Atomiser, Source, Inductively-coupled plasmas in Atomic fluorescence spectrometry (ASIA): a study of chemical and ionisation interference effects

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A Study of Chemical and Ionisation Interference Effects

by

Mahmood Shaker Salman, B.Sc., M.Sc.

A doctoral thesis
submitted in partial fulfilment of the requirements
for the award of
the degree of Doctor of Philosophy of the Loughborough University of Technology
July, 1989

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DEDICATION

"To my mother"
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 acknowledgement or in footnotes, and that neither the thesis or the original work contained therein has been submitted to this or any other institution for a higher degree.

Mahmood Shaker Salman
ACKNOWLEDGEMENTS

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Table 6-1. Detection limits p.p.b. for ICP-AES and ICP-AFS with laser, HCL and ICP as excitation source
PUBLICATION OF RESULTS

The work described in this thesis has been the subject of several publications and presentations, which are listed below.

Publications


Presentation


Additional Publication and Presentation

This work described in this thesis has also been mentioned in the papers and presentations listed below.


The aim of this work is to evaluate aspects of the performance of a novel atomic fluorescence spectrometer. This instrument uses two inductively coupled plasmas, one as the light source and one as an atom and ion reservoir. The technique is referred to by the acronym ASIA - Atomiser, Source, Inductively coupled plasmas in Atomic fluorescence spectrometry.

A comparison was made between a commercially available GMK nebuliser and a de Galan nebuliser combined with a cyclone spray chamber and an impact wall spray chamber. The results showed that the combination of a de Galan nebuliser with a cyclone spray chamber on the source plasma and a GMK nebuliser on the atomiser plasma gave the best performance, with the available nebulisers.

A comprehensive comparison of two optimisation strategies has been made in both emission and fluorescence modes. The alternating variable search (AVS) and simplex methods were compared on the basis of the time taken and the signal to background ratio (for emission) and total fluorescence produced. The AVS method of optimisation is described in detail and results are presented demonstrating the effect of changing the order in which the variables are taken. The results show that the order in which the five variables are taken is not critical. The simplex method was unable to satisfy the conditions for termination in the case of the atomic fluorescence studies and was much slower than the AVS method to implement as the latter method used direct visual feedback from the output as a measure of the figure of merit, total fluorescence.

Stable compound formation and easily ionised element interference effects have been investigated by studying the effects of phosphate, aluminium, sodium and potassium on the atomic fluorescence of calcium at 422.7 nm and on the ionic fluorescence at Σ393.4-396.8 nm when the operating conditions were optimised for maximum fluorescence signal from a solution containing no interferents. Interference effects were observed which were interpreted in terms of stable compound formation, ionisation suppression and fluorescence quenching. These effects may be removed by optimising the operation parameters for minimum interference.
CHAPTER 1
LITERATURE SURVEY

1.1 Development of the Inductively Coupled Plasma as a Source for Emission Spectrochemical Analysis

1.2 Plasma Initiation

1.3 The Effect of Different Injector and Plasma Gases on ICP-AES

1.4 Thermal Isolation and Stabilisation of ICP

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1.5.4 Types of atomic fluorescence

(a) Resonance fluorescence

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(i) Direct-line fluorescence

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(iii) Stepwise-excitation fluorescence

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1.5.5 Quenching of fluorescence

1.5.6 Basic instrumentation

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1.5.8 The ICP as an excitation source for fluorescence spectroscopy

1.5.9 The ICP as an atomisation cell for fluorescence spectroscopy

1.5.10 The ICP as an excitation source and atomisation cell for fluorescence spectroscopy
1.1 Development of the Inductively Coupled Plasma as a source for Emission Spectrochemical Analysis

In any study of inductively coupled plasmas (ICPs), the first papers of interest are those of Babat, who in 1942 published the results of his researches into the properties of electrodeless discharges [1]. This work became more widely known from a later English paper [2]. Babat found that a ring discharge, once established, could be maintained while the pressure was increased up to atmospheric pressure. He produced an electrodeless discharge within a quartz cylinder 15 cm in diameter and 150 cm long, containing air at pressures ranging from 0.1 to 760 torr, using a high-frequency (2 to 77 MHz) push-pull vacuum tube oscillator of his own construction. The plasma was initiated at low pressure and maintained as the pressure was gradually increased. The induction coil used was about five turns and made from square section copper tube (1x1 cm). Babat reported experiments concerning a non-flowing plasma. He also noted that the higher the frequency of the generator the lower the current and power consumption required to form a stable plasma.

This work was followed by Reed [3] who described an ICP torch operating at atmospheric pressure on argon gas and argon mixtures powered by a 10 kW high frequency 4 MHz power supply. The torch consisted of a quartz tube with a brass base having one tangential gas entry placed within the five turn work coil of the generator (Fig. 1-1). A pilot plasma was formed by the temporary insertion of a carbon rod into the torch thus producing thermal electrons by heating the carbon in the alternating magnetic field. These electrons provided the initial ionisation of the argon gas enabling coupling to occur between the oscillating field and the gas and a plasma to be formed. Reed considered that a tangential gas entry was necessary in order to create a vortex in the gas stream which could maintain the plasma and prevent the tube walls from melting. He showed that a plasma can be sustained in argon, and argon mixtures containing 20% air, helium, or hydrogen, or 50% oxygen. Argon was the simplest gas in which to start and operate the discharge due to its low heat capacity and thermal conductivity. In a later publication [4] Reed described a torch with three concentric quartz tubes with a centre
Fig. 1-1. Early Torch of Reed (Ref. 3)
powder feed for use in crystal growing which was one of his major goals (Fig. 1-2). Each tube had an independent gas flow: the outer flow was at high velocity to stabilise the plasma and to keep the hot discharge away from the outer quartz tube: the plasma was formed in the intermediate gas flow at low velocity; powder was carried in the innermost, high velocity flow. The possible application as a spectral source for solid samples was suggested [5].

Because a plasma offered such attractive properties, its use as a source for spectrochemical analysis was investigated independently by two groups of workers, one in Great Britain led by Greenfield and other in the United States led by Fassel.

In 1963 the ICP was first put to use as a spectroscopic source by Greenfield and co-workers who made a patent application for the plasma torch [6]. It was Greenfield who made the next important modification of the plasma by forming an annular shaped discharge. The torch consisted of three concentric tubes as shown in (Fig. 1-3). The two outer quartz tubes were used to contain the plasma and the inner tube of borosilicate glass was used to inject an aerosol through the plasma, once it had been formed. The 2 kW, 36 MHz generator was used to produce an argon plasma. The gas was fed tangentially into the inner tube (A) the high frequency field applied by the work coil and a plasma produced after seeding with electrons from a Tesla coil. Once the plasma formed, the argon gas was introduced tangentially into outer tube (B) to stabilise the plasma and keep it away from the walls of the torch. A hole was then punched through the flattened base of the plasma by the introduction, through the injector (C), of a sample containing aerosol in argon gas is (see Fig. 1-4 a).

In 1965 Wendt and Fassel [7] published their independent observations on the ICP. They used a 3.4 MHz, 5 kW generator to form the plasma. They described an inductively coupled plasma, with laminar flow (Fig. 1-5) which produced a solid ellipsoidal plasma similar to that produced by Reed [4]. The sample did not penetrate the plasma but passed around the outside of the core (Fig 1-4(b)), they claimed less turbulence and greater stability than was obtained with vortex flow (Fig. 1-6). This paper also contained the first publication of detection limits for inductively coupled plasma-atomic emission spectrometry (ICP-AES).
Fig. 1-2. Torch used by Reed for Crystal growing. (Ref. 4)

Fig. 1-3. Early Torch of Greenfield. (Ref. 6)
Fig. 1 - 4. Sample particle paths for several plasma shapes.
Fig. 1 - 5. Torch of Wendt and Fassell (Ref. 7)
Fig. 1-6. Two plasma torch gas flow patterns
The detection limits quoted were very low, and it is probably their use of an ultrasonic nebuliser which contributed greatly to their achieving such low detection limits.

Veillon and Margoshes [8] used a similar arrangement. They reported serious chemical interference resulting, presumably, from the inefficient heating of analyte as it passed around, instead of through, the discharge due to their torch not having an injector tube at all, as shown in (Fig. 1-7).

In 1965 Greenfield [9] found that the well known interference of phosphorus and aluminium on the flame emission for calcium was completely eliminated when using an ICP, thereby establishing one of the techniques most important analytical characteristics, relative freedom from chemical interference..

Also in 1965, Greenfield et al. published [10] preliminary studies made with a large generator (6 MHz, 25 kW) using a similar torch. They claimed that the detection limits obtained for a number of elements were one or two orders of magnitude better than those obtained with a D.C. arc and a Hilger and Watts large Quartz spectrograph.

Since then a large number of workers have explored the analytical potential of the ICP source. The work of Dunken and Pforr in 1966 [11] who used a 1-2 kW, 40 MHz generator in conjunction with an ultrasonic nebuliser was an early contribution to the field. Both atomic and ionic lines of the introduced elements were found in the spectrum and each showed high sensitivities. Hoare and Mostyn [12] designed a system for solution and powder sample analysis and freedom from matrix effects were reported.

In 1969 Dickinson and Fassel [13] in their continuing investigations on the analytical application of the ICP reported improvements in the detection limit of 3 to 4 order of magnitude compared to those observed by flame atomic absorption (FAA) and flame atomic emission (FAE) techniques. The improvements were achieved through desolvation of the sample aerosol before introduction into the plasma and the formation of a toroidal shaped plasma which allowed more efficient introduction of the aerosol residue into the plasma.

Kleimann and Svoboda [14,15] described a low power (120-220 W) generator operated at 40 MHz to power a single-tube torch with separate vaporisation of the sample.
In 1970, Truitt and Robinson [16,17] described the introduction of organic material into a torch similar to that of Wendt and Fassel [7] but with a long outer tube under a number of plasma conditions (Fig. 1-8). At the same time, Pforr and Aribot [18] have determined Ca, Mg, Ti, Fe and Al in quartz using a powder injection system.

In 1974, Scott et al. [19] used a three-tube torch which is shown in (Fig. 1-9) with vortex stabilisation without the intermediate gas in what is described as a compact design. The aerosol was produced using a pneumatic nebuliser. With an input power of 1.3 kW one might presume a power in the plasma of between 650 and 900 W. They obtained linear calibration curves over five decades of concentration.

Over this period instrument manufacturers had become gradually aware of the potential of (ICP-AES) and 1974 saw the first commercial ICP instrument [20,21].

During the mid 1970's, the ICP characteristics and its potential advantages as an emission source for spectrochemical analysis were well documented and instrumental developments, publications, conferences and lectures, and applications of ICP were reported in a monthly newsletter, edited by Barnes [22]. A number of reviews have appeared in the literature describing the development, principle operations and the applications of the ICP source. The author recommends the reviews of Greenfield et al. [23] and Barnes [24] for their comprehensiveness. In addition to these categories there are several books such as, A handbook of ICP-spectrometry [25], Application of plasma emission spectrochemistry [26], Development in atomic plasma spectrochemical analysis [27], Inductively coupled plasma emission spectroscopy Part 1 and 2 [28] and Inductively coupled plasma in analytical atomic spectrometry [29].

During the last ten years, numerous publications have appeared describing the fundamental developments and interpretation of the ICP emission spectrum. In addition the use of the ICP source for simultaneous multi-element analysis [14,30-33]. An ICP with a 30-channel direct-reading spectrometer with fully automatic sequential sampling and read-out had been used for practical analysis in an industrial laboratory for over four
Fig. 1 - 7. Torch of Veillon and Margoshes. (Ref. 8)

Fig. 1 - 8. Torch of Truitt and Robinson. (Ref. 16, 17)
Fig. 1 - 9. Torch of Fassel et al. (Ref. 19)
years [34].

Sample introduction into the ICP has received attention by various analysts, a separate section is given discussing the various method of sample introduction into ICP. Samples may be introduced into plasma, as solids, liquid or gases. The most commonly used technique for the introduction of liquid samples is based on the production of an aerosol by means of a pneumatic nebuliser [35-40].

The versatile characteristics of the ICP good atom or ion excitation cell have extended the application of the ICP to atomic absorption [41-43], fluorescence and mass spectrometry. The development of commercially available ICP-atomic fluorescence spectrometry (ICP-AFS) by Demers and Allemand [44] has stimulated research and application of ICP-AFS for minor element analysis. The principles and developments of ICP-AFS are given later in this chapter. The next application of the ICP is probably the use of ICP as an ion source for mass spectrometry (MS) and it is commercially available [45,46]. Reliable systems have been developed by Houk et. al. [47], Date and Gray [48,49]. Douglas et. al. [50] compared ICP-MS with optical emission methods and concluded that ICP-MS has the advantage of simple spectra. This is because in ICP-MS, only the masses of the ions are present in the spectrum whilst in ICP-AES, the emission lines of atoms and ions of many excitation states are present.

The development of low power ICP torches is gaining attention from both users and manufacturers of instruments because they are an essential part of a complete low-cost ICP system. Savage and Hieftje [51,52] described a plasma torch (Fig. 1-10) 33% smaller than a Fassel torch but otherwise conventional in design, which operated at 1 kW of power with 8 l min\(^{-1}\) argon coolant gas. They claimed the analytical characteristics of this torch seem to be very similar to the conventional size of torch. Other authors reporting small torches are Allemand et al. [53]. The various approaches to reduce both the power and the coolant argon gas consumption have been
Fig. 1-10. Torch of Hieftje (Ref.51)
reviewed by Hieftje [54]. Miniature torches [55] and externally cooled torches [56] have been investigated, however, the acceptance of any one of these depends on their analytical performance in the future.

Kawaguchi et al. [57] described a water cooled torch as shown in (Fig. 1-11) in which total argon flows as low as 1.4 l min⁻¹ have been investigated.

### 1.2 Plasma Initiation

The source of events leading to the formation of an inductively coupled argon plasma have been described by Fassel et al. [58,59], Sharp [60] and recently reviewed by Davies and Snook [61]. When high frequency (h.f.) power is supplied to the load coil, the h.f. current flowing in the load coil generates an oscillating magnetic field whose lines of force are axially oriented inside the quartz tube [62] as shown in (Fig. 1-12). This in turn induces the free electrons produced from argon ionisation by the Tesla coil to flow in closed annular paths around the field lines and accelerate during each half cycle of the h.f. supply. These fast electrons gain sufficient energy from the field to ionise additional argon atoms and a stable plasma is formed at the open end of the tube (Fig. 1-13) due to the recombination of ions and electrons establishing an equilibrium between the forward and reverse processes:

$$\text{Ar} + e^- \underset{\text{Ar}^+ + 2e^-}{\rightleftharpoons}$$

Argon ions will be consumed either by

(a) radiative recombination with electrons, producing continuum radiation.

(b) Collisions with species present in the plasma to form species in an excited state through charge transfer processes.
Fig. 1 - 11. Torch of Kawaguchi. (Ref. 57)

All Dimensions in mm.
Fig. 1 – Magnetic fields (H) and eddy currents (shaded) generated by high frequency currents (I) flowing through coil. (62).
Fig. 1-13. Schematic configuration of an Inductively Coupled Argon Plasma
\[
\text{Ar}^+ + X \rightarrow X^{+(\ast)} + \text{Ar} \\
X^{+(\ast)} \rightarrow X^+ + \text{hv} \quad \text{(ion line)} \\
X^{+(\ast)} + e^- \rightarrow X^* \quad \text{(Recombination)} \\
X^* \rightarrow X + \text{hv} \quad \text{(atom line)}
\]

Where \( X \) is the species present in the plasma.

(c) radiative de-excitation producing the argon line spectrum

1.3 The Effect of Different Injector and Plasma Gases on ICP-AES

Usually, high power is used with nitrogen-argon and low power with pure argon ICPs. This association of power level and type of gas is qualitatively understandable in terms of the difference in heat content between molecular and atomic gases. A molecular gas will require more energy than an atomic gas to reach a temperature where it is sufficiently ionised to sustain a discharge.

The effect of different injector and plasma gases on analyte emission intensity of the ICP was first reported by Greenfield et al. [9]. They found that the emission intensity decreased in the order argon > nitrogen > air > oxygen, used as injector gas, and consequently the use of argon as injector gas was recommended. For plasma gases emission intensity was found to decrease in the order nitrogen-argon > oxygen-argon > helium > argon. The amount of diatomic gas that could be mixed with argon was limited by the power available from the generator.

Greenfield and co-workers [9,23,63-66] developed the nitrogen-argon ICP as a useful analytical tool and advanced various arguments in favour of the use of nitrogen as
the outer gas in combination with high-power (5 kW or more), viz., high temperature, high electron density, high sensitivity, better freedom from interferences, and better tolerance for samples of high salt content, concentrated acids and organics, in comparison with low-power argon ICP's [23, 67, 68]. Currently Greenfield is using an Ar-Air plasma as the source of excitation for the determination of elements and for measuring their atomic fluorescence spectra [69,70].

Montaser and Montazavi [71] considered the realization and evaluation of an ICP generator running on an economic diatomic gas, such as N₂. They used a 2.5 kW, 27.32 MHz in combination with a Fassel torch, normally used for operating argon ICPs. They introduced N₂ only as the outer gas, the carrier gas still being argon. For initiating the ICP they used the following procedure. The plasma was first generated in the conventional way in an all-argon atmosphere. Nitrogen was then introduced in the outer gas flow by gradually decreasing the outer flow to zero, while increasing the nitrogen flow so that the total outer gas flow remained constant at 15 l min⁻¹. The change-over from 100% argon to 100% N₂ extended over a time interval of about 2 min. An initial comparison of the detection limits of 16 elements in Ar and N₂-Ar ICPs operated at identical power and flow rates indicated that the pure argon plasma generally yielded better detection limits.

A similar procedure has been described by Barnes and Meyer [72] for generating an all N₂ ICP with a Fassel torch, operating on 25 l min⁻¹ outer, 3.5 l min⁻¹ intermediate, and 1.5 l min⁻¹ carrier gas flows and about 1.5 kW forward power.

In a subsequent investigation, Montaser et al. [73] covered substantially broader ranges of the ICP parameters. In addition, they used an ultrasonic nebulizer with desolvation facilities. Ebdon et al. [74] performed optimization studies for ICP's with N₂ and Ar as the outer gas.

Boumans et al. [75] used a generator capable of delivering 2 to 3 kW and an ultrasonic nebuliser with desolvation system. They reached acceptable detection limits with a resonably low argon consumption of 2 l min⁻¹ carrier gas and 2.5 l min⁻¹ intermediate gas, while a 40 l min⁻¹ N₂ outer flow was required.

Meyer and Barnes [76] investigated analytical inductively coupled nitrogen and air
plasmas using a specially designed torch having approximately the same diameter as a Fassel torch. They also investigated the direct injection of fine powders into air and argon ICPs. The results were consistent with a previous prediction [77] that the molecular gas ICP is more effective than the argon ICP for sample decomposition. The use of an \( \text{N}_2\text{-Ar} \) ICP has been applied to the determination of phosphorus and aluminium in phosphate rock [10], the analysis of organic solutions [78] and aluminium alloys [79].

Recently several workers [80-82] have published the results of an extensive study of mixed gas ICPs.

1.4 Thermal Isolation and Stabilization of ICP

A plasma formed in the above way attains a gas temperature of such magnitude, that some thermal isolation from the quartz cylinder must be provided. This thermal isolation is achieved by the vortex stabilization technique used by Reed [3,5] using a flow of argon that is introduced tangentially or by the laminar (coaxial) flow pattern (Fig. 1-6) as used by Fassel [7,58]. The flow of argon which is typically 10 to 15 l min\(^{-1}\) goes upwards, cooling the inside walls of the outermost quartz tube and centering the plasma radially in the tube. It also serves as the primary sustaining flow. The plasma itself is anchored near the exit end of the concentric tube arrangement.

Temperatures measured above the coil region and estimated by extrapolation down into the induction region are shown in Fig. 1-14(a). Figure 1-14(b) shows that the distribution of the temperature has, in general, a plateau at the centre of the tube and drops off sharply near the walls. The plateau is quite flat, and in the central part there is a slight dip of approximately several hundred degrees.

The benefits of the ICP stem not only from the very high temperature of the source, but also the unique method of heating the sample. The sample is introduced along a central tunnel (Fig. 1-14a) and the temperature in this tunnel, although sufficient
Fig. 1 - 14(a) Temperature measurement above the coil region. (Ref 83).

Fig. 1 - 14(b) Radio frequency plasma. (Ref. 60)
to volatilize and atomise the sample, is nevertheless relatively cool in comparison to the surrounding toroidal plasma. The sample is therefore heated from the outside by the plasma, with a broad temperature profile within the tunnel. The ICP method of heating offers a much better chance of avoiding the self-absorption and self-reversal effects which are characteristic of arc and flame sources [25].

The conclusion from this brief historical survey is that ICP research has been explorative and involved the use of variety of torches and r.f. generator design. The primary aim of previous research workers was to establish the effects of essential parameters, including the torch configuration, on the analytical characteristics of the ICP to optimise the analytical performance. The relevant literature reflects the explorative nature of such research and covers a diversity of torch configurations and operating conditions.

The various developments have led to a few standardised torches of the conventional type at present used in commercial equipment. These torches, in turn, serve as starting points in the development of a second generation of ICPs that are being developed, with the primary goal of reducing the operating cost (lower argon consumption or replacement of argon by nitrogen or air) and generator cost (lower power <2 kW), without losing the excellent analytical performance achieved with classical torches. The quality of a torch can be judged by its analytical behaviour, detection limits, interferences, stability of background and analysis signal, maintenance during routine operation and gas consumption.

The literature shows the controversy between ICP spectroscopists, as to the rewards and penalties of high (larger than 2 kW) or low power (less than 2 kW) ICPs and nitrogen argon or pure argon ICPs, where high power is usually linked with nitrogen-argon and low power with pure argon ICPs. Argon is the most commonly used gas for plasma generation. A monoatomic gas requires less power than a diatomic gas. The capabilities of ICP-AES described in the literature can be summarised to include
i. Analyses involving major and trace elements

ii. Chemical interferences for refractory elements such as Al, Ti, W, and Zr are almost non-existent in the high temperature and inert atmosphere of the ICP; this contrasts with the relatively cold and chemically complex environment of the flame.

iii. ICP-AES has a linear dynamic range of 4-6 orders of magnitude and therefore requires less frequent dilution of samples.


However, one cannot bypass the problem of spectral interferences encountered in any AES method using a high-temperature source. This severe problem may be encountered in trace analysis.

The ICP-MS technique is confined to the analysis of simple solutions. Aerosol desolvation and a total salt concentration of less than 10 p.p.m. is required in order to prevent blockage of the mass spectrometer orifice and to ensure mass spectral interference is limited (section 6.1)
1.5 Atomic Fluorescence Spectrometry

1.5.1 Historical Aspects

Atomic fluorescence spectrometry (AFS) is based upon the absorption of radiation by an atomic vapour and subsequent deactivation of the excited atoms by the emission of radiation. The wavelengths of the absorbed and emitted radiation are characteristic of the atomic species present.

The fluorescence of atomic vapours has been studied by physicists since the late 19th century [84], but, in spite of the fact that the principles of atomic fluorescence have been known for years, the application of AFS as an analytical tool was first demonstrated in 1964 by Winefordner and Vickers [85].

Since then, AFS has gone through a period of very rapid growth and much of the credit for this can be attributed to two research groups, in particular, Winefordner's group at Florida state university [86] and West's group at Imperial College, London [87,88].

However, AFS has not been a commercial success, mostly because of the overwhelming popularity of atomic absorption spectrometry (AAS) whilst AFS was under development. Therefore, as AFS became more viable, it had to compete with a well established technique which meant that AFS had to be viable. The potential advantages of AFS over AAS include better detection limits, greater linear working range and freedom from spectral interference [89].

During the early development of AFS, flames were used as the only atomisation source available at that time. Winefordner and Staab [86] presented the results of some of their preliminary experiments, which demonstrated the feasibility of the technique for elements, such as Cd, Hg, Zn.

Continuum source [84] excited AFS has been proposed to offer many advantages in multi-element analysis. Amongst them are the good detection limits obtained. But in contrast to fluorescence measurement with line source excitation, the spectral interference
problems are severe in the continuum source excitation mode. Some early studies using xenon arc continuum source and H$_2$/C$_2$H$_2$ flame in AFS for the determination of 13 elements, have been reported by Veillon et al [90]. Further reports have appeared on continuum source in AFS [91-93].

West and Williams [98] first described the use of flameless atomisation device in AFS. They observed a large improvement in the fluorescence signal, due to the high atomic vapour density achieved with this type of atomisation device and the elimination of background noise commonly present in flames. Later, West's group reported [95-97] further work, using the graphite filament in AFS. Kirkbright [98] and Winefordner and Vickers [99] have extensively reviewed the use of non-flame cells in AFS.

Recently a tungsten filament atomiser has been successfully used in AFS by Muzgin et al. [100]. They have reported low limits of detection for some of the refractory elements.

AFS has been reviewed regularly [99,101-102]. Recently Horlick [103] has reviewed developments in the instrumental techniques for (AA, AF and AE spectrometries).

1.5.2 Theoretical Considerations

Atomic fluorescence is an emission phenomenon which relies upon radiational excitation, rather than thermal excitation. It involves excitation of atomic vapour by a radiation of characteristic wavelength from a suitable source, followed by deactivation by emission of radiation [104].

The intensity of the fluorescence radiation ($I_f$) is measured in a direction perpendicular to the exciting source of intensity ($I_o$) and is dependent on several parameters according to the equation given as:
where

\[ I_f = I_o \omega \Omega A_T \phi \]  

is the intensity of the exciting beam

\( \omega \) is the width of exciting beam

\( \Omega \) is the solid angle over which the excited fluorescence is detected and measured

\( A_T \) total absorption factor for the spectral line at which fluorescence is excited, depending both upon the path length of absorption cell and atom concentration

\( \phi \) Quantum efficiency of the fluorescence transition i.e. the fraction of absorbed photons per unit time which is re-emitted as fluorescence radiation per unit time, and the value of \( \phi \) for a particular fluorescence transition will depend on the type of fluorescence and on the quenching of fluorescence which occurs in the cell (see section 1.5.5)

This equation will hold providing the saturation of upper energy levels involved is not reached. The fluorescence intensity is linearly dependent upon the source intensity and the concentration of atoms if the atom density is low. At high atom densities self-absorption of the fluorescence radiation occurs.

1.5.3 Evaluation of Analytical Curves of Growth

In AFS either a line source or a continuum source can be used. When using a line source, the source line width is assumed to be much narrower than the absorption line width. When using a continuum source, or a broad-line source, the source half-width is
assumed to be much wider than the absorption line width. Therefore, evaluation of the basic fluorescence expression, equation 1.1, will depend on the type of source used [105]. Equation 1.1 can be more conveniently and meaningfully handled if only the limiting cases most useful to AFS are considered namely the cases of low and high atomic concentration with continuum source and with a narrow line source.

a. **Continuum source**

For the continuum source the intensity of fluorescence:

at low optical density is,

$$I_f = N_0 \Delta \lambda_D B_{c\lambda u} Y X_1 \Omega \cdot C_1 K_{lu} \left( \frac{L}{A_s} \right)$$  \hspace{1cm} 1.2

and at high optical density is,

$$I_f = \Delta \lambda_D 2B_{c\lambda u} Y \Omega \cdot \sqrt{\frac{C_2 L^2}{\sqrt{\pi}}} \cdot \left( \frac{1}{A_s} \right)$$  \hspace{1cm} 1.3

where:

- $N_0$ is the concentration of atoms in the ground state.
- $\Delta \lambda_D$ is the Doppler half-width of absorption line.
- $B_{c\lambda u}$ is the spectral radiance for continuum source.
- $Y$ is the fluorescence power yield.
- $X_1$ is the fraction of analyte atoms in the lower state involved in the absorption transition.
- $\Omega$ is the solid angle of exciting radiation collected.
C₁ and C₂ are constants defined as

\[ C₁ = \frac{\sqrt{\alpha}}{2} \sqrt{\ln 2} \quad , \quad C₂ = \frac{\sqrt{\alpha}}{\ln 2} , \]

\( K_{lu} \) is the modified atomic absorption coefficient for pure Doppler broadening

L₁, l₁ is the absorption path length

\( A_s \) is the total atomiser cell surface area.

b. Line source

For the line source the intensity of fluorescence;

at low optical density is,

\[ I_l = N_o \cdot B_s \cdot Y \cdot \frac{\Omega}{4\pi} \cdot K_{lu} \cdot \frac{L_1}{l_1} \cdot \frac{1}{A_s} \]  \hspace{1cm} (1.4)

and at high optical density is,

\[ I_f = \frac{1}{\sqrt{N_o}} 2B_s \cdot Y \cdot \frac{\Omega}{4\pi} \sqrt{\frac{qL}{\pi K_f X_f}} \cdot \left( \frac{1}{A_s} \right) \]  \hspace{1cm} (1.5)
where:

- $B_s$ is the radiance of line source.
- $af$ is the damping constant for absorption of fluorescence.
- $K_f$ is the modified absorption coefficient (same as $K_{lu}$) but for reabsorption of fluorescence.
- $X_f$ is the fraction of atoms in the lower state involved in reabsorption of fluorescence.
- $f_f$ is the absorption oscillator strength for reabsorption of fluorescence.

From the intensity expressions for fluorescence, growth curves for AFS can be determined. Many of the parameters in the intensity expression are either constant (for example, $\Delta \lambda_D$, $K_{lu}C_1$, $C_2$), or dependent only on the instrumental system (for example, $B_{c\lambda_{sp}}$, $B_s$, $A_s$, $L_{ill}$, $\Omega_{sp}$), or change little with small changes in atom source composition and temperature (for example, $f_f$, $Y$, $K_f$, $a_f$). Essentially therefore, a plot of integrated intensity versus atom concentration, $N_o$, should give a growth curve having a slope of unity for low atomic concentration with both continuum and line sources (see equation 1.2 and 1.4 and Fig. 1-15). At high atomic concentration and with a line source, the curve is independent of $N_o$ whereas with a continuum source at high atomic concentration the curve is proportional to $1/N_o^{1/2}$ (see equation 1.3 and 1.5 and Fig. 1-15).

As well as the radiance aspects, any expression for fluorescence intensity should also take into account the effects of atomiser cell geometry [106]. The atomisation cell is the volume of space occupied by atomic species, that is illuminated by the excitation beam and viewed by the detector. Inner filter effects shown as pre-filter and post-filter effects can reduce experimental fluorescence intensities. Pre-filter effects [89,107] occur because of weakening of the excitation beam in a region that is not observed by the detector. Post-filter effects occurs if there is an unexposed region between the illuminated volume and detector see Fig. 1-16. Atoms present in this region can absorb
Fig. 1 - 15. Theoretical working curves for line and continuum sources.
the fluorescence emitted from the illuminated volume. The best situation is obtained by having a cell length sufficient to absorb most of the source radiation and a cell width short enough to minimise self-absorption.

1.5.4 Types of Atomic Fluorescence

In atomic fluorescence spectrometry, radiation of a certain wavelength is used to excite an atomic vapour into a higher energy state. Emission of fluorescence radiation then occurs as the excited atoms return to a lower energy state.

The wavelength of the fluorescence radiation can either be the same, larger or occasionally shorter than the excitation radiation wavelength [108-110].

Ions can undergo fluorescence, similar in mechanism and characteristics to the neutral atomic fluorescence transitions [111-114]. The process is known as ionic fluorescence and can be observed if a significant proportion of atoms are ionised by the atomisation source. The main types of atomic fluorescence processes are:

A. Resonance fluorescence

Resonance fluorescence occurs when the atom re-emits a spectral line of the same wavelength as that used for excitation, Fig. 1-17(a).

Many of the AFS measurements made by analytical chemists, involve this type of fluorescence [104].
Fig. 1-16 The inner filter effect
B. Non-Resonance fluorescence

In non-resonance fluorescence the excitation and fluorescence radiation are of different wavelength.

Non-resonance fluorescence can occur as follows:

i. Direct-line fluorescence

In direct-line fluorescence an atom is excited (usually from the ground state) to a higher electronic state and then undergoes a direct radiative transition to a metastable state above the ground state as shown in Fig. 1-17(b). Direct-line fluorescence is normally less intense than resonance fluorescence. The use of direct-line fluorescence gives complete freedom from the effects of scattered source radiation. An example of this type of fluorescence is the absorption at 383.3 nm by lead atoms [115] in the ground state and the subsequent emission of the 405.7 nm and 722.9 nm lines. A similar mechanism is shown by thallium, indium and gallium [116]

ii. Stepwise-line fluorescence

Stepwise-line fluorescence is shown in Fig. 1-17(c). It occurs when an atom is initially excited to a higher excited state from the ground state, the atom which may undergo deactivation (often by a collision or other radiationless process) to a lower excited state rather than return directly to the ground state. The process is likely to occur when the intermediate excited level separation from the initially excited level is extremely small.
iii. Stepwise Excitation fluorescence

Stepwise excitation fluorescence occurs as the result of a stepwise absorption of energy, firstly thermally owing to relatively high temperature of a fluorescence cell followed by a radiative transition from this level. This type of stepwise excited fluorescence will be observed only when the lower level of the absorption line is relatively close to the ground state. This is illustrated in Fig. 1-17(d). A typical example occurs with thallium which quite strongly absorbs at 535.0 nm, so that fluorescence is observed at both 535.0 nm (resonance) and 377.6 nm (stepwise).

iv. Sensitized fluorescence

Sensitized fluorescence is obtained when an atom which has been excited by normal absorption of resonance radiation is able to transfer this energy to another atom during a collision, thus raising the second atom to an excited level from which a radiative transition is possible. In order to obtain sufficient collisional excitation of this kind a high density of the donor atoms is needed.

The mechanism can be represented by three equations as follows,

\[
\begin{align*}
A + hv & \rightarrow A^* \\
A^* + M & \rightarrow A + M^* \\
M^* & \rightarrow M + hv
\end{align*}
\]

A is the atom molecule at high concentration.

M is the metal atom at low concentration.
Fig. 1-17 Types of atomic fluorescence
(a) Resonance fluorescence  (b) Direct line fluorescence
(c) Stepwise line fluorescence  (d) Stepwise excited fluorescence
The classical example of sensitized atomic fluorescence are when a mixture of mercury and thallium atoms is strongly irradiated with mercury resonance radiation at the atomic line 253.7 nm, it is possible to observe sensitized fluorescence of thallium at the 377.6 nm and 535.0 nm lines.

1.5.5 Quenching of fluorescence

There are several types of quenching processes [107] as described below.

i. Quenching by collisions with free electrons

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

This process is mainly transfer of energy between the excited atom and the much smaller mass and higher velocity of the quenching electrons. This is unlikely to be of any consequence in present applications of AFS in which flame atom cells are used, because the free electron concentration outside the primary reaction zone is relatively low in most of the flames employed. The process may become significant if attempts are made to use plasma as atom cells devices which contain far higher electron populations.
ii. Quenching by collision with other atoms

\[
\begin{align*}
A + hv & \rightarrow A^* \\
A^* + B & \rightarrow A + B^*
\end{align*}
\]

This can only occur when the two atoms have excited states of very similar energy. It is simply the process of sensitized fluorescence described in section 1.5.4.

iii. Quenching by collision with molecules

\[
\begin{align*}
A^* + BC & \rightarrow A + BC^*
\end{align*}
\]

This is the most important process for consideration of quenching in flame AFS applications. The ability of many of the simple molecules found in flame gases to quench efficiently a wide variety of excited atoms is generally attributed to the ease with which the electronic energy of the atoms is converted to vibrational energy within the molecules.

1.5.6 Basic Instrumentation

The typical experimental arrangements [84,89] which may be used for atomic fluorescence, atomic emission and atomic absorption are illustrated by the block diagrams in Fig. 1-18. In AFS the atomic vapour generated in the flame cell is irradiated by excitation sources. The atoms absorb light of the appropriate wavelength and excited to a higher energy state. In the fluorescence spectrum obtained when excited atoms return to
Fig. 1-18 Basic instrumental system for Atomic Emission (AE), Atomic Absorption (AA), and Atomic Fluorescence (AF), Flame Spectrometries.
ground state, the wavelengths of emitted lines are characteristic of the element. Fluorescence is emitted in all directions equally, and some of this radiation falls on the detector which views the flame at 90° to the excitation beam.

The basic instrument consists of an excitation source with appropriate power supply, an atomiser, a method of isolating the wavelength region of interest, a photodetector, and an electronic amplifier/readout system.

The excitation source can be either a spectral line (e.g. metal vapour discharge lamp, microwave-excited electrodeless discharge lamp, one of the various types of hollow-cathed lamp, ICP, laser) or a continuum source (e.g. high-pressure xenon arc lamp). The fluorescence intensity is proportional to the intensity of the exciting radiation as indicated in section 1.5.2. Consequently, sources of high radiance are required for good limits of detection. The general requirements for an excitation source are as follows.

1. High radiance over the centre of the absorption line for the analyte atoms.
2. Good short-term and long-term stability.
3. Availability for a large number of elements.
4. Simplicity of operation.
5. Long lifetime.
6. Short warm-up time.
7. Low cost of source and associated power supplies.

The atomiser is usually a nebuliser burner system producing either a turbulent or laminar flame of the type commonly used in atomic absorption and emission spectrometry, or an electrothermal atom reservoir (e.g. electrically heated graphite furnace or metal filament operated in an inert gas atmosphere). The main requirements of an atom cell in fluorescence spectrometry are;
1. High density of analyte atoms.
2. Long residence time of the analyte atoms in the optical path.
3. High volatilisation efficiency
4. Low quenching properties.
5. Low radiance from analyte atoms or background.
6. Good homogeneity and stability.
7. High reproducibility
8. Simplicity and ease of handling.

Lenses are normally used both to focus the exciting radiation on the atomic vapour, and to focus the emitted fluorescence onto the entrance slit of a monochromator or a detector window; mirrors may be used to increase the amount of radiation reaching the detector.

The photodetector types employed are, without exception, photomultiplier tubes either of the conventional type or especially sensitized. The electronic measurement devices used range from a simple d.c. amplifier and direct read-out system to a more complex tuned a.c. phase-sensitive amplifier and recorder readout system or a photon-counting detection system. When a.c. systems are used, the excitation source output is either electronically modulated or mechanically modulated.

A commercial instrument designed for atomic fluorescence spectrometry has been introduced by the Technicon Instrument Corporation, Tarrytown, N.Y., U.S.A. [84] The instrument involves the use of a pulsed hollow-cathode lamp, rotating interference filter wheel, a casse grain mirror system, a flame cell, and logic circuitry to measure the fluorescence of each metal when the proper interference filter is in place. A schematic diagram of the instrument is given in Fig. 1-19. Each hollow-cathode lamp emits a 32-msec pulse of radiation, square-wave modulated at 500 Hz.
Fig. 1-19. Schematic diagram of the Technicon AFS-6 multichannel atomic fluorescence flame spectrometer.
1.5.7 Atom Formation

Chemical analysis by plasma methods requires the reproducible and effective conversion of the sample into the gaseous state in the plasma. When atomic absorption or fluorescence methods are applied, or when atomic emission lines are used in the analysis, at least part of the sample must be atomised, i.e. converted into free atoms in the gaseous state [117,118].

Figure 1-20 shows the different stages of sample transformation into an optical signal and the processes that subsequently play a role herein. The analyte is assumed to be present as a salt or in a complexed form in solution. After fragmentation of the liquid sample into a fine haze of spray droplets, by means of a nebuliser, the solvent is evaporated-desolvated. The dry aerosol particles in the solid or molten state are subsequently volatilized due to the high temperature of the plasma to yield gaseous atoms or molecules. Whereas desolvation and volatilization proceed in an irreversible way, rapid and reversible chemical reaction normally equilibrium between the atomic and molecular species in the gaseous state. The same holds also for the disintegration of neutral metal atoms into free ions and electrons, and the inverse recombination process. Fig. 1-20 shows how, finally, free metal atoms produce an emission, absorption or fluorescence line spectrum.

Each of the processes of desolvation, volatilisation dissociation, affect the spatial distribution of the concentration of analyte atoms in the plasma. Once the gaseous atomic reservoir is created a number of processes occur. Resultant species can be lost by excitation and/or ionisation via collisional paths ways and by compound formation via recombination, making them unavailable for radiational excitation which is the primary requirement in fluorescence measurement.

Dissociation and equilibria of the vapourised species in the most important step. Since, in addition to high temperature and the relatively long residence time of vapours in the plasma, there is also a chemically inert atmosphere, the prerequisite for a high degree of atomisation are fulfilled. However, some problems still occur, particularly with refractory oxide forming elements (Ti, W, Ta, Zr, ...etc), due to the entrainment of
Fig. 1-20  Transformation of sample during its passage through nebuliser and flame
air from the plasma surroundings. These refractory oxides remain undissociated. Incomplete dissociation of molecules containing atoms of analyte element obviously reduces the sensitivity of the determination of the element by AFS as well as AA.

1.5.8 The ICP as an Excitation Source for Fluorescence Spectroscopy

The properties which have made the ICP an excellent source for emission and the annular discharge spectroscopy are: its high excitation capability which gives it a wide dynamic range, low detection limits and the high temperature which gives it the ability to dissociate refractory compounds and thus reduce chemical matrix effects in both emission and fluorescence spectrometries. In addition, the ICP is remarkably free from self-absorption and self-reversal problems at least at the high typical analytical observation zones [119, 120]. Thus it is possible to aspirate a high concentration of the element to be determined, into the plasma, the limiting factor being nebuliser clogging. The ICP possesses the requisite property of being a good line source for atomic fluorescence spectrometry.

The use of an ICP as line source in atomic absorption was demonstrated in 1968 by Greenfield et al. [121].

The use of an r.f. inductively coupled plasma (36 MHz, 2 kW) as an excitation source for the atomic fluorescence in flames was first reported by Hussein and Nickless [122]. Relatively poor detection limits were obtained which probably contributed to the absence of further development and improvement of the ICP as a source for AFS. Significant improvements in sample introduction and plasma stability as well as the availability of intense atomic and ionic line radiation sources for many elements aspirated into the plasma, have more recently encouraged workers to use the ICP as an excitation line source for fluorescence measurement in flames [120, 123-124]. Typically the use of ICP as a line source is based on the nebulisation of a high concentration (10 - 20 mg l⁻¹) of the sought element into the plasma. Radiation from the ICP discharge was modulated and focused by spherical quartz lenses onto the air-acetylene flame into which the sample
was introduced. Detection limits for elements such as Ca, Cd, Co, Cr, Fe, Mg, Mn, and Zn are equivalent to or better than atomic absorption detection limits for these elements [127]. Cavalli et al. [126,127] have used the system for the determination of palladium in nuclear-waste samples and cadmium in lake sediments.

Recently, Omenetto et al. [128] have described a method for correcting the scattering in atomic fluorescence spectrometry excited by an inductively coupled plasma. The effectiveness of the method was demonstrated for cadmium atomised in a separated air-acetylene flame in the presence of a $10^6$ fold excess of aluminium.

Despite the analytical potential of the ICP as an excitation line source with a flame as the atomisation source, the technique still suffers from

i. quenching effects,
ii. flame noise,
iii. low atomisation efficiency,
iv. chemical and ionisation interferences and,
v. poor detection limits for refractory elements.

These problems could be ameliorated by using an ICP as an atomisation cell due to its high temperature and the relatively long residence time of the analyte.

1.5.9 The ICP as an Atomisation Cell for Fluorescence Spectroscopy

The same combination of properties which make the ICP an excellent atom cell for AES should enable its employment as an improved atom cell for AFS particularly for complex samples.

The first study using a high frequency plasma as an atomic cell for fluorescence measurements was undertaken by Hontaser and Fassel [129] who utilised microwave
excited electrodeless discharge lamps to stimulate fluorescence for several elements introduced into an ICP source. The AF detection limits for Cd, Zn and Hg were claimed to be superior to those by AE by a factor of 2 to 8. Three torch designs were examined. However, these sources are not yet commercially available for a wide enough range of elements.

One approach to ICP-AFS systems, demonstrated [130] in early 1981 and now commercially available, is the stimulation of atomic fluorescence from atoms in the plasma tailflame using hollow cathode lamps, see Fig. 1-21.

To date this is the only commercially available atomic fluorescence spectrometer and was designed by Demers and Allemand and built by the Baird Corporation [131] in which the plasma is employed as an atom cell and an array of up to 12 interchangeable optical modules are employed for excitation and detection. Each module consists of a hollow cathode lamp, an appropriate filter and a photomultiplier tube. This array surrounds the centrally placed low power argon plasma. Each hollow cathode lamp (HCL) is pulsed in sequence at a frequency of 500 Hz, that is only one HCL is on at any one time, so only one element is being excited with its resultant fluorescence emission being detected synchronously. The characteristic radiation from a given HCL is absorbed by atoms in the plasma and part of the fluorescence radiation is collected by a lens assembly and passed through the filter to fall on the PMT of the same module. Solution samples are introduced into the plasma by means of a cross-flow nebuliser mounted on a glass-horn spray chamber. The torch used was that of the Fassel type Fig. 1-9 but with the coolant tube extended 48 mm above the aerosol tube nozzle. Good detection limits were obtained for 32 elements, but detection limits for refractory elements were two orders of magnitude inferior to those obtained by conventional ICP-AES. Applications of HCL-ICP-AFS to analysis of low alloy and stainless steel has been reported by Lancione and Drew [132,133]. Additional refinements to the Baird plasma were reported by Demers [134] for the determination of refractory and non-refractory elements.

The influence of r.f. power, carrier gas flow rate and the use of ultrasonic nebulisation on detection limits and matrix effects has been discussed by Jansen and Demers [135].
Fig. 1 - 21. Baird Atomic fluorescence spectrometer with inductively coupled plasma and hollow cathode lamps.
Recently, Sanzolone [136,137] has used commercially available HCL-ICP-AFS manufactured by the Baird corporation to determine six elements (Cd, Cu, Fe, Pb, Mg and Zn) in a variety of geochemical materials. Mercury determination has been carried out, with slight modifications in the instrument, by using the cold vapour technique [142]. This has resulted in superior limits of detection for the element.

Baird Corporation described the determination of metals in petroleum, petroleum products and drinking water [139].

Atomic and ionic fluorescence in an ICP using HCL pulsed at high currents were used [140] as atoms and ionic fluorescence sources to excite atoms and ions in an ICP. Atomic fluorescence was measured for Cu, Ag, Zn, Al, Cr and Mo, while ionic fluorescence was measured for Cu, Cr, Zn and Sr.

Laser-excited atomic fluorescence spectroscopic techniques were first established in plasmas by Pollard et al. [141]. They investigated the application of a continuous-wave laser for the generation of fluorescence from barium, sodium, lithium and vanadium in the ICP. Analytical calibration curves for Ba and Na were presented covering about six orders of magnitude.

Nitrogen-pumped [142-144] and flash lamp-pumped [145] dye lasers were used as excitation sources for the fluorescence of atoms and ions in ICP by Omenetto and Uchida respectively. Analytically useful fluorescence signals from Al, B, Ba, Mo, Pb, Si, Sn, Ti, Tl, V, Y, Zn and U using ICP as atom/ion reservoir and a high power pulsed laser as excitation source have been reported by Omenetto and Human [146].

A pulsed tunable dye laser-excited ICP system was employed by Kosinski [147]. He claimed such a system has the advantages of,

i. high spectral irradiance;
ii. pulsed output;
iii. narrow spectral bandwidth of the excitation source;
iv. wide range of wavelength tunability and
v. high beam collimation.
The combination of eximer pumped dye laser as the excitation source and a 27.2 MHz ICP with an extended-sleeve torch as the atomisation cell for fluorescence measurement has been used [148,149].

A study of plasma diagnostics, quantum efficiencies, excited atom lifetimes, the vertical distribution of atomic and ionic fluorescence intensities, spectral interference and chemical interference using laser induced fluorescence have been recently reported [150-162].

Omenetto et al. [163] have used a combination of a tunable dye laser pumped with a pulsed nitrogen laser as an excitation source, with a conventional short torch as the atomisation cell for fluorescence measurements. Detection limits for 13 elements (mostly refractory) were obtained with a sensitivity better than those obtained using a hollow-cathode lamp as light source.

The pulsed hollow-cathode lamp, although commercially available in an HCL-ICP-AFS, yields limited radiance and may prove difficult to use for stimulation of fluorescence from analyte ions in the plasma. Unfortunately, laser techniques are costly, and of limited wavelength range.

1.5.10 The ICP as an Excitation Source and Atomisation Cell for Fluorescence Spectroscopy.

In 1968, Greenfield [121] was working with inductively coupled plasma for both line sources and atomisers in atomic absorption and postulated the use of two ICPs in one instrument. In 1981 he returned to his idea of using one plasma as a source and another as atomiser, but this time for atomic fluorescence spectrometry. This technique, viz, Atomiser Source, Inductively coupled plasma in Atomic fluorescence spectrometry (ASIA), has been shown to have relative freedom from spectral interference [69]. A typical layout for an ASIA system is shown in Fig: 1-22: [164].
Fig. 1 - 22. A typical layout for an ASIA system
Winefordner [165,166] also assembled an atomic fluorescence system, using two plasmas. The source ICP was operated at 2 kW using a conventional short torch and an analyte solution of 20 mg ml\(^{-1}\) was aspirated, to yield the line source radiation. The radiation emitted from 10-30 mm above the load coil was chopped and focused into the atomisation ICP at 60-80 mm above the load coil. The atomisation ICP is an extended-sleeve torch run at 0.9 kW for atomic lines and 1.0 kW for the ionic lines of non-refractory elements. Emission, excitation and fluorescence analytical curves of growth, and the vertical distribution of zinc atomic and calcium ionic fluorescence intensities were obtained.

Greenfield and Thomsen [167] used an ASIA spectrometer. Detection limits for several elements in both fluorescence and emission modes were compared directly. They found that the detection limits for the non-refractory elements were, in general, better in the fluorescence rather than the emission mode while for the refractory elements the converse was true. All limits of detection were in the p.p.b. range. Later, they introduced an organic additive into the atomiser plasma. The limit of detection for tungsten improved by a factor of two, by using ethanolic solution instead of adding traces of hydrocarbon gases [168].

An ICP-excited ICP resonance monochromator and fluorescence spectrometer for the analysis of trace to major sample constituents was presented by Krupa et al. [169,170]. The sample was aspirated into the source ICP and, by measuring its emission using the second plasma as a resonance monochromator, a linear dynamic range of up to \(5 \times 10^7\) was claimed. An important feature of this experimental set up (ICP-ICP-AFS), is the ability to analyse solutions of high concentration without unnecessary dilution.

Recently, Greenfield studied resonance and non-resonance atomic transitions in plasma spectrometry as well as demonstrating that the ASIA instrument has freedom from spectral interferences [70].

A growing number of papers for AFS techniques are being published, the theory of the method, improvements and modification in the instrument are being reported continuously [174-178], as will be described in chapter five.
CHAPTER 2
GENERAL INSTRUMENTAL ASSEMBLY
AND OPERATING PROCEDURE

2.1 Inductively Coupled Plasma
2.2 High Frequency Generator
2.3 Plasma Torches and Gas Flow
   (i) Greenfield torch
   (ii) Long sleeve torch
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2.4 Optical System
   2.4.1 AFS optical system
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2.11 Sample Introduction System
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Chapter Two
General Instrumental Assembly and
Operating Procedure

2.1 Inductively Coupled Plasma

The instrument used in this study was the atomiser, source, inductively coupled plasmas in atomic fluorescence spectrometry (ASIA) instrument [167] (see Fig. 2-1). It is a dual inductively coupled plasma instrument that can be operated as an atomic fluorescence spectrometer, or, by moving the chopper as indicated by the dashed line in Fig. 2-1, as an atomic emission spectrometer.

2.2 High Frequency Generator

The function of the radiofrequency (r.f.) generator in the ICP system is simply to provide a high-frequency current in the induction coil.

One group of generators, the free-running generators, allow the frequency of the oscillating current to change as the plasma impedance changes. Another type of generator, the crystal-controlled generator, maintains constant frequency by using the vibration of a piezoelectric crystal to regulate the frequency of the current. Both types are in widespread commercial use and both systems are clearly capable of giving entirely satisfactory results.

The high-frequency (h.f.) current produced by the generator in the coil provides the oscillating magnetic field which is necessary for the operation of the ICP. The waste heat generated in the coil is normally dissipated by water cooling. The coil is made of copper.
Fig. 2-1. ASIA Instrument.
In the present study two generators were used. The Radyne generator RD150 of 15 kW output at 7 MHz was used to power the light source plasma, and a smaller Radyne SG15 of 2.4 kW output at a frequency of 36 MHz used to power the atomiser plasma. Both these generators, which are free running have an efficiency of power transfer of about 50%.

The power from the generator was transferred via a coaxial cable to the copper coil. A fan incorporated in the generator served to cool the final power amplifier valve.

2.3 Plasma Torches and Gas Flows

The design and development of different torches for the ICP have been outlined in chapter one. There is some confusion in the use of the terms coolant and plasma gases in the literature. For example, Fassel et al. [177] refers to them as the plasma and auxiliary gases respectively while Greenfield [167] used the terms coolant and plasma respectively. Others, such as Huang et al. [152] used the terms coolant and auxiliary respectively. In order to clarify their functions, the following terms are used in this work.

1. **Coolant gas**: refers to the outermost gas flow which enters the tube tangentially in all torch types used in this work and swirls upwards. It's function is to cool the upper portion of the torch and sustain the discharge in Fassel and long extended sleeve torches.

2. **Plasma gas**: refers to the intermediate gas flow. Its function is to raise the discharge, reduce salt build up on the injector tip, as in the Fassel torch, and sustain the discharge, as in the Greenfield torch. Plasma gas was not found necessary for a long sleeve torch, because the coolant gas serves to build up and stabilise the discharge as well as cool the torch [152].
3. **Injector gas** (nebuliser gas): refers to the innermost gas flow which carries the sample aerosol to the plasma.

The gases were supplied from separate cylinders. The gas streams were passed through separate, calibrated flow-meters and the flow was finely controlled before entering the torch to allow optimum operating conditions to be obtained.

Three plasma torches were used. These are described below.

(i) **Greenfield torch**

The source ICP was induced in a Greenfield torch which consists of a plasma torch (Fig. 2-2) and injector (Fig. 2-3), made from silica and pyrex respectively. The torch holder was made from Teflon. A brass base was designed for this holder to allow the torch to be positioned in any perpendicular direction centrally inside the h.f. coil. The brass base was used only during assembly when the torches were glued to the base and then removed after about 2 hours, when the epoxy resin had hardened. The use of epoxy resin for fixing the quartz tube into the base has been reported by Lichte and Koirtyohann [178]. The injector was positioned inside the central tube of the plasma torch. The torch outer tube was terminated 5 mm above the water cooled three turn load coil, with the injector tube 2-3 mm below the tip of intermediate tube.

The observation height above the working coil in the ICP can be adjusted by vertically moving the whole plasma torch assembly, without moving the optical system. The optimum observation height and power setting for the ICP depends upon the element under investigation.

The torch was capable of handling the aspiration of solutions of high salt content (up to 40% of some elements) into the plasma without blockage of the injector.
Fig. 2 - 2. Diagramatic representation of the plasma cell in the Greenfield torch.
Fig. 2 - 3. Diagramatic representation of the injector used in the Greenfield torch
(ii) **Long sleeve torch**

The atomiser plasma was induced in an long sleeve torch (Fig. 2-4) which minimised the effect of air entrainment and diffusion of analyte atoms into the surrounding air, thereby reducing fluorescence quenching. The torch consisted of a centrally positioned non-detachable injector, surrounded by two concentric quartz tubes. The plasma was sustained in the flow of argon in the outer coolant tube. No *plasma* gas (flow in the inner tube) was used because it was not necessary for the operation of the torch as an atomiser in fluorescence studies. The torch outer tube was terminated 6.5 cm above the water cooled one and a half turn load coil.

Observation height adjustment can be performed in a similar manner to that of the source ICP.

(iii) **Fassel torch**

A Fassel torch (Fig. 1-9) was used in the emission studies with the Radyne SC15 plasma generator. The torch consisted of two concentric quartz tubes with the injector positioned inside the central tube of the pyrex plasma torch. The outermost tube was encircled by a one and a half turn water cooled copper coil. It was terminated 1.5 cm above the load coil, with the injector tube 2 mm below the tip of the intermediate tube.

The load coil and plasma torch were housed in an aluminium box in order to prevent h.f. radiation from interfering with nearby electronics. The box had an opening at the top to allow the plasma gases to exit to the extraction system positioned above, with rectangular openings in appropriate locations to allow light to escape to the detector. The box was provided with a cobalt blue glass viewing window. The plasma torch was mounted on a racking mechanism which allowed the assembly to be removed along a perpendicular axis, colinear with the monochromator entrance axis.
Fig. 2 - 4. The extended tube torch.
2.4 Optical System

2.4.1 AFS Optical System

The optical system for the AFS studies consisted of four, 2 inch diameter, fused quartz convex lenses (see Fig. 2-5).

A 1:1 image of part of the tail flame of the source ICP was brought into focus at the aperture of the light chopper using the first lens. The image formed at the chopper was focused by the second lens, centrally on the tail-flame of the atomiser ICP forming an image of breadth 3 mm and height 1 cm (see Fig. 2-6).

A 1:1 image of part of the atomiser tail-flame was focused onto the entrance slit of the monochromator by the other two lenses.

The observed fluorescence intensity depends upon the volume of the atomiser tail-flame illuminated by the source radiation and observed by the monochromator. The monochromator had a fixed slit height of 10 mm and a maximum slit width of 3.6 mm. Since the breadth of the exciting beam in the atomiser was 3 mm, the maximum volume from which fluorescence can be observed was 108 mm$^3$ (see Fig. 2-6). In order to obtain the desired theoretical fluorescence curve of growth, complete illumination of a particular volume in the atomiser tail-flame was required, thereby avoiding pre-filter and post-filter effects (inner filter effects) Fig. 1-16.

The illumination geometry of the ASIA spectrometer was investigated by using it to obtain the fluorescence curve of growth for copper (log Cu fluorescence signal against log Cu concentration in the atomiser plasma, with a fixed concentration of Cu in the source plasma) and comparing its shape with that of the theoretical curve of growth.

The results indicated that the instruments illumination geometry gave no significant inner filter effects, the copper curve of growth (Fig. 2-7) giving values near the theoretical values of +1 for the positive slope and -1/2 for the negative slope, in addition, the source ICP acted as a line source of excitation [84].
L1 - fused silica lens,
   \( f = 5.08 \text{cm}, \; d = 5.08 \text{cm}, \; u_1 = v_1 = 2f = 10.16 \text{cm} \).
L2 - \( f = 5.08 \text{cm}, \; d = 5.08 \text{cm}, \; u_2 = 30.48 \text{cm}, \; v_2 = 6.10 \text{cm} \)
L3 - \( f = 5.08 \text{cm}, \; d = 5.08 \text{cm}, \; u_3 = v_3 = 2f = 10.16 \text{cm} \)
L4 - \( f = 5.08 \text{cm}, \; d = 5.08 \text{cm}, \; u_4 = v_4 = 2f = 10.16 \text{cm} \)
C1 - position of chopper in fluorescence,
C2 - position of chopper in emission

Fig. 2-5. Design of the optical system on the ASIA spectrometer.
Fig. 2.6. X-section of atomiser plasma

I the image of source plasma (3 mm across)
the image height is 10 mm
Monochromator slit width 3.6 mm
Observation cell = 3 mm x 3.6 mm x 10 mm
Fig. 2 - Copper AFS curve of Growth, 100 p.p.m. in the source plasma; \( \lambda = 324.8 - 327.4 \) nm; slit width = 3.6 mm.
2.4.2 Atomic Emission Optical Systems

In the emission studies using the Radyne SC15 plasma generator and the Fassel torch, the third lens was used to focus a 1:1 image of part of the ICP tail-flame into the aperture of a light chopper (refer to the dashed lines in Fig. 2-1). The image formed at the chopper was then focused onto the entrance slit of the monochromator by the fourth lens (see Fig. 2-5).

2.5 Monochromator

The monochromator consists of entrance and exit slits, a focusing mirror, lenses and a diffraction grating. The mirror and grating are mounted in a light-tight box.

The work described in this thesis has been conducted with a single channel detection system. The 0.75 m, f/14 monochromator used in this study (Optica, U.K.) consisted of a Czerny-Turner mount optical arrangement incorporating a 600 lines/mm grating, blazed at 300 nm and giving a reciprocal linear dispersion of 1.6 nm mm\(^{-1}\). It had a maximum slit width of 3.6 mm and a minimum slit width of 20 micrometers, giving spectral band passes of 5.76 nm and 0.032 nm respectively. The instrument had a fixed slit height of 10 mm, and was capable of scanning from 180 to 1000 nm at speeds of either 5 or 10 nm min\(^{-1}\).

2.6 Photomultiplier

The photomultiplier used had wide spectral response (u.v. and vis.) bi-alkali photomultiplier tube (EMI 9789 QB) with a maximum gain rating of 10\(^8\). Its greatest sensitivity was in the 400 to 500 nm wavelength region and it was kept turned on continually in order to stabilise the dark emission count rate.
2.7 Lock-in Amplifier

The amplifier was a Brookdeal model 9503 with a model 5002 current pre-amplifier. It received a reference signal from the light chopper and amplified signals from the photomultiplier that had been modulated to the chopping frequency of the chopper, before sending the signal to the computer or chart recorder.

2.8 Light Chopper

The light chopper was a Brookdeal instrument consisting of 30 blades and capable of chopping at frequencies of between 5 Hz to 1 kHz. A chopping frequency of 977 Hz was used throughout the project.

The technique enables fluorescence radiation to be distinguished from unchopped light by modulating the excitation radiation prior to it reaching the atoms in the atomiser plasma. Light that is not modulated by the chopper will not be amplified.

2.9 Computer System

The computer system consisted of an Apple IIe 128K micro-computer with a dual disc drive, monitor and a Canon PW 1080A dot matrix printer.

It was interfaced to the amplifier and computer program was written by Thompsen and modified by Malcolm [179] to integrate the signals received from the amplifier, displaying the signal intensities in millivolts on the monitor screen and printer, all signals were integrated for 10 seconds.

As well as aiding fluorescence studies, the computer program also speeded up the optimisation in emission work, by measuring emission and background intensities and quickly calculating signal to background ratios.
2.10 Chart Recorder

The chart recorder (Gould BS-271) was capable of receiving signals from the lock-in amplifier and was used to record fluorescence and emission spectra.

2.11 Sample Introduction System

Several different types of nebuliser and spray chamber were used in this project. A detailed study of the sample introduction system is described in chapter three.

(i) GMK nebuliser

The aerosol for the atomiser ICP was produced by a GMK nebuliser and spray chamber system (Fig. 2-8).

The supply of solution to the nebuliser was provided by a peristaltic pump. In the nebuliser, solution flows over an argon gas outlet forming an aerosol which was transported to the plasma torch. Large droplets were broken up by an impact bead and any solution hitting the spray chamber walls went to waste.

(ii) de Galan nebuliser

The aerosol for the source ICP was produced by a de Galan nebuliser (Fig. 2-9) and cyclone spray chamber (Fig. 2-10) system. The de Galan nebuliser consisted of a cylindrical plastic block, with a V-groove cut across it's diameter. At the bottom of the groove appeared two narrow channels, one for a flow of argon and the other for the sample solution flow. A peristaltic pump was used to supply solution to the nebuliser and to remove waste solution from the bottom of the spray chamber.
Fig. 2-8. Components of the GMK Nebuliser System.
Fig. 2 - 9. de Galan nebuliser.
The aerosol produced is collected from the central region of the spray chamber and transported to the plasma torch.

to drain

glass frit

glass flask (500ml)
de Galan nebuliser

glass flask (500ml)
de Galan nebuliser

Fig. 2 - 10. Diagram of a cyclone spray chamber.
(iii) Meinhard nebuliser and Scott spray chamber

To compare the alternating variable search and simplex methods of optimisation, an ICP powered by the Radyne SC15 plasma generator and induced in a Fassel torch was employed.

The Meinhard nebuliser and Scott spray chamber (Fig. 2-11) were used [19] to produce the aerosol because of their speed of response when optimising signal to background ratios in atomic emission studies.

Solution was drawn up into the nebuliser by natural suction (i.e. no pump was required) because of low pressure, generated as the flow of argon passes around a narrow orifice.

2.12 Operation Procedure

The following routine was adopted to operate the system each time the generator equipment was used after having been completely turned off, and relates only to the initiation of the plasma.

A. Emission mode

1. Load the computer, Turn on cooling water, power supplies, argon supplies.
2. Place nebuliser tube into distilled water and open argon injector, coolant and plasma flow-meter tap fully for two minutes then close off.
3. Turn the wheel of the generator fully anti-clockwise; switch on the h.f. generator.
4. When the, on switch has illuminated (after three minutes) open the coolant flow-meter tap to give a flow of 11 l min\(^{-1}\) argon, press the r.f. button on the generator, turn the r.f. level dial to give full forward power, turn on the Tesla coil. The plasma should pop and form spontaneously and the Tesla coil can then be switched off.
Fig. 2 - 11. (a) Scott spray chamber.
(b) Meinhard nebuliser
5. *Turn down* the r.f. power to about 500 w and *fully open* the injector flow-meter tap and *adjust* the plasma gas flow-meter tap to a flow of 21 min⁻¹.

6. *Switch on* the chopper, select operating conditions

*To shut down the system.*

1. Press the STOP r.f. button

2. Wait three minutes for the torch to cool then turn off the gas and water flows.

3. Wait five minutes for the h.f. generator to cool down switch off the generator, turn off the power supplies.

**B. Fluorescence mode**

(i) *The small Radyne plasma generator SG15*

Follows the steps as in emission mode, except the plasma gas is *turned off.*

(ii) *Radyne plasma generator RD150*

Follows the steps as in emission mode, but instead of turning on the coolant flow-meter tap turn on the plasma flow-meter tap to give 12 l min⁻¹ argon, then turn on the coolant flow-meter tap to give 30 l min⁻¹ air when the plasma forms.
CHAPTER 3
EVALUATION OF SAMPLE INTRODUCTION SYSTEMS AND FUNDAMENTAL STUDY OF LEAD SPECTRUM

3.1 Introduction

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Chapter 3
Evaluation of Sample Introduction Systems and
Fundamental Study of Lead Spectrum

3.1 Introduction

The ICP-AES technique has been successfully applied to the analysis of samples introduced to the plasma as solids, solutions and vapours. The different methods of sample introduction into the ICP have been extensively reviewed by Barnes [24], Browner [180] and Boumans [28]. The major routes available for sample introduction to the plasma are shown in Fig. 3-1. As can be seen, liquid sampling is the normal method of sample introduction and can be performed in several ways. This is due to its simplicity, versatility and well characterised nature. In addition, dissolution may be a necessary step in sample preparation, in order to provide a representative sample of the analyte. In the study reported here, a comparison was made between a commercially available GMK nebuliser and two de Galan nebulisers (SG1 and SG2). These were used in combination with a cyclone spray chamber and an impact wall spray chamber on the ASIA instrument. Also included in this comparison was an ultrasonic nebuliser. A complete optimisation procedure was carried out by using a cyclic alternating variable search. The figure of merit used was the total fluorescence signal for lead at $\Sigma 280.2-283.3$ nm. The effect of using a desolvating system was also investigated. Recycling of the solution on the source plasma was achieved. Furthermore, the fundamental studies of the fluorescence spectrum for lead at different ranges were carried out.
Fig. 3-1 Sample introduction Routes for plasmas
3.2 Pneumatic Nebuliser

Liquid sample introduction with pneumatic nebulisation, is the approach used in the vast majority of atomic spectroscopy determinations. It is the most popular form of sample introduction as it is simple, inexpensive and robust, without being particularly prone to memory effects. The pneumatic nebuliser may be of a concentric, cross flow, Babington or fritted disc design [25].

3.2.1 The Concentric Nebuliser

The concentric nebulisers, generally of metallic construction, which have been used in flame spectrometry, are of limited use in ICP work. This is due to the high flow of gas required to operate the nebuliser, which is too high for the optimum ICP operating conditions. This problem has led to the development and design of specialised pneumatic nebulisers for use at low flow rates. The nebulisers have to have extremely fine orifices for both gas and liquid flows. These are difficult to fabricate, are fragile when made of glass and block easily when solutions containing high dissolved solids are being aspirated. The concentric nebuliser of the type developed by Meinhard [181] is the most popular nebuliser for ICP work. The geometry of a typical Meinhard nebuliser is shown in Fig. 2-11. This consists of a narrow annulus surrounding a narrow sample capillary tube, the nebuliser is generally constructed from glass. The passage of gas at high velocity through the annulus creates a low pressure region which causes solutions to be drawn up to the tip and shattered by the high gas velocity into an aerosol. Most Meinhard nebulisers are designed to operate at 1 l min\(^{-1}\) gas flow at between 20 and 50 psi. with the sample uptake rate between 1 to 4 ml min\(^{-1}\). The aerosol droplet size is dependent on nozzle geometry, the smallest capillary bore that will achieve a particular uptake rate should yield the finest disintegration of analyte [26]. The main disadvantage of Meinhard nebulisers, as with any nebuliser employing a narrow sample capillary, is
the ease of blockage. Consequently considerable care has to be taken to avoid blockages, such as routine aspiration of appropriate solvent usually water and avoiding the use of solutions containing a high concentration of dissolved salts or suspended particles. Some minor blockages in the sample capillary can be cleared by various simple methods, e.g. back-flushing the nebuliser from a syringe or holding the nebuliser in an ultrasonic bath. Recently, Baginski and Meinhard [182] reported an improvement in the design of Meinhard concentric nebulisers for aspiration of solutions containing high concentrations of dissolved salts (Meinhard type C), by using a recessed capillary tip nozzle.

However, the Meinhard concentric nebuliser has shown advantages, such as its simplicity and ease of operation (self-feeding) and, fixed configuration so that it does not require further adjustment. Several workers [74,183,184] report using Meinhard concentric nebulisers with an ICP.

3.2.2 The Cross-flow Nebuliser

In the last few years, cross-flow nebulisers have become increasingly popular for ICP work. A typical diagram of the nebuliser is shown in Fig. 3-2. Here two capillaries are mounted at right angles, one is for the sample solution and the other is for the injector gas flow. This design (as well as the concentric nebuliser) could block easily when suspended particles, or concentrated solutions which tend to crystallise at the nebuliser tip, are aspirated. Although this problem was avoided using a cross flow nebuliser provided with disposable tips [38], poor stability over long periods of time was obtained. This resulted from a dimensional change in the supporting PTFE block. This problem was overcome recently by Meddings et al. [185] and Novak et al. [186] by making fixed cross flow nebulisers as shown in Fig. 3-3, in which the fine capillaries were replaced by glass tubes drawn down to fine jets at the ends. The jets were then positioned so that a given solution uptake rate was achieved at the required gas flow and pressure. The tubes were then joined by a glass bar which was bent to achieve alignment of the capillary tips.
Once constructed, the nebuliser required no further adjustment during routine operation. Using this nebuliser, detection limits obtained were similar to those obtained with the Meinhard at comparable gas flow rates [186]. Nevertheless, the nebulisers were found to block when solutions containing high salt content (5-10%) were nebulised. The cross flow nebulisers are widely used with the ICP [187,188].

3.2.3 The Babington Type Nebuliser

The problem of the blockage of cross flow nebuliser when solutions containing high salt were nebulised, was overcome by using nebulisers developed by Suddendorf and Boyer [189] and Wolcott and Sobel [190]. In these designs the sample solution was pumped into a V-groove channel and made to flow over a small hole which serves as the gas exit, at which the solution was converted to a fine aerosol by pressurised injector gas flowing through the orifice. These nebulisers, which are based, on the principle of the Babington [191] nebuliser, and often called Babington type nebulisers were used to aspirate slurries of finely divided particles, such as powdered coal and rock [192].

A number of Babington type nebulisers were used in ICP systems [193]. The GMK nebuliser (Fig. 2-8) constructed by McKinnon and Giess in 1978 [194] was developed later by the Labtest equipment company and is commercially available.

A plastic nebuliser was developed by Ebdon et al. in 1982 [35]. Ebdon's nebuliser was constructed from a single length of PTFE rod which is easier to manufacture than the other types as well as a de Galan nebuliser.

Recently Cecconie et al. have characterised a micro-Babington nebuliser and compared its performance with that of a cross-flow nebuliser for ICP-AES [195].
3.2.4 The Fritted Disc Nebuliser

Another new type of nebuliser which does not require the passage of solution through a fine capillary tube is the glass frit nebuliser as shown in Fig. 3-4. This was developed by Apel et al. [196] in 1977 and modified recently by Layman and Licht [197]. In this design, sample solution is pumped onto the face of a fine glass frit through which the nebuliser gas is passed, producing an aerosol of sample solution. It was observed that the nebuliser was highly efficient at only low liquid flow rates, with some memory effects. A combination of a glass frit disc with a Meinhard nebuliser was used by Luffer and Salin [198].

3.3 Ultrasonic Nebuliser

Ultrasonic nebulisers operate on a somewhat different principle from pneumatic nebulisers. The sample solution is subjected to agitation in the MHz frequency range, produced by a transducer. An aerosol of the solution, containing a higher proportion of smaller droplet sizes than that produced pneumatically, is continuously broken away from the surface of the liquid. Consequently, more of the aerosol generated can be passed directly to the plasma which results in a lower detection limit. Values 5-10 times better than those obtained with pneumatic nebulisers have been reported [34]. In addition the independence of aerosol production on the transport gas flow, facilitates individual control of the gas flow rate and aerosol generation rate, which is not possible with pneumatic nebulisers.

The relationship of aerosol droplet diameter \(d_0\) generated by ultrasonic nebulisation with the ultrasonic frequency is given by the following formula [199,200]

\[
d_0 = 0.34 \left(\frac{8\pi \sigma}{\rho f^2}\right)^{\frac{1}{3}}
\]
Fig. 3 - 2. Cross-flow nebuliser

Fig. 3 - 3. Fixed cross-flow nebuliser

Fig. 3 - 4. Fritted glass disc nebuliser
where
\[
\begin{align*}
\sigma & \text{ is the surface tension of the solution (dyne-cm}^{-1}) \\
\rho & \text{ is the specific gravity} \\
f & \text{ is the frequency (Hz)}
\end{align*}
\]

Therefore, it is possible to reduce droplet size simply by increasing the frequency at which the transducer operates.

Ultrasonic nebulisers, however suffer from a number of disadvantages [201] among which are the following:

1. Complexity and expense
2. Long washing time
3. The requirement for desolvation apparatus to prevent the plasma from being extinguished or from suffering considerable reduction in its excitation temperature [202]

Since the early work on ICP-AES, ultrasonic nebulisation has been recognized as a powerful method for aerosol generation [7,203]. Two types of ultrasonic nebulisers have been developed; in the first type the analyte solution flows over the surface of the transducer as described by Boumans and de Boer [203] and later on by Olson et al. [205]. Whereas, in the second type, the ultrasonic energy is focussed on a Mylar-film forming the bottom of a vessel containing the analyte solution, as described by Wendt and Fassel [7] and later on by Mermet et al. [204]. Recently Fassel et al. [205,206] have reported an extensive study of ultrasonic nebulisation.
3.4 Other Methods

A number of alternative means of sample introduction into the plasma have also been developed and used.

1. Swirl cups

Powders may be injected into the plasma from an agitated cup by gas displacement [6]. The basic device involves a downward injection of a flow of argon into a sample cup which also acts as a swirl chamber. The cloud of powder thus formed is led to an outlet and then to the torch. The centrally injected gas flow displaces the powder from the base of the sample cup onto the walls.

2. Fluidised bed

Another technique for introducing solid sample powders used a fluidised bed chamber [12]. In this device, powdered sample is placed on a sintered glass disc through which argon is flowing.

3. Electro-thermal atomisation

Rapid thermal vaporisation combined with ICP has been used for solid samples and solid residues from sample solutions. Substrates which have been used for the volatilisation include tantalum filaments [207] and graphite rods [208].
4. Direct insertion

The direct introduction of solids into an ICP using a rod or cup device has been reported by a number of workers [209,210]. The first of these used a graphite rod as a sample elevator to introduce the sample directly into the torch in the region of the plasma coils.

5. Arc or spark chamber

Microarcs and spark discharges have been employed for the vaporisation of solid samples [211,212]. The sample after sparking is transported from the spark sampling chamber to the ICP directly by the gas which flows over the microarc electrodes.

6. Direct laser ablation

Laser ablation, in which the power from a focused ruby laser is used to vaporise a spot of material directly from a solid surface has been used [213,214].

7. Slurry nebulisation

Slurry nebulisation using a Babington type nebuliser to introduce slurries in which powders are suspended with or without agitation in either aqueous or organic solvents, has been reported by a number of workers [35,215].
3.5 Spray Chamber

In addition to the nebuliser itself, the function of the spray chamber is critical to successful liquid sample introduction. The primary purpose of the spray chamber is to remove the larger droplets (larger than 10 µm) from the aerosol before it enters the ICP torch [216]. The most commonly used design of spray chamber for the ICP system is a dual concentric chamber, based on the design of Scott et al. [19]. In this design, the aerosol from the nebuliser enters initially a chamber of approximately 2.5 cm internal diameter. The aerosol laden gas stream passes through this tube, and then back through an outer concentric tube of larger diameter, before exiting to the plasma injection tube. A typical design is shown in Fig. 2-11.

Certain spray chambers, such as the spray chamber used by Greenfield [34], impart a centrifugal motion to the aerosol. The action of the cyclone is to impart a spiral motion to the aerosol. Consequently, particles of larger diameter, on entering the chamber, possess a higher angular momentum, and tend to strike the walls of the spray chamber. This design of spray chamber has proved to be effective as a means of removing larger droplets from the aerosol spray [34].

Another type of spray chamber design is based on the fact that if an aerosol passes through the device, each component droplet will rapidly reach its own terminal settling velocity, under the influence of gravity [217]. In many cases some type of impactor bead is used. This not only helps to remove the larger droplets but may generate more small droplets as the larger droplets are caught and further fragmented.

For most nebuliser/spray chamber systems now in use, the proportion of solution going to waste is large. The transport efficiency is usually below 2% and may be less than 1% [35].
3.6 Experimental

3.6.1 Reagents

i. Source ICP

All solutions for the source plasma were prepared by dissolving AnalAr (BDH) grade lead nitrate salt Pb(NO₃)₂ in tri-distilled water.

ii. Atomiser ICP

Solutions for the atomiser plasma were prepared by using standard 1000 p.p.m. lead nitrate SpectrosoL (BDH) solution and diluting with tri-distilled water as necessary. Solutions greater than 1000 p.p.m. were prepared by dissolving specpure grade lead nitrate salt in tri-distilled water.

3.6.2 Optimisation Procedure

The twelve experimental variables Table 3-1 excluding the spectrometer slit width were optimised for lead at wave lengths ∑280.2-283.3 nm in the fluorescence mode of operation for the ASIA instrument with different nebulisers. The technique used for the optimisation was a cyclic alternating variable search (discussed in more detail in chapter 4). The search began with the source plasma followed by the atomiser plasma. The process was repeated in a cyclic manner until the figure of merit used showed no significant change. The figure of merit used was total fluorescence signal [167].
3.6.3 Sample Introduction System

a. Nebuliser

i. GMK nebuliser

The commercial GMK nebuliser was used Fig. 2-8. In this design two capillaries are mounted at right-angles, one acting as the sample delivery (by a pump) and the second carrying the gas flow. The accurate positioning of the capillaries is vital in order to achieve efficient nebulisation, and initially this was achieved by careful adjustment of the capillaries. The spray impinges onto an impact bead about 0.5 mm from the nebuliser tip.

ii. de Galan nebuliser (SG1 and SG2)

The de Galan nebuliser is shown in Fig. 2-9 and consisted of a cylindrical plastic rod with a V-groove cut across its diameter. In the bottom of the groove were two narrow holes one for a flow of argon and the other for the sample solution flow. There is little difference in the gas flow rate between SG1 and SG2 see Fig. 3-5.

iii. Ultrasonic nebuliser

A schematic set-up for ultrasonic nebulisation is shown in Fig. 3-6. Nebulisation is induced when the test-solution is pumped over the surface of a Mylar film (nebulisation cell). A piezoelectric crystal vibrates with a set frequency, and the acoustic wave is propagated in distilled water. The vibrations are transmitted through a Mylar film to the analyte solution. A stream of argon carries the aerosol into the plasma through a round chamber. The residual analyte is pumped away from the cell after analysis. The desolvation system is built-in with the nebuliser.
Fig. 3-5. de Galan SG1 & SG2 calibration curve
b. **Spray chamber**

i. **Cyclone spray chamber**
   A schematic diagram for the cyclone spray chamber is shown in Fig. 2-10. The aerosol is introduced tangentially into a cyclone chamber, the larger droplets falling to the drain at the base and the aerosol leaving from a tube at the centre of the chamber. The drainage tube was covered by a coarse glass frit, which allowed smooth drainage of waste liquid and provided the back pressure necessary for aspiration of aerosol into the plasma [198].

ii. **Impact wall spray chamber**
   A schematic diagram of the impact wall spray chamber is shown in Fig. 3-7. The spray impinges onto a wall about 4 cm from the nebuliser tip. This may have the effect of further reducing the number of large droplets entering the plasma.

3.6.4 **Desolvation System**

In this design the aerosol passes through a glass tube heated externally by a furnace with a variable control (temperature about 200 °C). All the water droplets are evaporated leaving an aerosol of solute particles. The gas then passes through a water-cooled condenser where the water vapour condenses on the cold surface, but the solute particles remain suspended and pass to the plasma.
Fig. 3-6. Ultrasonic nebuliser with the desolvat system.
Fig. 3-7. Impact wall spray chamber.
3.6.5 GMK Nebuliser on Atomiser Plasma

The complete optimisation procedure was carried out for the source plasma with the GMK nebuliser, the de Galan nebuliser SG1 with the cyclone spray chamber and the de Galan nebuliser SG1 with the impact wall spray chamber as shown in Table 3-1.

3.6.6 GMK Nebuliser on the Source Plasma

The complete optimisation procedure was carried out for the atomiser plasma with the de Galan SG1 nebuliser with both the cyclone spray chamber and the impact wall spray chamber as well as with the ultrasonic nebuliser as shown in Table 3-2.

3.6.7 Comparison of de Galan Nebuliser SG1 and SG2

A comparison of the de Galan nebulisers, operated with the cyclone spray chamber was made on the source plasma whilst keeping the GMK nebuliser on the atomiser plasma under the optimised conditions. In addition the instrument response was obtained

(a) with the de Galan SG1 nebuliser and cyclone spray chamber were on the source plasma while the de Galan SG2 nebuliser and cyclone spray chamber on the atomiser plasma and;

(b) with the de Galan SG1 nebuliser and cyclone spray chamber on the source plasma and the GMK nebuliser was on the atomiser plasma.
3.6.8 Aerosol Desolvation on the Atomiser Plasma

The desolvator system was combined with the GMK nebuliser and the de Galan SG1 with the cyclone spray chamber. The effect of desolvating the aerosol on the atomiser plasma, while keeping the GMK nebuliser on the source plasma and the effect of using the desolvator system with the ultrasonic nebuliser was investigated on the atomiser plasma as shown in Table 3-3.

3.6.9 Aerosol Desolvation on the Source Plasma

The combination of the GMK nebuliser and the de Galan SG1 with the cyclone spray chamber were investigated on the source plasma with the desolvating system. While keeping the GMK nebuliser on the atomiser plasma.

3.6.10 Detection Limit

The detection limits obtained for lead at wavelengths 280.2-283.3 nm with the various nebuliser system are given in Table 3-7. Here the detection limit is calculated as the concentration equivalent to a signal intensity equal to three times the standard deviation of background signal $3s_b$. Ten consecutive ten-second integrations were made.

3.6.11 Recycling Solution on the Source Plasma

Recycling of the solution on the source plasma was achieved by pumping the solution drained from the spray chamber back into the vessel from which it was originally drawn (see Fig. 3-8). The fluorescence signal for lead under optimised condition was measured as a function of time, with a fixed concentration of lead. Concentrations of 100
Fig. 3 - 8. Recycling sample introduction system on source plasma
p.p.m. in the atomiser plasma and 20% in the source plasma were used with a combination of the de Galan nebuliser and cyclone spray chamber.

3.4.12 Excitation Curve of Growth

To obtain the AFS excitation curve growth for lead, increasing concentrations of lead solutions (0.1-20%) were aspirated into the source plasma, while aspirating a fixed concentration (100 p.p.m.) into the atomiser plasma and measuring the fluorescence intensity produced. The wavelength and slit width settings of the monochromator were 283.3 nm and 0.2 mm (spectral bandpass 0.32 nm) respectively.

3.6.13 Curves of Growth

To obtain AFS curves of growth for lead, the fluorescence intensities produced at a particular wavelength (283.3 and 405.7 nm) were measured while aspirating increasing concentration of lead solutions (10-50,000 p.p.m.) into the atomiser plasma. A fixed concentration was introduced into the source plasma.

A slit width setting of 0.2 mm was used in each case. The log (fluorescence signal intensity) against log (lead concentration in atomiser plasma) curves were plotted.

3.6.14 AFS Spectra

To obtain various AFS spectra of lead, a lead solution (10 p.p.m.) was aspirated into the atomiser plasma, while aspirating a 20% solution into the source plasma and recording the AFS spectra using the chart recorder. The monochromator scanned between 275-290 nm and 400-410 nm at a speed of 5 nm min⁻¹ and with a slit width of 0.2 mm. Further more, the spectrum in the region 272-292 nm at different slit widths was obtained.
3.7 Results and Discussion

Table 3-1 shows the 12 variables which were optimised for wavelengths \( \sum 280.2-283.3 \text{ nm} \) in the fluorescence mode of operation of the ASIA instrument with different nebulisers and spray chambers on the source plasma while keeping the GMK nebuliser with the atomiser plasma.

The results show the total signal obtained was similar for the de Galan SG1 with cyclone spray chamber and for the GMK nebulisers. The signal obtained with the de Galan nebuliser in combination with the impact wall spray chamber was slightly less.

The general shape of the power versus fluorescence curve for lead is shown in Fig. 3-9. This curve illustrates the optimisation of the power in the source plasma. It can be seen that the fluorescence signal increases up to a maximum at 5.9 kW. At a power somewhat above 5.9 kW it deteriorated, very dramatically. The power was therefore set to 5.9 kW.

The effect of varying the sample flow rate on different nebulisers on the source plasma is shown in Fig. 3-10. This shows that, for lead the fluorescence signal depends on the sample flow rate. The SG1 nebuliser with impact wall spray chamber showed a maximum at 3 ml min\(^{-1}\). The fluorescence signal increased gradually for the de Galan SG1 nebuliser with the cyclone spray chamber. The fluorescence signal for GMK nebuliser improved modestly as the sample-rate increased until the flow-rate reached 5.1 ml where a plateau occurred. The sample flow rate, for de Galan SG1 with the impact wall spray chamber, corresponding to a fluorescence signal maximum was lower than for the others.

A comparison was made of the de Galan SG1 with the cyclone spray chamber, the de Galan SG1 with the impact spray chamber and ultrasonic nebulisers while keeping the GMK nebuliser on the source plasma. The complete optimisation was carried out and the results are given in Table 3-2. The results indicated the signal from the de Galan SG1 nebuliser with the impact wall spray chamber was lower than that obtained with the GMK nebuliser and that obtained with the de Galan SG1 with the cyclone spray chamber. When the ultrasonic nebuliser was used, it gave a mean fluorescence signal 3-4 times as great as all the pneumatic nebulisers, but its precision was poor and a long washout time
<table>
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<td>GMK nebuliser</td>
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<td>SGI + Impact</td>
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Table 3.1 Comparison of nebulisers on the source plasma

- Concentration lead p.p.m.
- Coolant gas flow L min⁻¹
- Plasma gas flow L min⁻¹
- Injector gas flow L min⁻¹
- Sample flow rate mL min⁻¹
- Viewing height above the coil cm.
- Power in the plasma kW
- Fluorescence signal mV
- Relative standard deviation
| GMR nebuliser | Ultrasonic nebulizer | SG1 + syringe chamber | Concentration load | PPM | Coolant gas flow | 1 min$^{-1}$ | Plasma gas flow | 1 min$^{-1}$ | Injucer gas flow | 1 min$^{-1}$ | Sample flow rate | ml min$^{-1}$ | Plasma height above coil | cm | Power in the plasma | kW | Source plasma | Coolant gas flow (A) | Plasma gas flow (A) | Injucer gas flow (A) | Sample flow rate (A) | Height above coil | KW | Fluorescence signal | mg ml$^{-1}$ | Relative standard deviation |
|----------------|----------------------|-----------------------|-------------------|-----|-----------------|-------------|---------------|-------------|----------------|-------------|---------------------|--------------|---------------------|-----|------------------|----|----------------|----------------|--------------------------|----------------|------------------|----|----------------|----------------|-------------------------|
| ×              | 10                   | 8.5                   | No                |     | 2.2             | 5.1         | 10.1          | 3.9         |                   |             |                     |               |                     |     |                 |    |               |                |                          |               |                  |    |               |                |                          |               |                  |
| ×              | 10                   | 8.5                   | No                |     | 3.2             | 3.5         | 10.1          | 3.9         |                   |             |                     |               |                     |     |                 |    |               |                |                          |               |                  |    |               |                |                          |               |                  |
| ×              | 10                   | 8.5                   | No                |     | 4.0             | 4.0         | 10.1          | 3.9         |                   |             |                     |               |                     |     |                 |    |               |                |                          |               |                  |    |               |                |                          |               |                  |
| ×              | 10                   | 8.5                   | No                |     | 4.3             | 0.5         | 10.1          | 3.9         |                   |             |                     |               |                     |     |                 |    |               |                |                          |               |                  |    |               |                |                          |               |                  |

Table 3-2 Comparison of nebulisers on the atomiser plasma
Fig. 3-9. Power curve for lead, 20% lead in source plasma, 100 p.p.m. lead in atomiser plasma, \( \lambda = \sum 280.2 - 283.3 \text{ nm} \)
Fig. 3-10. The effect of varying the sample flow-rate on different nebulisers on the source plasma:
- de Galan SG1 with impact wall spray chamber
- de Galan SG1 with cyclone chamber
- GMK nebuliser
was needed. The optimum sample flow-rate for de Galan SG1 nebuliser with the cyclone spray chamber was lower than for the GMK nebuliser and for de Galan SG1 nebuliser with the impact spray chamber, but not as low as for the ultrasonic nebuliser see Table 3-2.

The results of the studies of the effect of desolvation of the aerosol introduced into the atomiser are shown in Table 3-3. In all cases the total signal was less with the desolvator on. It is suggested in all probability that this effect is due to the dry aerosol increasing the temperature of the atomiser plasma reducing the population of the free atoms in the ground state. It was not possible to run the power down as part of a reoptimisation procedure because below 0.39 kW, the plasma became unstable.

The results of the studies of the effect of desolvation of the aerosol introduced into the source plasma shown in Table 3-4. The results show an increase in the fluorescence signal with desolvation on.

The results of the comparison of de Galan nebulisers is shown in Table 3-5. It can be seen that the de Galan SG1 nebuliser yielded a better fluorescence signal (24%) compared with the de Galan SG2 nebuliser.

Table 3-6 shows that using the de Galan SG1 nebuliser with the cyclone spray chamber on the source plasma while keeping de Galan SG2 nebuliser on atomiser plasma did not help to generate a better fluorescence signal than GMK nebuliser on the atomiser plasma.

The results of the detection limit studies are shown in Table 3-7. For pneumatic nebulisers, it can be seen that best detection limit was obtained with the arrangement of the de Galan SG1 nebuliser with the cyclone spray chamber on the source plasma whilst the GMK nebuliser was with the atomiser plasma.

The result of recycling 20% of lead solution on the source plasma is shown in Fig. 3-11. A stable fluorescence signal was obtained during a recycling time of two hours.
Table 3-3 Effect of desolvating the aerosol on the atomiser plasma, on the fluorescence signal while GMK nebuliser on the source plasma

<table>
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<th>GMK nebuliser</th>
<th>SG1 + cyclone chamber</th>
<th>Ultrasonic nebuliser</th>
<th>Desolvator</th>
<th>Concentration p.p.m</th>
<th>Fluorescence signal (mV)</th>
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<td>151</td>
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</tr>
<tr>
<td>x</td>
<td>on</td>
<td>10</td>
<td></td>
<td></td>
<td>121</td>
<td>1.5</td>
</tr>
<tr>
<td>x</td>
<td>off</td>
<td>10</td>
<td></td>
<td></td>
<td>55</td>
<td>1.3</td>
</tr>
<tr>
<td>x</td>
<td>on</td>
<td>10</td>
<td></td>
<td></td>
<td>48</td>
<td>1.78</td>
</tr>
</tbody>
</table>
Table 3-4  effect of desolvation of the source plasma aerosol for fluorescence signal while a GMK nebuliser with the atomiser plasma

<table>
<thead>
<tr>
<th>Concentration p.p.m. lead</th>
<th>Atomiser plasma</th>
<th>Source plasma</th>
<th>Fluorescence signal (mV)</th>
<th>Relative standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GMK nebuliser</td>
<td>SG1+cyclone chamber</td>
<td>Desolvator</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>×</td>
<td>off</td>
<td>75</td>
<td>1.53</td>
</tr>
<tr>
<td>10</td>
<td>×</td>
<td>on</td>
<td>103</td>
<td>1.15</td>
</tr>
<tr>
<td>1</td>
<td>×</td>
<td>off</td>
<td>15</td>
<td>1.66</td>
</tr>
<tr>
<td>1</td>
<td>×</td>
<td>on</td>
<td>23</td>
<td>1.09</td>
</tr>
</tbody>
</table>

**Notes:**
- The table shows the effect of desolvation on the fluorescence signal while using a GMK nebuliser with the atomiser plasma.
- The data is presented for different concentrations of lead.
<table>
<thead>
<tr>
<th>nebuliser system</th>
<th>fluorescence signal mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomiser</td>
<td>Source</td>
</tr>
<tr>
<td>GMK nebuliser</td>
<td>SG1+ cyclone</td>
</tr>
<tr>
<td>GMK nebuliser</td>
<td>SG2+ cyclone</td>
</tr>
</tbody>
</table>

Table 3-5 Comparison of de Galan nebulisers at identical conditions, 10 p.p.m. lead in atomiser plasma, 20% lead in source plasma.

<table>
<thead>
<tr>
<th>nebuliser system</th>
<th>fluorescence signal mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomiser</td>
<td>Source</td>
</tr>
<tr>
<td>SG2 + cyclone</td>
<td>SG1+ cyclone</td>
</tr>
<tr>
<td>GMK nebuliser</td>
<td>SG1+ cyclone</td>
</tr>
</tbody>
</table>

Table 3-6 Fluorescence signal obtained for de Galan nebulisers SG1, SG2 and GMK nebuliser, SG2 at identical conditions.
<table>
<thead>
<tr>
<th>nebuliser set-up</th>
<th>detection limit p.p.b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomiser</td>
<td>Source</td>
</tr>
<tr>
<td>GMK</td>
<td>GMK</td>
</tr>
<tr>
<td>GMK</td>
<td>SG1+ cyclone</td>
</tr>
<tr>
<td>GMK</td>
<td>SG2 + cyclone</td>
</tr>
<tr>
<td>ultrasonic</td>
<td>GMK</td>
</tr>
</tbody>
</table>

Table 3-7 Detection limits obtained for atomic fluorescence at different set-ups of nebuliser, \( \lambda = \sum 280.2 - 283.3 \) nm
Fig. 3_11. Recycling 20 % lead solution on source plasma 100 p.p.m. lead into atomiser plasma
3.7.1 Curves of Growth and Spectrum for Lead

The excitation curve of growth is shown in Fig. 3-12. The plot shows linearity at concentrations between 0-4% lead in the source plasma and a gentle curvature at higher concentration, caused by self-absorption of radiation in the source plasma. The lead calibration curves at different fluorescence wavelengths are shown in Fig. 3-13.

The spectrum displayed in Fig. 3-14 was obtained by scanning between 275-290 nm at a slit width setting of 0.2 mm. The peak at 283.3 nm was predominantly the result of ground state resonance fluorescence. Fig. 3-15 was obtained by scanning 400-410 nm at a slit width 0.2 mm.
Fig. 3.12. Lead excitation curve of growth, 100 p.p.m. lead in atomiser plasma and 0.2 mm slit width
Fig. 3.13. Lead calibration curve at different wavelengths, 
- $\lambda = 280.1 - 283.3$ nm and $\circ \lambda = 405.7$ nm
Fig. 3.14. Lead fluorescence spectrum at different slit widths, 10 p.p.m. lead in atomiser plasma, 10% lead in source plasma, (a) 0.2 mm and (b) 3.6 mm multiply Y-axis by 10
Fig. 3.15. Lead fluorescence spectrum, 100 ppm. lead in atomiser plasma, 20 % lead in source plasma, 0.2 mm slit width
CHAPTER 4
OPTIMISATION OF PLASMA PERFORMANCE

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Chapter 4
Optimisation of Plasma Performance

4.1 Introduction

The employment of an expensive atomic-emission spectrometer using the inductively coupled plasma in the most efficient and cost-effective manner requires a knowledge of the optimum operating conditions for the plasma in single-element and simultaneous multi-element analysis modes.

In the previous studies in this laboratory [167] it has been shown that the measured emission from a plasma source is dependent upon the following parameters; viewing height, power of the plasma and the three gas flows (nebuliser gas flow-rate, plasma gas flow-rate and coolant gas flow-rate).

The aim of this present study is to compare the performance of an alternating variable search method (AVS) and a modified simplex method of optimisation in three situations. Firstly for the location of the maximum of model response surface, secondly for the location of the maximum signal to background ratio for a plasma spectrometer for atomic emission spectrometry and thirdly for the routine operation of a dual plasma atomic fluorescence spectrometer.
4.2 Simplex Optimisation

4.2.1 Historical Aspects

The simplex optimisation method has been used in analytical chemistry for many years. The original technique was derived by Box and Wilson [218] in 1951, then developed by Spendly et al. [219] in 1962, and later applied to analytical chemistry by Long [220] in 1968. Deming and Morgan [221,222] have helped to clarify the technique for the analyst. The use of simplex optimisation in analytical chemistry has been reviewed by Deming and Parker [223]. Nelder and Mead modification [224] of the original sequential simplex procedure of Spendley et al. [219] has been most widely applied. The computer, of course, plays a large role in the application of this technique. Berridge [225] has reported using an interactive simplex programme (written in Basic) for several years.

4.2.2 Simplex Rules Consideration

A simplex is a geometric figure defined by a number of points equal to the number of parameters considered in the optimisation plus one (i.e. one more than the number of dimensions of the factor space). For the simplest multi-factor problem, namely the optimisation of two parameters, the simplex is therefore a triangle. In the following discussion a two parameter optimisation will be considered since this is the most easily to visualise, however, the theory applies equally well to any number of variables. Consider the response surface in Fig. 4-1(a) with parameters $X_1$ and $X_2$. The contours are lines of iso-response. The highest response is required. The optimisation starts with points 1, 2 and 3. These points form an equilateral triangle with point 1 showing the worst response of the three. It is logical to conclude that the response will probably be higher in the direction opposite to this point. Therefore the triangle is
Fig. 4-1. (a) Single step size simplex.
(b) Variable step size simplex.
reflected about the side joining points 2 and 3 to produce point 4. The response is evaluated at the new point 4 and the triangle is reflected away from the new point, which in this case is point 2. In this way, using successive simplexes, one moves along the response surface towards the optimum. This gives rise to the first rule of the simplex method:

**Rule 1:** The new simplex is formed by rejecting the point with the worst result in the preceding simplex and replacing it with its mirror image across the line defined by the remaining two points.

In the initial stages of an optimisation the new point in a simplex will usually yield a better result than at least one of the two remaining points, because the simplexes will tend to move towards a maximum. When the new point has the worst response of the simplex, this usually occurs as the maximum is approached, application of Rule 1 would lead a reflection back to the point which was itself the worst in the preceding simplex. The repetition of rule 1 would then lead to an oscillation between the two simplexes thus halting the progress of the procedure. For example, consider simplex 8, 10, 11 in Fig. 4-1(a) the worst response is at point 11, applying Rule 1 would lead back to point 9, and then again point 11 etc. Thus the second rule must be used.

**Rule 2:** If the newly obtained point in a simplex has the worst response, do not apply rule 1 but instead eliminate the point with the second lowest response and obtain its mirror to form the new simplex.
This effect usually occurs as the maximum is neared and the simplex *overshoots*. Applying Rule 2 allows the simplex to continue, changing direction and again to approach the maximum. In the region of the maximum, the simplex circles around the provisional maximum. In Fig. 4-1(a) the provisional maximum is vertex number 10. If, however, the response at any point was measured erroneously high, the simplex would hold onto a false maximum. To counter this Rule 3 is used.

**Rule 3:** *If one is retained in three successive simplexes (in the case of *n* variables in *n+1* successive simplexes), determine again the response at this point. If it is the highest in the last three simplexes it is considered to be the maximum which can be attained with the simplex chosen.*

If not, the simplex has become fastened to a false maximum and the optimisation is restarted.

Finally, because the factor space chosen will not be infinite due to the physical constraints of the system, it is possible that the new vertex will fall outside the factor space and hence have an unknown response. Thus Rule 4 is formulated.

**Rule 4:** *If a point falls outside one of the boundaries, assign an artificially low response to it and proceed with rules 1-3.*
The effect of applying Rule 4 is that the outlying point is automatically rejected without bringing the succession of simplexes to an end.

These four basic rules form the simplex method first devised by Spendley et al. [219].

4.2.3 The Modified Simplex Method

In the original simplex method the step size is fixed. If the initial step size is too small compared to the factor space the maximum will be approached slowly; if is too large, the maximum is determined with insufficient accuracy. In the later instance a new simplex with smaller step size can be started at the provisional maximum. This was the method used by Long [220]. However, a modified simplex method in which the step size is variable throughout the whole procedure offers a more efficient solution as shown in Fig. 4-1(b). The principal disadvantage is that the simplicity of the calculation in the original simplex method no longer exists. This can, however, be outweighed by the reduction in the number of steps required to reach the maximum.

Nelder and Mead [224] formulated a method for introducing a variable step-size into the simplex procedure. This can be visualised by considering the initial triangle (i.e. simplex) BAW in Fig. 4-2 in this case it is not necessarily an equilateral triangle. Instead of the single reflection of the basic simplex method, Nelder and Mead's modification allows the simplex to move in one of four ways. Let each point on triangle BAW in Fig. 4-2 have a position vector B, A, W respectively, then the basic step can be defined by:

\[ R = P + (P - W) \]

where:

- \( P \) is the centroid of the line joining B and A
- \( W \) is the point of the worst response
- \( R \) is the new simplex vertex
This is equivalent to the basic reflection in the original simplex method. The effect of this is shown in Fig. 4-2(a). This can be modified by expanding the new simplex to produce E Fig. 4-2(b) defined by:

\[ E = P + \alpha(P-W) \]

where:

\( \alpha > 1 \) is the expansion factor usually 2

A contraction of the simplex can be made to produce \( C_r \), Fig. 4-2(c) defined by:

\[ C_r = P + \beta(P-W) \]

where:

\( \beta < 1 \) but >0 is the contraction factor usually 0.5

Finally a contraction back into the preceding simplex Fig. 4-2(d) is defined by:

\[ C_w = P - \beta(P-W) \]

To ascertain which of the four points is used to construct the next simplex the following procedure is used. The response at \( R \) and \( C_r \) is observed if the response at \( R \) is greater than at \( C_r \) then calculate \( E \). If the response at \( E \) is greater than at \( R \) use \( E \), if not use \( R \). If the response at \( C_r \) is greater than at \( R \) calculate \( C_w \). If the response at \( C_w \) is greater than at \( C_r \) use \( C_w \), if not use \( C_r \).

Thus the method of Nelder and Mead modifies Rule 1 of the basic simplex procedure allowing the expansion and contraction of each new simplex speeding the progress to the maximum. Rules 2-4 remain unaltered and are applied in the same manner as for the basic simplex.
Fig. 4-2. Variable size simplex steps
A comparison of the modified simplex method with the basic simplex on the same response surface are shown in Fig. 4-1(a) and Fig. 4-1(b) from which it can be seen that the variable step simplex contracts down to identify the maximum without the need for cycling around a provisional value.

4.2.4 Setting up and Calculation of the Simplex Optimisation

The choice of initial simplex is a critical feature of the optimisation procedure. Yarbro and Deming [226] have demonstrated that it is desirable to begin with a large step size to ensure that most of the vector space is explored before the simplex collapses on the optimum. These authors described a method for matrix and accompanying equations Table 4-1. The value $X_i$ is called for the $n$th variable, this is calculated by subtracting the lowest feasible value for that variable from the highest feasible value. For the ICP these lowest and highest values depend on the physical constraints of the instrument and whether or not a stable plasma can be formed. The values $p_i$ and $q_i$ can be calculated for each variable and by adding these values to the appropriate $X_i$ value, as shown in the matrix, the initial simplex can be defined.

The calculations involved in setting up the initial simplex can be set out on a simplex worksheet an example of which is shown in Table 4-2. This may be used to help make the calculations easier. Calculation of the four possible sets of new variables can be done by using the equation in the bottom left of the worksheet.
where:

\[ p_i = \frac{X_i}{i\sqrt{2}} (\sqrt{i+1} + (i-1)) \]

\[ q_i = \frac{X_i}{i\sqrt{2}} (\sqrt{i+1} - 1) \]

denotes:

Table 4-1 Initial simplex matrix
### Table 4-2 Simplex worksheet

<table>
<thead>
<tr>
<th>Vertex</th>
<th>Injector $\text{L min}^{-1}$</th>
<th>Coolant $\text{L min}^{-1}$</th>
<th>Height cm</th>
<th>Power kW</th>
<th>Plasma $\text{L min}^{-1}$</th>
<th>SBR $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \Sigma \]

\[ P = \frac{\Sigma}{n} \]

\[ P - W \]

\[ \frac{1}{2} [P - W] \]

\[ R = P + [P - W] \]

\[ E = P + 2[P - W] \]

\[ C_r = P + \frac{1}{2}[P - W] \]

\[ C_w = P - \frac{1}{2}[P - W] \]

$\Sigma$ is the summation of the co-ordinates exclusive the worst response

$^*$SBR is the Signal to Background ratio
4.3 The Alternating Variable Search Method (AVS)

In the AVS method each independent variable is considered in turn and altered until a maximum of the function is located, the remaining (n-1) variables remaining fixed [227]. The current best point therefore moves parallel to each axis in turn, changing when a maximum in the current direction of search is reached.

If the contours of the objective function are hyperspherical then, in this case, five linear searches should find the maximum. If, however, the contours are elongated in some direction, as is shown in Fig. 4-3 for two variables only small steps can be taken and the method may be time consuming. A wide sweep can be made and the problem of scale is avoided, AVS methods can be classified into several categories as follows:

(i) Fixed step size method

Two methods were used which differed only in the rule for changing direction [228]. In the first, (Fixed AVS-1) the search changed direction after one step in a bad direction (i.e. a decrease in response) whereas in the second (fixed AVS-2) a change of direction was made after two successive bad steps had been taken.

(ii) Rosenbrock's method

This is a variable step size method in which the step size was increased by a factor of 3 if the search was proceeding in a good direction. If the search direction was bad a contracted step of half the previous step size was taken. The search direction was changed after a contracted step had been taken [229].
Fig. 4 - 3. Alternating Variable Search method, with two variables.
4.4 Application of Simplex and AVS Method in ICP

The application of the modified simplex method to the optimisation of the operating conditions in ICP-AES has received considerable attention [74,230-239]. It has been employed by Ebdon et al. [74] to compare a modified torch with the Greenfield design. The experiment was carried out for the Mn 357.6 nm ion line and both argon and nitrogen as a coolant were used. A univariate search was then made to confirm that the simplex method had located the maximum.

Ebdon et al. [240] used the modified simplex procedure to optimise a direct current plasma for atomic emission spectrometry. Again the univariate search procedure was used to indicate the significance of each parameter with respect to response.

Carpenter and Ebdon [235] used a modified simplex method to compare ICP torches and sample introduction systems.

Moore et al. [234] used a modified simplex method to remove matrix effects due to easily ionisable elements using a nitrogen-cooled ICP for direct reading multi-element analysis. Recently [238], the same authors have optimised the same instrument for the multi-element analysis of aluminum and iron. Difficulty was experienced with termination of the simplex optimisation, so the compromise parameters were calculated as the average of the final values for the simplex vertices taken. The whole procedure took approximately 2 hours.

Greenfield and Burns [241] have successfully used an AVS method for optimising an ICP-AES. Greenfield and Thomsen [167] used the AVS method for optimising the ASIA instrument in both the emission and the fluorescence mode. In 1988 Greenfield et al. [174] studied all possible permutations of the order of the five variables for ICP-AES for the determination lead at, 405.78 nm and compared the results with those obtained from a modified simplex procedure for a series of elements such as sodium, calcium and aluminium. Recently Greenfield et al. [242] have compared alternating variable search and simplex methods of optimisation for inductively coupled plasma optical emission and atomic fluorescence spectrometry.
Long and Brown [243] have used the univariate search to optimise an ICP-MS instrument. The performance of ICP-MS was investigated as a function of a number of parameters associated with sample introduction and plasma operation.

Most previous studies of the simplex optimisation of ICP-AES do not give details of the time involved. For example, in a comparison of two sample introduction configurations reported recently [235], a manually calculated simplex optimisation of 3 variables (injector gas flow, power and observation height) was followed by approximately an additional 20 points in 3 univariate searches from the simplex optimised conditions. The authors claimed that simplex optimisation has been shown to be a rapid and effective technique for element optimisation in ICP-AES. A 4-parameter optimisation of a nitrogen-cooled ICP for maximum, signal to background ratio, (SBR), and minimum matrix interference was stated to have taken 2 hours. The authors used their experience to terminate the simplex [238].

One advantage that the AVS methods have over the simplex methods is that at the end of the search, information about the shape of the response surface is available in a form that the analytical chemist requires. For example [74] in a study of the differences in behaviour of a nitrogen-cooled ICP and an argon-cooled ICP and of the possible reasons for the observed differences, the experimental strategy was to optimise the 5 variables (injector, plasma and coolant gas flow, observation height and power coupled into the plasma) using a manually calculated simplex procedure. Having done this, univariate searches of variable step size were conducted either side of the optimum value for each factor.
4.5 Experimental

4.5.1 AVS Method

4.5.1.1 Atomic Emission Spectrometry

All possible permutations of the order of the five variables were taken resulting in 120 (factorial 5) optimisation experiments. In the AVS optimisations procedure four variables were held constant while the remaining variable was altered in a stepwise fashion and set to give a maximum value of the response (SBR). Then the next variable in the order was altered and set to give a maximum value and so on taking the 5 variables in a pre-set order. After all 5 variables had been set to give the maximum response, one cycle of the optimisation was complete and a second cycle commenced. The search continued until the figure of merit showed no significant difference after a complete cycle. For all methods an estimate of the standard deviation of the SBR was made after the first successful cycle by replication of measurement. The search was terminated when the SBRs obtained at the end of two successive cycles were within two standard deviations. The experimental variables were optimised for lead (10 p.p.m., 405.58 nm). The instrument was optimised for a further series of elements including sodium (1 p.p.m., 589.0 nm), calcium (1 p.p.m., 422.6 nm), aluminium (10 p.p.m., 396.1 nm), manganese (10 p.p.m., 279.48 nm), tin (100 p.p.m., 326.2 nm) and calcium ionic emission (1 p.p.m., 393.3 nm) as a further check on the suitability of this particular order of variables as shown in Table 4-5.
4.5.1.2 The Range and Step-size of Parameters

The instrument has five continuously variable operating parameters, power in the plasma, observation height, and three gas flow-rates (coolant, plasma and injector). The boundary conditions were set at the limits for easy plasma operation, for example, a plasma gas flow-rate of lower than $0.3 \text{ L min}^{-1}$ causes the plasma tube to burn, but a plasma gas flow rate of greater than $2 \text{ L min}^{-1}$ causes the plasma to be extinguished. The initial step-size was that which was easily controllable with the equipment available and caused a measurable change in the figure of merit. The hybrid method (as it will be described below) was applied to the step-size to reduce the time taken for the optimisation procedure. The range, the step size and the starting points of parameters are given in Table 4-3.

4.5.1.3 Hybrid Method

In this method the first cycle used a fixed step-size. For subsequent cycles the initial step-size was increased by a factor of three if the search was proceeding in a good direction. As long as the response increased the initial step size was repeated followed by a *triple jump*. If the factor of 3 expansion gave a bad response, a step (of initial size) was taken in the reverse direction (equivalent to a replacement step of factor 2 expansion). The search direction was then changed. When a bad response was obtained for the initial step size following a triple jump a further unit step was taken. If two successive bad steps had then been taken, the search direction was changed otherwise a triple jump was taken. The flow diagram of this hybrid method is shown in Fig. 4-4.
Table 4-3 Boundary conditions and step size for the AVS method for the emission studies

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Starting conditions</th>
<th>Step size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma gas flow (l min⁻¹)</td>
<td>0.3-2</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>Injector gas flow (l min⁻¹)</td>
<td>0.5-1.5</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Coolant gas flow (l min⁻¹)</td>
<td>9-20</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Power in the plasma (W)</td>
<td>485-930</td>
<td>485</td>
<td>30</td>
</tr>
<tr>
<td>Viewing height above the coil (cm)</td>
<td>3.1-6.2</td>
<td>3.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Variable</td>
<td>Range</td>
<td>Step size</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>Source plasma</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injector gas flow (l min⁻¹)</td>
<td>0.8-3.6</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Plasma gas flow (l min⁻¹)</td>
<td>20-30</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Coolant (air) flow (l min⁻¹)</td>
<td>30</td>
<td>fixed</td>
<td></td>
</tr>
<tr>
<td>Power in the plasma (kW)</td>
<td>2.6-6.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Position of the coil below the optical axis (cm)</td>
<td>1-5</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Atomiser plasma</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injector gas flow (l min⁻¹)</td>
<td>1-3.6</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Coolant gas flow (l min⁻¹)</td>
<td>8-20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Power in the plasma (W)</td>
<td>422-771</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Viewing height above the coil (cm)</td>
<td>7-12</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Solution uptake rate (ml min⁻¹)</td>
<td>1.3-5.0</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-4 Boundary conditions and step size for the AVS method for the fluorescence studies
Fig. 4-4 Flow diagram of hybrid AVS method
4.5.2 The Modified Simplex Method

The computer program used for the simplex optimisation was kindly supplied by Ebdon [244] and modified slightly to incorporate the short program described above to record the SBR as a subroutine to be called when the simplex asked for a value of the response factor.

The simplex optimisations were carried out as follows using the modified program. The variable names were entered into the microcomputer together with their ranges, see Table 4-1. Also entered was the precision to which each could be measured. The program then generated the six sets of operating conditions needed to form the initial simplex and printed worksheets for each set. After the experiments were performed the actual variable values used and the SBR obtained were entered. The program calculated the next set of conditions (i.e. the next vertex) and printed another worksheet. As before, the results were entered into the microcomputer and another set of experimental conditions was generated. The process was continued until the conditions for termination were satisfied. When the vertex is outside the boundary conditions a new vertex is generated by entering data via the keyboard. For the same experimental was done, the previous value was entered to save time.

The simplex method and the hybrid method were compared with lead (10 p.p.m., 407.67 nm), sodium (1 p.p.m., 589.0 nm), calcium (1 p.p.m., 422.6 nm) and aluminium (10 p.p.m., 396.1 nm) as test elements.
4.5.3 Atomic Fluorescence Spectrometry

4.5.3.1 AVS Method

The optimisation procedure was carried out in the same manner as described above for nine variables, see Table 4-4. The order of the variables, step size and the boundary conditions are given in Table 4-4.

Optimisation for calcium (1 p.p.m., 422.7 nm), copper (1 p.p.m., 324.8-327.4 nm) and chromium (1 p.p.m., 357.9-360.5 nm) were performed. The total fluorescence signal was used as the figure of merit.

4.5.3.2 Simplex Method

The same program as described early was used in this optimisation with the same nine variables used in the AVS method. Calcium and copper were used as the test elements.

4.5.4 Solutions

The solutions used in the experiments were all prepared from either AnalaR or SpectrosoL grade reagents and were diluted with tri-distilled water.
4.5 Results and Discussion

4.6.1 Atomic emission spectrometry

In order to establish whether the sequence in which the five variables were taken had any effect on the optimisation, all possible permutations of the five variables were taken and an optimisation carried out using the AVS method. The results of the experiment are shown in Table 4-5 and the order of the variables in this example was as follows: injector, coolant, height, power, and plasma. For the AVS method 106 of the 120 optimisations were completed in three cycles, with the remaining 14 orders requiring four cycles of the optimisation; the SBR still showed a significant improvement after three cycles but only very marginal in each instance.

The percentage optimisation after the first cycle against the number of orders is plotted in Fig. 4-5. This gives an indication of how well the optimisation procedure is doing after one cycle. For most of the experiment the optimisation was at least 70% complete after only one cycle. A complete optimisation experiment took, on average, 2 h to perform with approximately 45 min being spent on the first cycle.

The AVS optimisation of lead is mapped for the five variables, height, power, plasma, coolant and injector respectively in Fig. 4-6(a) to 4-6(e). It can be seen that for the final variable, the injector gas flow-rate, the values of the SBR in second and third cycles overlap as the maximum is reached. These plots of the SBR against the variable for all the cycles of optimisation give a good indication of the behaviour of the variable and how sensitive the figure of merit is to small changes in the value of each variable.

The additional information available from the AVS method is illustrated by these figures. Further points have been added to these curves to give a fuller picture of the variation of the response with each variable. The plots for the first and second cycles also contain useful information in that they demonstrate to the operator to what extent the response is dependent on a particular variable.

The progress of the AVS method for six experiments is summarised in Table 4-5. The order of the variables was selected from the results of studying all 120 orders.
<table>
<thead>
<tr>
<th>Element</th>
<th>Status</th>
<th>Injector 1 min⁻¹</th>
<th>Coolant 1 min⁻¹</th>
<th>height cm</th>
<th>power kW</th>
<th>plasma 1 min⁻¹</th>
<th>SBR</th>
<th>% SBR after 1st cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>start</td>
<td>0.5</td>
<td>20</td>
<td>3.5</td>
<td>485</td>
<td>2.0</td>
<td></td>
<td>1.08</td>
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<td></td>
<td>end 1st cycle</td>
<td>0.9</td>
<td>15</td>
<td>4.5</td>
<td>612</td>
<td>0.5</td>
<td></td>
<td>2.58</td>
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<tr>
<td></td>
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<td>1.0</td>
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<td>4.6</td>
<td>612</td>
<td>0.3</td>
<td></td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>end 3rd cycle</td>
<td>1.0</td>
<td>11</td>
<td>4.6</td>
<td>644</td>
<td>0.3</td>
<td></td>
<td>3.01</td>
</tr>
<tr>
<td>Na</td>
<td>start</td>
<td>0.5</td>
<td>20</td>
<td>3.1</td>
<td>485</td>
<td>2.0</td>
<td></td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>end 1st cycle</td>
<td>1.0</td>
<td>17</td>
<td>4.8</td>
<td>517</td>
<td>2.0</td>
<td></td>
<td>20.6</td>
</tr>
<tr>
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<td>12</td>
<td>4.8</td>
<td>580</td>
<td>2.0</td>
<td></td>
<td>55.9</td>
</tr>
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<td>11</td>
<td>4.8</td>
<td>549</td>
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<tr>
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<td>20</td>
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<td>485</td>
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<td></td>
<td>1.10</td>
</tr>
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<td>2.97</td>
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<td>739</td>
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<tr>
<td>Ca(I)</td>
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<td>20</td>
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<td>485</td>
<td>2.0</td>
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<td>1.01</td>
</tr>
<tr>
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<td>0.9</td>
<td>16</td>
<td>4.6</td>
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<td>2.0</td>
<td></td>
<td>4.65</td>
</tr>
<tr>
<td></td>
<td>end 2nd cycle</td>
<td>1.2</td>
<td>12</td>
<td>4.7</td>
<td>612</td>
<td>2.0</td>
<td></td>
<td>6.58</td>
</tr>
<tr>
<td></td>
<td>end 3rd cycle</td>
<td>1.2</td>
<td>11</td>
<td>4.7</td>
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<td>2.0</td>
<td></td>
<td>6.65</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>start</td>
<td>0.5</td>
<td>20</td>
<td>3.1</td>
<td>485</td>
<td>2.0</td>
<td></td>
<td>1.22</td>
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<tr>
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<td>20</td>
<td>4.4</td>
<td>549</td>
<td>2.0</td>
<td></td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>end 2nd cycle</td>
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<td>4.5</td>
<td>676</td>
<td>1.3</td>
<td></td>
<td>3.42</td>
</tr>
<tr>
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<td>end 3rd cycle</td>
<td>0.6</td>
<td>19</td>
<td>4.5</td>
<td>676</td>
<td>1.1</td>
<td></td>
<td>3.48</td>
</tr>
<tr>
<td>Mn</td>
<td>start</td>
<td>0.5</td>
<td>20</td>
<td>3.1</td>
<td>485</td>
<td>2.0</td>
<td></td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>end 1st cycle</td>
<td>0.8</td>
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<td>4.6</td>
<td>549</td>
<td>2.0</td>
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<td>5.75</td>
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<tr>
<td></td>
<td>end 2nd cycle</td>
<td>1.0</td>
<td>16</td>
<td>4.6</td>
<td>549</td>
<td>1.1</td>
<td></td>
<td>6.58</td>
</tr>
<tr>
<td></td>
<td>end 3rd cycle</td>
<td>1.0</td>
<td>16</td>
<td>4.6</td>
<td>549</td>
<td>1.0</td>
<td></td>
<td>6.61</td>
</tr>
<tr>
<td>Sn</td>
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<td>20</td>
<td>3.1</td>
<td>485</td>
<td>2.0</td>
<td></td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>end 1st cycle</td>
<td>0.7</td>
<td>19</td>
<td>4.4</td>
<td>517</td>
<td>2.0</td>
<td></td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>end 2nd cycle</td>
<td>0.8</td>
<td>18</td>
<td>4.4</td>
<td>549</td>
<td>2.0</td>
<td></td>
<td>4.43</td>
</tr>
<tr>
<td></td>
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<td>0.8</td>
<td>16</td>
<td>4.4</td>
<td>517</td>
<td>2.0</td>
<td></td>
<td>4.48</td>
</tr>
</tbody>
</table>

Table 4-5 Progress of AVS searches using the best order of variables
Fig. 4.5. Progress of hybrid AVS optimisation after one cycle.
Fig. 4-6. Full exploration of factor space for lead
(b)

Response (SBR)

Legend
- 1st eye
- 2nd eye
- 3rd eye

Power in the plasma/W

400 500 600 700 800 900 1000

0 0.5 1 1.5 2 2.5 3
(C)

Response (SBR)

Legend
- 1st cycle
- 2nd cycle
- 3rd cycle

Plasma gas flow-rate/ml min

0 0.5 1 1.5 2
Legend
- 1st cycle
- 2nd cycle
- 3rd cycle
for the optimisation of the instrument for lead. As can be seen from the table, apart from sodium and aluminium this order gave at least 70% of the maximum SBR at the end of the first cycle. Optimisation for all the elements studied were completed within three cycles.

The modified simplex method was used for several elements and for the lead the progress of the simplex is shown in Fig. 4-7(a) to 4-7(e). The map of the simplex procedure with respect to the figure of merit is shown in Fig. 4-8. Twenty vertices were required to reach the optimum conditions. A summary of the optimum conditions found for the elements is given in Table 4-6, and the plot of SBR against vertex number for calcium, sodium and aluminium are shown in Figs. 4-9, 4-10 and 4-11 respectively. The values may be compared with the entries in Table 4-5, at the end of the third cycle for the corresponding elements. It can be seen that the optimum values of the variables are slightly different and that the final SBR is slightly lower for the simplex than for the AVS methods. This may be due to the fact that the optimum conditions given by the simplex method are those corresponding to the vertex giving the highest SBR in the final simplex. The simplex method took, on average, 2 hours to reach the conditions for termination.

The progress of the AVS method is shown in Fig. 4-12 as a plot of the current maximum SBR against step number. As each step represents one (sometimes two) changes of variable value, the number of steps is a good guide to the number of changes of variable that were required. Similar plots are given in Fig. 4-13 for the simplex optimisations of the same elements. It is thought such plots provide useful information such as the number of changes of variable and the progress as a function of vertex number. The progress of the simplex method for sodium is shown in detail in Table 4-7. Values underlined in the table indicate a value of a parameter outside the boundary conditions. When this occurred the appropriate entry was made via the keyboard and the program calculated a new vertex. In practice 104 changes of variable were made. This may be compared with the progress of the hybrid AVS method, for the same element shown in Table 4-8 which required 60 changes of the variable before termination.
<table>
<thead>
<tr>
<th>Element</th>
<th>injector cm/min</th>
<th>coolant cm/min</th>
<th>height cm</th>
<th>power W</th>
<th>plasma cm/min</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1.0</td>
<td>12.8</td>
<td>4.6</td>
<td>644</td>
<td>0.9</td>
<td>2.97</td>
</tr>
<tr>
<td>Al</td>
<td>1.1</td>
<td>13.1</td>
<td>4.8</td>
<td>771</td>
<td>1.3</td>
<td>4.61</td>
</tr>
<tr>
<td>Na</td>
<td>1.4</td>
<td>12.8</td>
<td>4.8</td>
<td>517</td>
<td>1.6</td>
<td>52.9</td>
</tr>
<tr>
<td>Ca</td>
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<td>13.9</td>
<td>4.9</td>
<td>612</td>
<td>1.1</td>
<td>5.62</td>
</tr>
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</table>

Table 4-6 Optimum conditions obtained with the simplex method
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<th>Vertex number</th>
<th>attempted move</th>
<th>injector 1</th>
<th>coolant height 1</th>
<th>Power kW</th>
<th>Plasma 1</th>
<th>SBR</th>
<th>Vertices in current simplex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>0.5</td>
<td>9</td>
<td>3.1</td>
<td>485</td>
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<td>1.25</td>
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<td>I</td>
<td>1.5</td>
<td>11.9</td>
<td>3.7</td>
<td>580</td>
<td>0.6</td>
<td>28.8</td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>0.8</td>
<td>19.9</td>
<td>3.7</td>
<td>580</td>
<td>0.6</td>
<td>7.15</td>
</tr>
<tr>
<td>4</td>
<td>I</td>
<td>0.8</td>
<td>11.9</td>
<td>6.0</td>
<td>580</td>
<td>0.6</td>
<td>9.73</td>
</tr>
<tr>
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<td>I</td>
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<td>3.7</td>
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<td>0.6</td>
<td>3.49</td>
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<tr>
<td>6</td>
<td>R</td>
<td>1.4</td>
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<td>5.2</td>
<td>735</td>
<td>1.4</td>
<td>20.4</td>
</tr>
<tr>
<td>7</td>
<td>R</td>
<td>1.3</td>
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<td>5.2</td>
<td>735</td>
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<td>20.4</td>
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<td>7.0</td>
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<td>644</td>
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<td>15.4</td>
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<td>10.6</td>
<td>4.6</td>
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<td>1.4</td>
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<td>4.8</td>
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<tr>
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<td>CW</td>
<td>1.3</td>
<td>11.9</td>
<td>3.7</td>
<td>580</td>
<td>0.6</td>
<td>2.7, 10, 11, 12, 13</td>
</tr>
<tr>
<td>16</td>
<td>R</td>
<td>1.3</td>
<td>11.9</td>
<td>3.7</td>
<td>580</td>
<td>0.6</td>
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<td>12.5</td>
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<td>549</td>
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<td>R</td>
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<td>R</td>
<td>1.3</td>
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<td>4.4</td>
<td>517</td>
<td>1.5</td>
<td>2.7, 10, 11, 12, 13, 14</td>
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</tbody>
</table>

Cw Contraction, E expansion, R reflection, Ch check as vertex appeared in n+1 successive values underlined are suggestions for points which lie outside the boundary conditions.

Table 4-7 Progress of simplex optimisation algorithm for sodium
<table>
<thead>
<tr>
<th>order</th>
<th>injector 1 min⁻¹</th>
<th>Coolant 1 min⁻¹</th>
<th>height cm</th>
<th>Power kW</th>
<th>Plasma 1 min⁻¹</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>original conditions starting 1st cycle</td>
<td>0.5</td>
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Table 4-8 Progress of the AVS method for sodium
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Table 4-8 Continued
Fig. 4.7. The map of the simplex procedure for lead
Coolant gas flow-rate/1 min⁻¹

Vertex number

(b)
(c)

Plasma gas flow-rate/lt/min

Vertex number

0 5 10 15 20 25
Fig. 4.8. Map of simplex response (plot of SBR against vertex number), for lead.
Fig. 4.9. Map of simplex response (plot of SBR against vertex number) for calcium.
Fig. 4.10. Map of simplex response (plot of SBR against vertex number) for sodium
Fig. 4.11. Map of simplex response (plot of SBR against vertex number) for aluminium
Fig. 4.12. Progress of hybrid AVS method of optimisation as a function of number of changes of variable for (a) lead (b) aluminium (c) sodium and (d) calcium.
Fig. 4.13. Progress of the simplex method of optimisation as a function of the vertex number and number of changes of variable for (a) lead, (b) aluminium, (c) sodium, and (d) calcium. The SBR value is the current optimum.
4.6.2 Atomic Fluorescence Spectrometry

The results obtained for the AVS optimisation are shown in Table 4-9. These values were obtained after two cycles which took approximately 45 min. The reason for the increase in speed over the same optimisation for the emission mode is that the value of the response (total fluorescence signal) is viewed directly on the lock-in amplifier. The behaviour of each variable as a function of the fluorescence signal for calcium, chromium and copper are shown in Fig. 4-14 to 4-22.

The progress of the simplex method as a function of the response for calcium and copper is shown in Fig. 4-23 and 4-24 respectively. The simplex maps for each variable for calcium are shown in Fig. 4-25(a) to 4-25(i). The simplex method was unable to satisfy the criterion for termination and the values shown represent the progress of the simplex over a four hour period. The values obtained from the best vertex during this period are given in Table 4-10. A comparison with the fluorescence signal values in Table 4-9 shows that although there is reasonable agreement between the two optimisation strategies for calcium, the simplex has been unable to find an optimum in the case of copper.
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Table 4-9 Optimum plasmas parameters (ASIA instrument) obtained with AVS method in fluorescence mode
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Table 4-10 Plasma parameters (ASIA instrument) obtained with simplex method after 48 vertices
Fig. 4.14. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the injector gas flow-rate on source plasma, using AVS optimised conditions:
- Ca 422.7 nm, Cr Σ 357.9 - 360.5 nm and Cu Σ 324.8 - 327.8 nm
Fig. 4.15. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the height above the coil on source plasma, using AVS optimised conditions
- Ca 422.7 nm, □ Cr 35.9 - 360.5 nm and ● Cu 324.8 - 327.8 nm
Fig. 4. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the power on the source plasma, using AVS optimised conditions: □ Ca 422.7 nm, ▪ Cr 357.9 - 360.5 nm and ● Cu 324.8 - 327.8 nm.
Fig.4.17. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the plasma gas flow-rate on the source plasma, using AVS optimised conditions
- Ca 422.7 nm, Cr 357.9 - 360.5 nm and Cu 324.8 - 327.8 nm
Fig. 4.18. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the injector gas flow-rate on the atomiser plasma, using AVS optimised conditions

- Ca 422.7 nm, o Cr Σ 357.9 - 360.5 nm and • Cu Σ 324.8 - 327.8 nm
Fig. 4.19. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the viewing height above the coil on the atomiser plasma, using AVS optimised conditions
- Ca 422.7 nm, Cr 357.9 - 360.5 nm and Cu 324.8 - 327.8 nm
Fig. 4.20. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the coolant gas flow-rate on the atomiser plasma, using AVS optimised conditions.

- Ca 422.7 nm, Cr 2357.9 – 360.5 nm and Cu 324.8 – 324.8 nm
Fig. 4.21. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the power in the atomiser plasma, using AVS optimised conditions

- Ca 422.7 nm, Cr $\Delta 357.9 - 360.5$ nm and Cu $\Delta 324.8 - 327.8$ nm
Fig. 4-22. Behaviour of Ca, Cr and Cu fluorescence signal as a function of the solution flow-rate on the atomiser plasma, using AVS optimised conditions
- Ca 422.7 nm, Cr \( \Sigma 357.9 - 360.5 \) nm and Cu \( \Sigma 324.8 - 327.8 \) nm
Fig. 4.23. Simplex method with calcium at 422.7 nm in fluorescence mode.
Fig. 4-24. Simplex method with copper at λ 324.8 - 327.8 nm in fluorescence mode
Fig. 4.25. Map of simplex method for calcium in fluorescence mode
(d)

Power in the atomiser plasma/W

Vertex number
Solution flow-rate on the atomiser/ml min$^{-1}$ vs Vertex number

(From the image, the graph shows a fluctuating trend in solution flow-rate with respect to vertex number.)
(h)

Power in the source plasma/kW

Vertex number
Plasma gas flow-rate on the source/l min⁻¹

Vertex number
CHAPTER 5
THE STUDY OF INTERFERENCES IN AFS

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Chapter 5
The study of Interferences in AFS

5.1 Introduction

The early literature on interferences in emission spectroscopy suggested that the higher temperatures obtained in the plasma would produce an ideal interference-free spectroscopic source. However, as the use of ICP-AES became more widespread, many varied and often conflicting reports on different types of interference were published [6,8], probably due to the use of different operating conditions and system designs. The literature on interferences has been reviewed most extensively by Kornblum and de Galan [245], and Barnes [24]. Robin [246], in his review, gives an interesting discussion on ICP-AES interferences.

The majority of ICP interferences can be categorised into one of the following headings;

(1) Transportation,
(2) Chemical and Ionisation,
(3) Spectral

5.1.1 Transportation

The variation of the uptake rate of the sample solution by the nebuliser has been found to be a source of interference in the plasma [147]. The viscosity of the sample solution can affect the uptake rate, and hence the amount of analyte reaching the plasma.

Greenfield et al. [247] have made a detailed study of the viscosity effect. They showed that the increased viscosity of some common solvents (e.g. phosphoric acid) can
markedly decrease the nebuliser uptake rate causing an apparent depression of the signal.
In order to counteract this effect, it was necessary to either match the viscosity of the
sample and standard solutions, making sure that the head of solution did not significantly
change during nebulisation or, more simply, to pump solutions into the nebuliser at a
constant rate so that the viscosity did not control the solution feed rate.

5.1.2 Chemical and Ionisation Interferences

The influence of phosphate on the signal from calcium is a classical example of
compound formation in the condensed phase of the flame; although the effect disappears
the use of a C₂H₂-N₂O flame [248]. This interference in ICP-AES has often been used
in the literature to demonstrate the superiority of ICP-AES over flame for analytical
applications [249]. Veillon and Margoshes, however have shown the interference to
exist [8] due to the use of a solid plasma. Larson [250] showed that by careful choice of
the viewing height and other operating parameters, the chemical and ionisation
interference effects of Al and Na on Ca could be virtually removed.

AFS studies of the interference effects from easily ionisable elements and
formation of stable compounds have received attention using different excitation sources
and the ICP as an atom or ion cell [147].

Montaser and Fassel [251] studied the influence of 10,000 fold excesses of 17
species (e.g. Al, PO₃⁻, K, Na, Mn) on the AF signal of 1 p.p.m. Cd and Zn which was
measured at about 75 mm above the load coil. They found a depression of about 10% in
the presence of Al, Ca, Mg, Na and Ni.

Demers and Allemand [131,252,253] investigated the interference effect of PO₃⁻ and aluminium on the calcium and zinc fluorescence intensity. They observed a classical knee interference effect on the calcium fluorescence signal at low radio-frequency powers, but, the effect was shown to be absent at high r.f powers. On the other hand, the interference effect of PO₃⁻ and aluminium on the calcium atomic fluorescence signal
was found to be of complicated behaviour. A depression of the calcium fluorescence signal was observed at low r.f. power and a slight enhancement in intensity noted at high r.f. powers.

Winefordner and coworkers [165,148,149,169] have reported different interference effects produced by phosphorus, aluminium, sodium and potassium on the calcium atomic and ionic fluorescence signal.

Kosinski et al. [165] observed an enhancement in the calcium ionic fluorescence signal with the addition of sodium and aluminium and a slight suppression in the presence of phosphorus at 1 kW, with an observation height of 20 mm above the top of the extended-sleeve torch. Kosinski et al. [148] found that the r.f. power greatly affected the behaviour of aluminium and sodium on the calcium ionic fluorescence signal. Later in their investigation, Krupa et al. [169] claimed solutions containing up to 50,000 p.p.m phosphate produced no depression or enhancement of calcium fluorescence signal. They attributed this to the high temperature of the plasma plume. They found the enhancement of atomic and depression of ionic calcium fluorescence by adding sodium as an interferent. In 1986 Huang et al. [149] reported on the interference effects of potassium on calcium fluorescence intensity from an extended sleeve torch. They observed a 4-fold increase in the atomic fluorescence intensity and a decrease of over 100-fold in the ionic fluorescence intensity by adding 1000 p.p.m. potassium to the calcium solution.

Recently, Gillson and Horlick [156] studied the effects of the addition of sodium on atomic and ionic fluorescence signal intensities generated in an MAK torch. They showed that the general effect of adding an easily ionised element (EIE), (e.g. sodium) was to depress the calcium ionic fluorescence and enhance the calcium atomic fluorescence intensities. The effect was studied as a function of power and observation height.

In conclusion, reports in the literature show that ionisation and stable compound formation interferences do occur in AF using a plasma as the atomic or ionic reservoir. These effects can usually be overcome by the appropriate choice of operating parameters, particularly r.f. power, viewing height and possibly injector flow-rate.
A close look at the literature shows conflicting reports were published, such as, an enhancement in the calcium ionic fluorescence signal with the addition of sodium was reported by Kosinski et al. [165] while a depression was reported by Krupa et al. [169], Huang et al. [149] as well as Gillson and Horlick [156]. Furthermore, an enhancement in calcium ionic fluorescence signal with the addition of aluminium was reported by Kosinski et al. [165] while a depression was reported by the same author [148]. These conflicting reports were probably due to the different conditions and systems that were used by workers in this field.

5.1.3 Spectral Interferences

Some limitations on the analytical performance of the ICP-AES still remain in the form of spectral interferences. Background radiation from the Ar ion recombination continuum and molecular emission degrade the signal-to-noise ratio and signal to background ratio in analytical measurements [28].

The fluorescence technique is considerably less susceptible to spectral interferences. This is due to fluorescence spectra containing fewer lines than those produced by collisional excitation [150].

Kosinski et al. [165] reported that ICP-ICP-AFS has relative freedom from spectral interferences for (i) Zn (213.856 nm) with Cu (213.853 nm); (ii) Co (231.160 nm) with Ni (231.096, 231.324 nm) [126]. Greenfield and coworkers show that with the ASIA instrument there is remarkable freedom from spectral interferences for elements that exhibit the effect in ICP-AES. They reported that the lead fluorescence spectrum showed an absence of spectral interference from iron and chromium. Furthermore, the copper fluorescence spectrum showed an absence of spectral interference from iron, chromium, aluminium and calcium [70].

Demers and Allemand reported that HCL-ICP-AFS was free from the background shift interference due to the recombination continuum that existed with ICP-AES and broadening of calcium lines [131]. More detail will be given later in section 5.3.1.
5.2 Experimental

5.2.1 Reagents

(i) Atomiser plasma

All calcium, chromium, iron and molybdenum standard solutions were prepared from SpectrosoL standard solutions and AnalaR grade reagents using AnalaR acids and deionised water. The solutions of phosphate were prepared from AnalaR orthophosphoric acid. The solutions for interelement experiments were prepared from pure aluminium metal dissolved in AnalaR nitric and hydrochloric acids and from solutions of AnalaR sodium and potassium chloride.

(ii) Source plasma

Calcium, chromium, iron and molybdenum were prepared from AnalaR grade reagents. Calcium chloride was dissolved in tridistilled water. Chromium and iron metal standards were dissolved in a minimum amount of AnalaR grade hydrochloric acid and the solution diluted as appropriate. Molybdenum oxide was dissolved in ammonia solution then acidified with AnalaR hydrochloric acid.

5.2.2 Optimisation

The complete optimisation procedure was carried out for iron at $\Sigma248.3-249.1$ nm, molybdenum at 313.2, 315.8, 317.0, 379.8, 386.4 and 390.3 nm calcium at 422.7 nm and chromium at $\Sigma357.9-327.4$ nm using the AVS method described in chapter four.
5.2.3 Excitation Curve of Growth

To obtain the excitation curve of growth for calcium, increasing concentrations of calcium solutions (0.1-20%) were aspirated into the source plasma, while aspirating a fixed concentration (0.1 p.p.m.) to the atomiser plasma and measuring the fluorescence intensity produced under the optimum conditions.

5.2.4 Linear Dynamic Range

Standards were prepared by serial dilution of the stock calcium nitrate solution and a calibration curve obtained. The calibration curve covered the range from the detection limit to the point where self-absorption produced curvature of the graph.

5.2.5 Interelement Effect

The effect of interferents on the calcium calibration curve was evaluated using a fixed concentration of the interferent elements (Na, K, Al and PO$_4^{3-}$).

In addition the interference of aluminium and phosphate, as well as potassium and sodium, on the calcium signal at atomic fluorescence line 422.7 nm and ionic fluorescence lines $\sum$393.4-396.8 nm was studied. A 1 p.p.m. calcium solution was used while varying the interferent concentration up to 9000 p.p.m. The interferences of chromium and molybdenum on iron were investigated in the same manner at iron atomic fluorescence lines $\sum$248.3-249.1 nm. Furthermore the interference of iron on chromium atomic fluorescence lines was evaluated at $\sum$357.9-360.5 nm. Light scattering effects in the atomiser plasma were examined for all the preceding experiments by spraying blank solutions containing the appropriate amount of concomitant. The levels of scattered light were found to be negligible for all solutions up to the highest concentrations.
The atomic and ionic fluorescence intensities of calcium suffer from chemical interferences as will be described in section 5.3. In order to overcome this problem, a reoptimisation of the atomiser plasma was carried out.

5.2.6 Reoptimisation

The reoptimisation was carried out in an attempt to overcome various effects. The experiments were carried out to compare the signal obtained from a 1 p.p.m. calcium solution, 1 p.p.m. calcium solution in the presence of 500 p.p.m. sodium or aluminium and a 1 p.p.m. calcium solution in the presence of 200 p.p.m. potassium at 422.7 nm. Also compared were a 1 p.p.m. calcium solution and 1 p.p.m. calcium in the presence of 500 p.p.m. sodium or potassium or aluminium at 393.4-396.8 nm. Furthermore the reoptimisation of 1 p.p.m. iron solution and 1 p.p.m. iron in the presence of 500 p.p.m. and 200 p.p.m. chromium was carried out at 248.3-249.1 nm. Minimum interferences were used as the figure of merit with the AVS method of optimisation.

5.2.7 Fluorescence Spectra and Spectral Interferences

To obtain fluorescence spectra of calcium atomic and ionic fluorescence, the monochromator was scanned between 405 and 435 nm and 380 to 405 nm at a speed of 10 nm min⁻¹ for various slit width settings. Copper atomic fluorescence spectra were recorded between 310 and 345 nm at 100 μm and 3.6 mm slit widths. A low concentration (p.p.m. level) solution was aspirated into the atomiser, while aspirating a percentage solution into the source plasma.

The spectral interferences for argon lines and hydrogen bands were evaluated when spraying deionised water into both plasmas. The monochromator was scanned
between 380 and 405 nm as well as when aspirating a 1 p.p.m. calcium solution into the atomiser plasma and a 3% solution of calcium into the source plasma.

The possible hydroxyl group spectral interference was evaluated by aspirating deionised water into both plasmas and scanning the monochromator between 280 and 335 nm.

5.2.8 Influence of the Power and Observation Height in the Atomiser Plasma

There was a hypothesis that there was a relationship between the viewing height and the power in the atomiser plasma. An experiment was carried out to find the influence of the power on the fluorescence signal with the variation of the height for copper. The powers used were 0.38 kW and 0.46 kW.

5.3 Results and Discussion

The excitation curve of growth for calcium is shown in Fig. 5-1. The curve yielded a limiting slope of unity at low atom densities in the source plasma and a slope approaching zero at high atom densities. These limiting slopes agree well with theory [120] and show that self-reversal is absent in the source plasma under the conditions used in this study. The same result was reported by Kosinski [147].

The optimum conditions for calcium are given in Table 4-9. Fig. 5-2 shows the calibration curve for calcium atomic fluorescence line at these optimum conditions. The linear range was approximately six orders of magnitude. Obviously this technique retained the large linear range advantage that ICP-AES has over AAS. The shape of the calibration curve showed that at low atom densities in the atomisation plasma, a limiting
Fig. 5.1. Excitation curve of growth of calcium at 422.7 nm 0.1 p.p.m. in the atomiser plasma.
Fig. 5.2. Calcium fluorescence calibration curve at 422.7 nm
slope of unity was obtained while at high atom densities a slope of -0.5 was obtained. According to theory [120] the source plasma was acting as a line excitation source compared with the absorption profile in the atomisation plasma. The detection limit was 0.7 p.p.b. the same method as described in section 3.6.10 was used.

The calibration curves for calcium in the absence of interferent and in the presence of 1000 p.p.m. phosphate, 1000 p.p.m. sodium, 500 p.p.m. potassium and 500 p.p.m. aluminium respectively are shown in Figs. 5.3-5.6. The negligible effect of phosphate on calcium can be seen, but sodium, potassium and aluminium all caused an interference effect. These effects will be discussed later. For the calcium atomic fluorescence at 422.7 nm the chemical interference is shown in Fig. 5-7. It can be seen that a phosphate concentration up to 9000 p.p.m. produced no depression or enhancement of the fluorescence signal. This was due to the high temperature of the plasma and the long residence time of the sample aerosol in the plasma [169] which, together produce complete dissociation of molecular compounds between calcium and phosphate. A depression in the presence of aluminium was observed. This was interpreted as the formation of a stable compound reducing the population of free calcium atoms in the region of observation height [104]. A signal enhancement on addition of sodium and potassium was observed. It was thought that this was due to the presence of an EIE causing a shift in the ionisation equilibrium to produce more atoms in the ground state. This would then increase the fluorescence intensity, suppression at high easily ionised element concentrations was due to the fluorescence quenching by electrons [104].

For the ionic calcium fluorescence at $\Sigma 393.4-396.8$ nm, Fig. 5-8 summarises the results. Again phosphate had no effect on the calcium ionic fluorescence due to the same reason given previously. But it was evident that the ionic fluorescence intensity suffered the greatest interference from an EIE as well as from aluminium. However a suppression occurred. The former effect may be due to the increase of electrons in the plasma that reduced the ground state ions for ionic fluorescence, causing a shift in equilibrium to atom formation as shown below. While the latter effect was due to stable
Fig. 5.3. Calcium fluorescence calibration curve at 422.7 nm.
- without $\text{PO}_4^{3-}$, • with 1000 p.p.m. $\text{PO}_4^{3-}$
Fig. 5.4. Calcium fluorescence calibration curve at 422.7 nm
- without Na, □ with 1900 p.p.m. Na
Fig. 5.5. Calcium fluorescence calibration curve at 422.7 nm.

○ without K, △ with 500 p.p.m. K.
Fig. 5.6. Calcium fluorescence calibration curve at 422.7 nm
- without Al, □ with 500 p.p.m. Al
Fig. 5.7. The effect of increasing concentrations of Na, K, Al and PO$_4^{3-}$ on the fluorescence signal at 422.7 nm of a 1 p.p.m. concentration of calcium under conditions optimised for maximum signal: ■ + Na, □ + PO$_4^{3-}$, ● + Al, ○ + K.
Fig 5.8. The effect of increasing concentrations of Na, K, Al and $\text{PO}_4^{3-}$ on the fluorescence signal at 393.4-396.8 nm of a 1 p.p.m. concentration calcium under conditions optimised for maximum signal.

- $\cdot + \text{Na}$, $\cdot + \text{PO}_4^{3-}$, $\cdot + \text{Al}$, $\cdot + \text{K}$
compound formation in the presence of aluminium.

\[
\begin{align*}
\text{Ca} & \quad \rightarrow \quad \text{Ca}^{2+} + 2e^- \\
\text{Na} & \quad \rightarrow \quad \text{Na}^+ + e
\end{align*}
\]

To reduce the interference, reoptimisation of the atomiser was carried out. Previously [245] it had been shown that injector gas flow-rate and viewing height could greatly influence the magnitude of interferences observed from concomitants. The reoptimisation behaviour of each variable as a function of the figure of merit is shown in Figs. 5-9 to 5-15. Typical results for the effect of increasing sodium, potassium and aluminium concentration on the fluorescence signal at the reoptimisation conditions (Tables 5-1 and 5-2), are shown in Fig. 5-16 and 5-17 for atomic and ionic calcium fluorescence respectively. At the optimum condition used for calcium very large enhancements were observed at low injector flow-rate and low viewing height in the presence of EIE. At high viewing heights and high injector flow-rates this enhancement was reduced. An increased injector flow-rate and viewing height would be expected for the reoptimised conditions. This was caused by the shorter residence time and cooler viewing region keeping the quantum efficiency the same. However, the opposite effect to that expected was observed with aluminium. It was necessary to decrease the viewing height and increase the injector flow-rate for the reoptimisation of the ionic fluorescence signal (Table 5-2).

The effect of the presence of aluminium on the calcium ionic fluorescence intensity at the reoptimisation conditions (minimum interference occurred for 1 p.p.m calcium and 500 p.p.m. aluminium) is shown in Fig. 5-18. The results were difficult to interpret but were in agreement with those reported by Kosinski et al. [165].

For the intermetallic interference, the effect of the presence of chromium and molybdenum on the iron atomic fluorescence intensity at \( \Sigma 248.3-249.1 \) nm is shown in
<table>
<thead>
<tr>
<th>Atomiser Plasma parameters</th>
<th>Max. signal optimum conditions</th>
<th>Min. Interference with Na</th>
<th>Min. Interference with K</th>
<th>Min. Interference with Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height above the coil (cm)</td>
<td>9.7</td>
<td>10.1</td>
<td>10.9</td>
<td>9.2</td>
</tr>
<tr>
<td>Power in plasma (kW)</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>Injector gas flow (1 min⁻¹)</td>
<td>2</td>
<td>3</td>
<td>3.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Plasma gas flow (1 min⁻¹)</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Liquid uptake rate (ml min⁻¹)</td>
<td>3.6</td>
<td>3.6</td>
<td>3.6</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 5-1. Calcium atomic fluorescence line at 422.7 nm. Optimum conditions for maximum signal, and the conditions where the minimum interferences occur with Na, K and Al.

*Minimum interference is the case of no interference.*
Table 5-2. Calcium ionic fluorescence lines at Σ393.4-396.8 nm. Optimum conditions for maximum signal, and the conditions where the minimum interferences occur with Na and K.

<table>
<thead>
<tr>
<th>Atomiser Plasma parameters</th>
<th>Max. signal optimum condition</th>
<th>Min. Interference with Na</th>
<th>Min. Interference with K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height above the coil (cm)</td>
<td>9.7</td>
<td>8.7</td>
<td>9.2</td>
</tr>
<tr>
<td>Power in plasma (kW)</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>Injector gas flow (1 min⁻¹)</td>
<td>2</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Plasma gas flow (1 min⁻¹)</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Liquid uptake rate (1 min⁻¹)</td>
<td>3.6</td>
<td>3.6</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Fig. 5.9. Reoptimisation behaviour of calcium at 422.7 nm in presence of 500 p.p.m. Na and Al for minimum interference as a function of injector gas flow-rate. ■ Na and □ Al
Fig. 5.10. Reoptimisation behaviour of calcium at 422.7 nm in presence of 500 p.p.m. Na and Al for minimum interference as a function of the height; ● Na and ▲ Al
Fig. 5.11. Reoptimisation behaviour of calcium at 422.7 nm in presence of 500 p.p.m. Na and Al for minimum interference as a function of power. Na and Al
Fig. 5-12. Reoptimisation behaviour of calcium at 422.7 nm in presence of 500 p.p.m. of Na and Al for minimum interference as a function of coolant gas-flow, ■ Na and □ Al
Fig. 5.13. Reoptimisation behaviour of calcium at 422.7 nm in presence of 500 p.p.m. Na and Al for minimum interference as a function of solution flow-rate. □ Na and ■ Al
Fig. 5.14. Reoptimisation behaviour of calcium at $\lambda$ 393.4-396.8 nm in presence of 500 p.p.m. Na, K and Al for minimum interference as a function of injector gas flow-rate. $\bullet$ Na; $\circ$ K and $\square$ Al.
Fig. 5.15. Reoptimisation behaviour of calcium at 393.4-396.8 nm in presence of 500 p.p.m K and Na for minimum interference as a function of the viewing height, ■ K and □ Na.
Fig. 5.16. The effect of increasing concentrations of Na, K and Al on the fluorescence signal at 422.7 nm of 1 p.p.m. concentration of calcium under conditions optimised for minimum interference, • + Na, ○ + Al, ● + K.
Fig. 5.17. The effect of increasing concentrations of Na and K on the fluorescence signal at 393.4–396.8 nm of a 1 p.p.m. concentration of calcium under conditions optimised for minimum interference, ■ +Na and □ +K.
Fig. 5.18 The effect of increasing concentrations of aluminium on the fluorescence signal at 393.4–396.8 nm of a 1 ppm calcium under conditions optimised for minimum interference.
Fig. 5-19 under the optimum conditions for iron (Table 5-3). The figure shows no effect on iron by chromium and a slight suppression by the presence of molybdenum at the high concentration.

The effect of the presence of iron on the chromium atomic fluorescence intensity at $\lambda_{357.9-360.5}$ nm is shown in Fig 5-20 under the optimum conditions for chromium Table 4-9. The figure shows a sharp decrease in the chromium fluorescence intensity and 100% depression at 500 p.p.m. iron due to the formation of a metallic compound between the chromium and iron. It was not possible to reduce the level of this interference by reoptimisation. No signal could be detected for molybdenum throughout the attempts to optimise conditions for this element. This was thought to be due to the formation of molybdenum oxide [107].

The vertical distribution of the fluorescence intensities for copper at $\lambda_{324.8-327.4}$ nm at powers of 0.48 and 0.74 kW are shown in Fig. 5-21. The phenomena reflect the population density of the copper atom ground state in the atomiser plasma at these powers.

5.3.1 Fluorescence Spectra and Spectral Interferences

The spectra of atomic and ionic calcium fluorescence and copper atomic fluorescence are shown in Figs. 5-22 to 5-24. Here the low background and freedom from interference exhibited by fluorescence meant that a wide slit setting could be used in routine analytical work. This produced a further enhancement of the fluorescence sensitivity for elements where there were several fluorescence wavelengths falling within the monochromator bandpass and which were unresolved. During both scans no baseline shift was observed.

Larson and Fassel [254] have shown that there are two argon lines at 394.8 nm and 394.9 nm in ICP-AES, due to radiative recombination. In contrast Fig. 5-25 shows
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Atomiser Plasma</th>
<th>Source Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height above the coil (cm)</td>
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<td>2</td>
</tr>
<tr>
<td>Power in plasma (kW)</td>
<td>0.48</td>
<td>6.1</td>
</tr>
<tr>
<td>Injector gas flow (1 min⁻¹)</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Plasma gas flow (1 min⁻¹)</td>
<td>-----</td>
<td>30</td>
</tr>
<tr>
<td>Coolant gas flow (1 min⁻¹)</td>
<td>11</td>
<td>30 Air</td>
</tr>
<tr>
<td>Liquid uptake rate (ml min⁻¹)</td>
<td>3.8</td>
<td>5.1</td>
</tr>
<tr>
<td>Monochromator slit: width (mm)</td>
<td>3.6</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5-3. Optimum conditions for iron fluorescence atomic lines $\sum 248.2-249.1$ nm.
Fig. 5-19. The effect of increasing concentrations of chromium and molybdenum on the fluorescence signal at \( \Sigma 248.2-249 \) nm of 1 p.p.m. concentration of iron under conditions optimised for maximum signal.

- Cr
- Mo
Fig. 5-20. The effect of increasing concentrations of iron on the fluorescence signal at Σ 357.9 - 360 nm of 1 p.p.m. concentration chromium under conditions optimised for maximum signal.
Fig. 5-21. The influence of power and viewing height on fluorescence signal for copper at $\lambda = 324.8 - 327.8$ nm, $485$ W, $739$ W.
Fig. 5-22. Calcium atomic fluorescence spectra, 5% calcium in the source plasma and in the atomiser plasma (a) 0.1 p.p.m. calcium, 3.6 mm slit width (b) 5 p.p.m. calcium, 0.2 mm slit width and (c) both plasmas tri-distilled water.
Fig. 5-23. Calcium ionic fluorescence spectra under high and low resolution, 5% calcium in the source plasma and in the atomiser plasma (a) 1 p.p.m. calcium, 3.6 mm slit width and (b) 5 p.p.m. calcium, 0.2 mm slit width
Fig. 5-24. Copper atomic fluorescence spectra under high and low resolution, 15% copper in the source plasma and in the atomiser plasma (a) 1 p.p.m. copper, 3.6 mm slit width and (b) 50 p.p.m. copper, 0.1 mm slit width
Fig. 5-25. Wavelength scan at the region 380-405 nm for (a) 2 p.p.m. calcium in the atomiser plasma, 3.6 mm slit width (b) water in both plasmas, 0.2 mm slit width.
scans which were obtained at high gain. It can be seen that the argon lines were absent as the ground-state to excited-state transitions of argon lie outside the uv-visible region. Although fluorescence from the excited state is possible, the frequencies involved were also mainly outside the spectral region used in atomic spectrometry [70,255].

Interference from a hydrogen band, centered at 397.007 nm was observed by Mermet and Trassy [256] on the prominent calcium ionic line at 396.847 nm for ICP-AES. Fig. 5-25 show the absence of this hydrogen band in the same region.

Hydroxyl OH is produced by the dissociation of water and this species has a rotational spectrum in the 281 to 295 nm and the 306 to 325 nm wavelength regions for ICP-AES, as reported by several worker [257,258]. Fig. 5-26 shows that there was no hydroxyl fluorescence signal in the regions under investigation. This might be due to the absence of the molecular emission from the source plasma due to the high power [70].
Fig. 5-26. Wavelength scan at the region 280-335 nm, water in both plasmas,
0.2 mm slit width
CHAPTER 6
GENERAL CONCLUSIONS AND SUGGESTIONS
FOR FURTHER WORK

6.1 Limitation and the Future
6.2 Suggestions for Further Work
Chapter 6
Conclusions and Suggestions for Further Work

The most interesting aspect of this work has been in demonstrating the use of the ICP as an excitation source and as atomisation cell for measurement of emission and fluorescence in the same instrument.

For the fluorescence mode, a wide slit width could be used, since this increased the amount of fluorescence radiation gathered by the monochromator. Wide slits also allowed several closely spaced lines for some elements, (for example lead and copper) to be monitored at the same time.

In this study of ASIA, several advantages have been noted including spectral simplicity and low background levels. The construction was such that future modification will be simple. Additionally it has been shown that the ICP was an efficient line source and its tailflame makes an efficient source of ground state species for both atomic and ionic fluorescence (see chapter five).

The comparison of the nebulisers showed that there was no significant difference between the commercial GMK nebuliser and the de Galan SG1 nebuliser with the cyclone spray chamber for solution introduction into the source plasma. The consistently high performance of the de Galan nebuliser and cyclone spray chamber has been demonstrated by its continuous and routine use in this laboratory. The nebuliser was free from salting-up and easy to set up (adjustment was not required), while for the commercial GMK nebuliser the setting up was important. The de Galan and GMK nebulisers worked well and have not blocked during several hours of work. While the GMK nebuliser gave a higher fluorescence signal on the atomiser plasma. The ultrasonic nebuliser had the lowest sample flow-rate and lowest detection limit, but this was impaired by poor precision and a long wash-out time.

The next stage in this work was to study the AVS method in the ICP-AES which accounted for all the variables in the system. These were coolant, plasma, and
nebuliser gas flow-rates, height of observation and power in the plasma. As all possible permutations of the 5 variables were taken, the results show that the order in which the variables were taken was not critical and made no difference at all to the optimisation. At least 50% of the final SBR was achieved after one cycle which took 45 mins. The modified simplex method of optimisation reached the optimum after about 20-25 vertices when the same 5 variables were taken and signal to background ratio was used as the figure of merit. There was no significant difference between the time required (about 2 hours) by each method to reach the final optimum (3.01 SBR for lead).

The real advantage of the AVS for ICP-AES was that the variables could be changed quickly and continuously over a wide range and the effect could be seen quickly. The problem of diagonal ridges did not occur for the elements under study. Also the advantage that information about the shape of the factor space was available which aided an inexperienced operator of such an instrument to become experienced.

With regard to ASIA, the AVS method performed significantly better than the simplex method, which could not take advantage of the benefits of immediate visual feedback of the value of the figure of merit.

In this work, the AVS method has been shown to be efficient for the study of different nebuliser and spray chambers as well as for the study of the effect of concomitant elements on the optimum conditions, and also as a method for minimising the interference effect of easily ionisable elements and stable compound formation.

For the study of the chemical and ionisation interferences, it has been shown that the well-known depressive effect of phosphorus on the flame emission spectra of calcium, which is largely absent in ICP-AES, was also largely absent in ASIA for the atomic line 422.7 nm and the ionic lines at $\lambda$393.4 - 396.8 nm. This state of affairs applied if the working conditions were optimised for maximum fluorescence signal.

Aluminium had a marked depressive effect on both the atomic and ionic lines when the working conditions are optimised for maximum fluorescence signal. However, this depressive effect was reduced in the case of the atomic line if the working conditions were re-optimised for minimum interference.
The ionisation interference of the alkali metals was greatly reduced for both the atomic and ionic lines of calcium when re-optimisation was carried out.

6.1 Limitation and the Future

The ICP is an extremely versatile source because even high concentrations, 1 to 2% for the low power plasma [165], and up to 40% with the high power plasma [167], of analyte result in spectral lines remarkably free from self-absorption at the observation heights commonly used in analytical measurements. The detectability of a number of elements obtained by different technique of spectrometries are listed in Table 6-1. The ICP-AFS results are compared with detection limits for ICP-AES, where pneumatic nebulisation of analytes was used to introduce the sample into the ICP. It can be seen that the HCL-ICP-AFS gave the lowest detection limits for elements such as Al, B, Ni, W and Zn. ICP-ICP-AFS detection limits for the elements determined with the ASIA instrument were comparable to those achieved by the two low power plasmas [165]. For all the elements, superior detection limits were obtained with the ASIA instrument. The detection limits for some elements measured with the Baird plasma AFS system (HCL-ICP-AFS) are comparable to those achieved by the ASIA instrument. However the ASIA instrument values were those better than from the Baird system for Ba and five times better for Na. The high power plasma as a source of light provided a powerful excitation source for the ASIA instrument.

The chief limitation of ICP-AFS is its inferior detectability for the refractory elements. This could be improved by adding propane gas (as shown in Table 6-1) to the atomiser cell through the injector gas flow.

The ICP-AFS provided the greatest spectral selectivity compared to ICP-AES (chapter five), inductively coupled plasma-mass spectrometry (ICP-MS) and similar to the AAS. ICP-MS has the mass spectral interference from the background spectra for distilled and deionised water, as described by Tan and Horlick [259].

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<table>
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<tr>
<td>Al</td>
<td>22.5</td>
<td>45 †</td>
<td>8000</td>
<td>0.02 †</td>
<td>0.4</td>
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<tr>
<td>B</td>
<td>4.8</td>
<td>56 †</td>
<td>—</td>
<td>0.5 †</td>
<td>4</td>
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<tr>
<td>Ba</td>
<td>1.31</td>
<td>8</td>
<td>—</td>
<td>500</td>
<td>200 †</td>
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<tr>
<td>Ca</td>
<td>0.2</td>
<td>0.5</td>
<td>60</td>
<td>0.4</td>
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<tr>
<td>Co</td>
<td>6</td>
<td>21 †</td>
<td>40</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cr</td>
<td>6.2</td>
<td>8 †</td>
<td>900</td>
<td>8</td>
<td>—</td>
</tr>
<tr>
<td>Fe</td>
<td>4.7</td>
<td>19</td>
<td>1300</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>Li</td>
<td>4.2</td>
<td>7</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Na</td>
<td>28.5</td>
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<td>100</td>
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<td>—</td>
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<tr>
<td>Ni</td>
<td>10.1</td>
<td>21 †</td>
<td>ND</td>
<td>7</td>
<td>—</td>
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<tr>
<td>Si</td>
<td>12</td>
<td>120 †</td>
<td>—</td>
<td>300</td>
<td>1</td>
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<tr>
<td>W</td>
<td>30</td>
<td>923 ‡</td>
<td>—</td>
<td>2 †</td>
<td>—</td>
</tr>
<tr>
<td>Zn</td>
<td>1.8</td>
<td>6</td>
<td>6</td>
<td>0.5</td>
<td>—</td>
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</tbody>
</table>

† propane gas added to injector flow
+ determined in Dioxane
++ determined in ethanolic solution
ND not detectable

Table 6-1 Detection limits (p.p.b.) for ICP-AES and ICP-AFS with laser, HCL and ICP as excitation source.
The linear range for the ICP-AFS is very similar to that obtainable by ICP-AES [175] and better than that obtainable by AAS.

The ICP torch as an atomiser cell and laser as an excitation source provided the most powerful single element atomic fluorescence spectrometric system, but the capital cost and the operating costs of a laser system can be high. Lasers are more difficult to use than sources such as the HCL and the electrodeless discharge lamp EDL, but the intensity of laser radiation is $10^6$ to $10^{12}$ times higher [261]. The plasma light have, source and atomic fluorescence selection mode have been shown to be a viable alternative to the high cost laser system (which is more difficult to operate) giving reasonable source intensity and avoiding the need for an expensive, high resolution monochromator.

The ASIA instrument provided good detection power for the refractory and non-refractory elements, large dynamic ranges and freedom from spectral interferences with few matrix interferences.

### 6.2 Suggestions for Further Work

The logical extension of the present study could be summarised as follows:

1. The optical transfer of radiation from the atomiser ICP to the monochromator could be improved by reducing the distance between the atomisation ICP and the monochromator (see Fig. 6-1). In addition, the radiation from the source ICP to the atomisation ICP could be improved by reducing the distance between these two ICPs (see Fig. 6-2). A modulated light source is required and the use of an optical chopper might be avoided if it was possible to devise an aerosol modulation introduction system [262]. A mirror placed behind the atomisation ICP in the direction of the fluorescence monochromator could be expected to improve detection power.
2. For the refractory elements propane could be used as a reducing agent to help scavenge oxygen in the tail-flame and reduce the formation of refractory oxides.

3. The possibility of using the system described as a resonance monochromator, for solutions with high percentage concentrations of an element, by aspirating these into high power source plasma while a fixed concentration was introduced into the low power plasma should be studied. This mode could allow slurry introduction into the high power source which would overcome the problems of blockage which arise with low power source and could also prevent the spectral interferences that can arise when slurry introduction is used.

4. A further extension of the present work would include the development of the technique for simultaneous or sequential multi-element analysis based on the use of a direct reading polychromator or with a computer controlled monochromator system with a computer controlled introduction system. This could be suitable for trace element analysis without spectral interference.

5. Another extension of the present work would be the development of the instrument for absorption spectrometry. Changes in the arrangement of the optical components would be needed to produce an initial arrangement for radiation from the source ICP and the detector. The atom cell could be a T-shaped torch [121] to provide a suitable path length for absorption.
Fig. 6.1. The suggested design of the optics of the AISA spectrometer.

L1 - fused silica lens, 
\[ f = 5.08 \text{ cm}, \quad d = 5.08 \text{ cm}, \quad u_1 = v_1 = 2f = 10.16 \text{ cm} \]

C - position of chopper

L2 - \[ f = 5.08 \text{ cm}, \quad d = 5.08 \text{ cm}, \quad u_2 = v_2 = 30.48 \text{ cm}, \quad v_2 = 6.1 \text{ cm} \]

L3 - \[ f = 5.08 \text{ cm}, \quad d = 5.08 \text{ cm}, \quad u_3 = v_3 = 2f = 10.16 \text{ cm} \]
L1 - $f = 5.08 \text{ cm}, \ d = 5.08 \text{ cm}, \ u_1 = 30.48 \text{ cm}, \ v_1 = 6.1 \text{ cm}$
L2 - $f = 5.08 \text{ cm}, \ d = 5.08 \text{ cm}, \ u_2 = v_2 = 2f = 10.16 \text{ cm}$
M - concave mirror
C - position of chopper in fluorescence, without aerosol modulation introduction system

Fig. 6.2. The suggested design of the optics of the ASIA spectrometer with aerosol modulation introduction system with source plasma
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