrangement of the system, particularly between the source and atomiser plasmas. It has been demonstrated in this thesis that considerable improvements in sensitivity
were achieved when the distance between the excitation radiation source and the atomiser plasma was reduced (See Chapter 3). The use of an ellipsoidal reflector placed behind the plasma to collect a much larger solid angle source radiation, could possibly increase the analytical sensitivity of the system. At present, based upon the solid angle considerations less than 1% of the source radiation is being collected. Furthermore, a mirror placed behind the atomiser plasma in the direction of the monochromator might improve sensitivity of the system.

3. In many applications often a need arises to determine both trace elements as well as major constituents of the sample. In such a case ASIA system could be useful in the resonance monochromator mode. In the resonance monochromator mode the sample is introduced in the source plasma and a constant concentration of about 1-100 \( \mu g \text{ ml}^{-1} \) of an analyte standard is introduced into the atomiser plasma. This study might increase the linear dynamic range and possibly could help in saving time which is consumed in diluting high concentration solutions when determinations are made using other techniques.

4. Further extension of the present work could possibly be the use of the system for multielement analysis. In this case, a cocktail solution of different elements could be introduced into the source plasma while, the sample solution is being introduced into the atomiser plasma. The resultant fluorescence lines could be separated and intensity measured using a polychromator with computerized detection and read-out system.

5. Clogging of the nebuliser of the torch in the source plasma occurs in some cases when 20% or higher concentration solutions are used. Also, the use of high concentration solutions in the source plasma, at the rate of 2-3 ml min\(^{-1}\) is another aspect which needs attention. In this respect, a study could be made for the possible use of controlled-dispersive flow analysis (CDA) method\(^{176,177}\) as sample introduction system for the source plasma. In this method solution is aspirated into a probe or pump tube by the precise rotation of a peristaltic pump driven by a stepping motor. The motor is
activated by pulses generated by a microcomputer. Only required amount of solution is used with no wastage. A schematic diagram of the CDA system is shown in Fig. 8.1. At the start of a cycle the reagent probe moves from the carrier solution (de-ionized water) to the analyte solution. The pump then rotates through a small angle, drawing analyte solution into the probe. The probe then returns to the carrier solution and the analyte slug is propelled through the coil into the nebuliser. To prevent the nebuliser running dry during the arm transfer phase a reservoir of carrier solution (de-ionized water) is connected to the system via a T-piece. When the pump is stationary the nebuliser will draw carrier from C'.

![Fig. 8.1 A schematic diagram of the controlled dispersive flow analysis system.](image)

6. Another possible extension of this work could be the development of a laminar flow plasma torch as an excitation source. It was noticed in the comparison work mentioned in Chapter 3, that lower standard deviation values were obtained for the blanks with BDHCIs as excitation sources compared to those with ICP as an excitation source. Clearly, one would expect an improvement in detection limit by reducing the noise originating from the excitation source plasma. Snook and co-workers\textsuperscript{107,110} have
investigated and shown that an improvement of an order of magnitude in detection limits is obtained when an extended tube laminar flow torch instead of the commonly used tangential flow torches, is used for ICP-AES. It is believed that the tangential force exerted by the plasma and the coolant gas flows causes disturbance in the laminar flow injector gas carrying the analyte aerosol.
Appendix I

11700 REM
11710 PRINT "This part of the program integrates signal for fluorescence measurements": PRINT
12000 PRINT: LPRINT: LPRINT: LPRINT "operator/Date"TAB(37)+D$
13000 REM
13010 CLS
13020 REM
13040 PRINT: PRINT: PRINT TAB(15)"F----------Fluorescence measurements"
13060 PRINT: PRINT: PRINT TAB(15)"O----------TO MAIN MENU"
13070 PRINT: PRINT: PRINT TAB(15)"Change current amplifier sensitivity"
13080 PRINT: PRINT: PRINT
13100 IF A$="F" OR A$="f" THEN 13500
13100 IF A$="O" OR A$="O" GOTO 1010
13500 IF A$="M" OR A$="M" THEN GOSUB 19000
13500 REM
14000 REM
14100 CLS
14200 PRINT: PRINT
14300 CALL ADC%(RETSTAT%)
14400 IF RETSTAT%<>O THEN 6760
14500 V=0:VTIME=T1
14600 GOSUB 20
14610 Z4=0
14620 V=TVDST
14630 Z4=FNP(V)
14700 PRINT: PRINT "INTEGRATED SIGNAL =";Z4; " nA"
14800 LPRINT " Integrated Signal"; TAB(38) Z4;TAB(47) "nA"
14900 PRINT: INPUT "Press ENTER key to repeat OR 0 for MENU

-194-
"BAS
15100 IF BAS="" THEN 14000
15200 GOTO 13000
19000 CLS
19300 PRINT: PRINT: PRINT
19500 G1$="N"
19600 PRINT "100pA-----P 1 nA-----Q"
19700 PRINT "10 nA-----R 100 nA-----S"
19800 PRINT "1 uA-----T 10 uA-----U"
19900 PRINT
20000 k$="amplifier gain code ":A1N$=G$
20100 GOSUB 8340
20200 G$=A1NS$
20300 IF ASC(G$)≥112 AND ASC(G$) <=117 THEN G=ASC(G$)-117
20400 G$=CHR$(G+85)
20500 IF ASC(G$)<80 OR ASC(G$)> 85 THEN 19600
20600 G=ASC(G$)-85
20700 RETSTAT%=0
20800 LAD%(1)=DEV28%
20900 LAD%(2)=199
21000 CALL WRSTR%(EOS%, TERM%, LAD%(1), G$, CNT%,
21100 RETSTAT%
21200 RETURN
21300 END
References


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References

References

References

References

References

References

References

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