Electrothermal Atomisation into a Low Pressure Microwave Plasma for Trace Metal Determinations

by

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ABSTRACT

An evaluation of the low pressure microwave induced plasma (MIP) for the determination of trace amounts of metals is described. For this purpose, a cell was designed so that the plasma is maintained at reduced pressure while the sample is introduced at atmospheric pressure. This system was used for the determination of cadmium, zinc, mercury, copper and manganese using a low pressure argon MIP. Calibration curves and detection limits are presented.

A survey of the proposed excitation mechanisms in these plasmas was carried out and the mechanisms put forward are discussed. The effect of the addition of matrix elements on the determination of metals in this plasma are studied and some interference mechanisms are proposed.

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CONTENTS

CHAPTER I

Introduction

1.1. The Nature of Plasma

Langmuir (1) (1930) first used the term plasma to describe the ionized gases found in discharges which were known to possess unusual physical and chemical properties. The degree of ionization may range from small, as in the case of the low power microwave induced plasma, to very high, as in systems studied by astrophysicists.

Within this range, gases show a wide variety of physical and chemical properties that are entirely different from their normal behaviour, thus justifying Crookes' early suggestion (2) that in the active condition, they represent a fourth state of matter.

The word plasma itself is now commonly used for that region in which the species are actually formed, i.e. the discharge itself which is usually characterized by intense luminosity and in which are found electrons and positive and negative ions as well as atoms.

The splitting of neutral gas molecules into positively charged ions and electrons results in both positive and negative charges. These are approximately equal so the plasma is neutral.

Initially, a discharge results from randomly occurring free electrons being accelerated in the electric field until they attain sufficient energy to cause ionization of some of the gas molecules.

The electrons formed in this ionization are in turn accelerated and produce further ionization. This progressive effect causes extensive breakdown of the gas, the current rises and the discharge is established.

Soon, a steady state is reached in which there is an equilibrium between the rate of formation of ions and the rate of their recombination; this recombination occurring mainly on the walls of the containing vessel when the pressure is of the order of a few Torr or lower.

The drift of electrons in the field is responsible for the electrical conductivity of the plasma since the electrons are the major current carriers. The contribution of the positive ions can be neglected because their drift velocity is low.

The complexity of the system is, however, considerably greater than that represented only by one species of positive ions together with electrons.

Broadly speaking, electrical discharges fall into two main classes (3).

A) The disruptive discharge - which comprises arc and spark types. Intense heat is produced resulting in melting of metals which is often accompanied by sputtering.

B) The non-disruptive discharge - which comprises among others, the glow and electrodeless discharge. Because this latter type of discharge is the one concerned in this thesis a more detailed description of it is warranted.

Electrodeless discharge

At lower frequencies the energy of the field is coupled into the ionized gas of the discharge by means of coils wound round the plasma tube (inductive coupling) or by separated electrodes attached to the outside of the tube (capacitive coupling). At higher frequencies, i.e.

2450 MHz, these discharges can be generated inside the tube coupling the power using resonant cavities.

Above 1000 MHz the main types of generators capable of producing power suitable for plasma chemistry work are magnetrons and klystrons. Because magnetrons are used to excite lower power microwave plasmas they will be described in more detail.

1.2. Frequency Generators

1.2.1. The magnetron (3) is a diode in which a magnetic field is applied at right angles to the electric field between cathode and anode. The tuning circuits included in the tube take the form of cylindrical cavities opening into the central portion via narrow slits. So, magnetrons are therefore a fixed frequency generator. The theory of operation is based on the motion of electrons in a combined electric and magnetic field. When these fields are perpendicular, electrons leaving the cathode tend to travel in cycloidal paths and on average do not change their kinetic energies. In an operating magnetron, in addition to the steady electric field furnished by the d.c. voltage between anode and cathode, there will be an alternating component from the oscillations of the tuned circuits. The alternating field between the anode segments may either increase or decrease the angular velocity of an electron depending on its position relative to the segments, a process that is equivalent to the absorption and release of energy. Electrons that acquire energy are accelerated and soon re-enter the cathode, those that give up energy are decelerated and drift towards the anode. In a properly designed magnetron the electrons absorb energy from the d.c. component of the field and deliver it to the alternating component, thereby sustaining the oscillations of the tuned circuits of cavities. Normally, magnetrons function only as oscillators. They are simple of operation, efficient and relatively low priced.

1.2.2. Klystrons (or velocity modulated tubes) are more expensive than magnetrons and the power requirements are more complex. Other types of generators less used are the backward wave oscillator and the travelling wave tubes.

1.3. The Microwave Discharge - has found increasing application for gaseous electronic studies, light sources, i.e. EDL's (4), production of free radicals (5) and recently, (1965), has been used for the determination of trace elements in different materials (6-11).

This discharge has many attractive characteristics as the production of a high degree of ionization and a large amount of molecular dissociation without heating the supporting gas. It also does not require electrodes and so it is possible to have reaction vessels free of contamination. The source presents no dangerously high voltages to soft tissue (12).

The need for an inexpensive, uncomplicated source of microwave power was achieved through the use of medical diathermy units which supply a maximum of about 200W at 2450 MHz.The usefulness of this power source depends on the discharge cavities whose purpose is to transfer power from the microwave power source to the gas, which is contained in a glass or silica tube. A resonant structure is then used to increase the electrical field in the gas. Any dielectric region completely enclosed by a conducting surface constitutes a cavity resonator and every resonator has an infinite number of natural frequencies and corresponding field patterns (3). However, for the practical purpose of imparting energy to a load such as a discharge apparatus, only a limited number of shapes and sizes are suitable.

The field pattern should also be simple so no multiplicity of regions of high intensity field will exist inside the resonator. The impedance of the cavity is matched to that of the coaxial line of the microwave power supply by a coupling device so that when the impedance of this structure is tuned to that of the power generator, the reflected power from the cavity is minimum, which means that the efficiency of the cavity and, consequently, the power transfer to the plasma is maximum.

The reason for always tuning to minimum reflected power is twofold. First, is that although the power generator is designed to tolerate a certain amount of impedance mismatch, the reflected power injures the components of the equipment as it is dissipated as heat in localised areas, depending upon the position of the maxima of the interference between the forward and reflected current wave; maxima of the voltage wave pattern may be so high as to cause breakdown of the insulation in the transmission line. Second, and more important for this study, is the necessity of describing properly the power dissipated in the plasma, in order to define and more particularly, to reproduce the conditions of operation. It is therefore expedient to tune the cavity to minimum reflected power before each measurement and, since this is only a few percent of the incident power as a rule, the conditions of operation, as far as this aspect is concerned, can be easily reproduced. The properties of the discharge change with different gases and pressures, so it is necessary to adjust the cavity tunning to minimum reflected power when using different conditions.

Five basic types of cavities have been presented by Fehsenfeld, Evenson and Broida (13). Although some of them are improvements of the first ones, each of them has a different optimum range of work. The work in this thesis has been carried out using Electromedical Supplies Model 214L which was found to exhibit a wide analytical useful pressure range of operation with both argon and helium, and a reflected power which can be tuned to nearly zero for the entire range of pressures and microwave power used.

An improvement on this cavity that avoids the necessity of tuning the reflected power to a minimum for each measurement has been described (11) and a new design for improving the efficiency of power transferred to the plasma has also been recently proposed (14). Both workers claim that, with these modifications, helium can be used as plasma gas, operating at atmospheric pressure with some possible advantages (11, 14). With the former Evenson type resonant cavity it was only possible to use helium at pressures below 200 Torr because of the inefficiency in transfer of microwave power (10, 14). The ionization potential of helium is 24.6 V compared with 15.8 V for argon.

1.4. The Nature of Atomic Emission

The basic principle of the radiation of light from excited atoms is well known and described in various texts as are the many applications of atomic emission from arcs, sparks, flames and plasmas (16-21) since Bunsen and Kirchhoff, using a pre-mixed air coal gas flame, observed the atomic emission of Cs, Rb, Tl, Ga and In (22). The particular aspects related to the excitation of atoms in plasmas are briefly described in section 2.4, but for a more profound explanation the reader is referred to several specialized texts (23-25). Analyte atoms excitation processes in low pressure plasmas have not been widely studied and are part of the subject of this thesis.

1.5 Atom Reservoirs

Flames have been widely used as atom reservoirs. Their popularity came from the simplicity of their use. The energy required for desolvation of the sample, evaporation of the solid left and dissociation of the molecules into atoms is provided by collision with flame gas molecules. So, in a primary sense, they are self supported. A wide combination of gases exist, so temperatures between about 2000 and 3000°K are attained. In this range even elements that form refractory oxides are atomized. Flames also are virtually free from memory effects.

In spite of the widespread use of flames as atom reservoirs, they do have some disadvantages:

1. Conventional methods of sample introduction are highly inefficient: normally, only 3-12% of samples reach the flame.
2. A minimum of 1-5 mls of sample is required to obtain a steady signal which is not available in some cases as e.g. clinical analysis.
3. In some cases, the efficiency of free atom formation from the sample nebulized into the flame is low (short residence time) and also metals that form refractory oxides are poorly atomized, since species like O and OH are present in the flame, even using nitrous oxide/acetylene flames.
4. The concentration of atoms in the flame is limited by the large dilution factor due to the large flow rate (typical flow rates used for emission C_2H_2, 1.8 l min^{-1}; air, 8.0 l min^{-1} and C_2H_2, 2.16 l min^{-1}; N_2O, 4.0 lmin^{-1})

and expansion of flame gases, although this is not entirely a disadvantage (26).

Some of these disadvantages, particularly compound formation and, to some extent, band spectrum interferences, can be overcome using other atom reservoirs such as inert gas plasmas.

The high electronic temperature attained (27, 28) and the use of an inert gas as plasma support, decreases the possibility of compound formation and consequently increases the atomization efficiency. Also, the background spectrum is much simpler and the flow rate of the support gas is also smaller than that employed in flames.

The residence time of atoms in the plasma is also greater than in flames; it could be as high as 10^{-2} s compared with 10^{-4} s in the latter (29).

Interferences produced by variations in the population of excited atoms will persist, however, as well as ionization problems. Although plasmas seem in some aspects more suitable as atom reservoirs, there are some disadvantages.

For high power plasmas, (5-10 kW) the power supply is bulky and expensive; the small powered microwave induced plasmas (up to 200W) do not have sufficient energy to atomize most samples, and more important, because of the small amount of energy available, the samples should be almost completely desolvated before going into the plasma region, otherwise it will be extinguished.

Because of this limitation, until recently these plasmas were only used for gas analysis and for monitoring effluent from a gas chromatograph.

1.6. Analytical Applications of Microwave Plasmas

The low power microwave induced plasma (< 200 W) has been used by a number of workers (30). It was pointed out that one of the main advantages of using such a plasma is the high electronic temperature obtained which enables the spectral lines of most elements to be excited with greater intensity than using flames system.

However, because the electronic temperature is a measure of the energy of the electrons rather than the kinetic temperature of the gas, the latter has a value of about 800^{o}K (31) while the electronic temperature could attain $30,000^{o}$K (27). This is due to inefficient transfer of kinetic energy of electrons to the gas molecules, although it should be pointed out that the concept of temperature in such non-thermodynamic equilibrium situations is somewhat futile. Since the theory via which the temperature is obtained is derived for an equilibrium distribution of energy within the system, the values obtained have no meaning than to illustrate the non-equilibrium situation.

Because of the low enthalpy of the gas, few samples could be atomized at the temperature attained and the samples also should be desolvated before entering the discharge. Water absorbs microwave radiation well at 2450 MHz due mainly to its high dielectric loss at that frequency. Other solvents too absorb in a similar manner - the extent depending upon their molecular properties.

Also, some samples are not efficiently vaporized into the plasma. This problem has been partially overcome by injecting the elements as chlorides.

Because of the limitations in the sample introduction as solutions, these plasmas have been used mainly for the analysis of gases (32-35) and as a detector for monitoring the effluent from a gas chromatograph column (6, 36-41). Only recently, solutions of elements previously dried on an ohmically heated filament or on a desolvation facility after a nebulizer have been introduced into the plasma and determined by atomic emission (8, 9, 30, 31, 42-46).

1.6.1. Gas Analysis

The first successful application of microwave discharges using a resonant cavity for spectrochemical analysis was the determination of nitrogen isotopes by Broida and Chapman in 1958 (47). Broida and Morgan (48) have investigated the analysis of hydrogen-deuterium mixtures. Sources at frequencies of 150 and 2450 MHz were tried; the 150 MHz source was preferred since the microwave source showed strong self-absorption. Opposite options were chosen by the same workers for the analysis of nitrogen for equally pertinent reasons.

Taylor et al. used an argon MIP, operating at atmospheric pressure to determine impurities on the support gas by AES (34). 0,05 ppm of carbon, 0,7 ppm of nitrogen, both added to purified argon were detected at 247.9 nm atomic C line and at 337.1 nm of N_2 band head. The precision attained was generally better than 10%.

1.6.2. Gas Chromatography Detectors

The first practical application of MIP as an emissive detector for gas chromatography appears in 1965. Cooke et al.(6) monitored the electronic spectra of the organic compounds in an argon carrier gas. The detector sensitivity was 2 x 20^{-16}g of hexane per second. They tried a variety of electrical discharges and found that the intensity of spectra emitted from a 2450 MHz source was significantly higher than the other sources.

The spectra recorded indicated rather complete fragmentation although recombination was also extensive, indicated by the presence of cyanogen bands.

Both helium and argon have been tried as carrier gas. When a low pressure discharge is used helium was the choice because it has fewer lines in its spectrum, but because of the complexity of the associated vacuum system, argon was used at atmospheric pressure.

The detection limit for I_2 was found to be 7 x 10^{-14}g I_2/s when using methyl iodide monitored at 206, 2 nm; for CS_2 at 257, 6 nm was 10^{-9}g/s; for phosphorus compounds, 253, 5 nm was found to be the most intense line and the detection limit was about 10^{-11}g/s. Sensitivity for chlorine was 2 x 10^{-12}g/s and for fluorine about 5 x 10^{-10}g/s.

This detector was used for the determination of organophosphorus insecticide residues (40) measuring the intensity of the 253, 5 nm phosphorus atomic line. The sensitivity obtained was about 10^{-12}g/s of phosphorus from potatoes, lettuce, grapes, etc.

Bache and Lisk (37) using a low pressure argon discharge, determined 6 x 10^{-13}g/s P at a S/N equal to 3 using the 253, 5 nm phosphorus atomic line in organo phosphorus compounds. The maximum response obtained was at 200 Torr for phosphorus using either atomic line or band emission. They reported that using a low pressure plasma not only increases the sensitivity but also selectivity.

Dagnall et al. (38) reported an atmospheric pressure plasma design for emissive gas chromatographic detector but a $\frac{3}{4}$-wave cavity was preferred because it produced a long stable discharge with negligible overheating of the quartz tube. They also recommended a low pressure plasma, because of the greater sensitivity provided by this system, although this is a function of the system used and the wavelength of the measurement.

An improvement in the G.C. detector has been attained (49) using low pressure (5-10 Torr) microwave induced helium plasma. Atomic lines of I_2, Cl_2, S, Bi and P were produced. Sensitivity for these elements were in order of 10^{-11}g/s using the atomic lines. An improvement of one order of magnitude was found for phosphorus (10^{-12}g/s).

Moye (39) improved the sensitivity and selectivity for several types of pesticides by mixing nitrogen, carbon dioxide, oxygen and helium with argon.

When using 100% argon, the detector shows an enhancement in sensitivity for reduced pressure over that obtained at atmospheric pressure. Maximum sensitivity was obtained at 25 Torr, the lowest pressure obtained with the system.

Optimum sensitivity of the detector was obtained with 85% helium, 15% argon mixture. N_2, CO_2 and O_2 gave a very high continuum radiation even when present in trace quantities. Limits of detection are in the ng range, although they varied with the pesticide analysed.

In gas chromatography detectors most authors claim the superiority of the helium plasma at low pressure over the argon at atmospheric pressure based on the high ionization potential of the former and its ability to prevent association of atoms into pairs with consequent emission of a complex spectrum. Stanton et al. (50) stress the importance of a scavenger gas to prevent carbon deposition on the walls of the tube. 20 pg of arsenic and 50 pg of antimony have been determined by Talmi et al. (41) in environmental samples using gas chromatography using an argon plasma at atmospheric pressure. The removal of the excited metals from the discharge by interaction on the relatively cold walls resulting in deposition of them has been noticed.

Houpt (10) applied a MIP helium gas discharge at 60 Torr for the continuous determination of methyl mercury chloride in environmental samples separated by gas chromatography. The detection limit reported was 5×10^{-14}g and the signal is proportional to the amount of mercury compound up to 5×10^{-9}g. He improves the selectivity by application of wavelength modulation. The method was also applied to the determination of stable isotopes of hydrogen, carbon and nitrogen and also for nanograms of halogens. Characteristics of these discharges are also reported for pressures between about 10-100 Torr.

An evaluation of a MIP helium plasma operating at atmospheric pressure as an element selective detector for gas chromatography has recently been reported by Beenakker (51). He used his own new design cavity that allows helium to be used at 760 Torr, and seems to improve the detection limits of carbon, hydrogen, sulphur, chlorine, bromine and iodine obtained using low pressure helium plasmas (10) and also better than those obtained using argon at atmospheric pressure. Using the latter, these elements can only be detected from diatomic band emission spectra which are somewhat difficult to identify. These bands can overlap sometimes and not always vary linearly with concentration. Detection limits are of the order of 10^{-10} mol/l and linear range over 10^{4}. Comparison with other detection limits with those obtained by the worker are reported. A mechanism for excitation in helium and argon plasmas is suggested. This will be discussed in section 2.4.

1.6.3. Trace Elements in Solutions

Although much attention has been directed to the development of capacitively and inductively coupled high powered plasma sources for metal analysis because of the excellent sensitivity, the apparatus is often complex, bulky and expensive. So, the low powered microwave induced plasma has been tried as an alternative to offer a rapid, sensitive method for the routine determination of trace elements in solutions. In 1969, Kirkbright et al. (7) developed a simple apparatus for this purpose. They used a Microtron 200 generator operating at 100W, an air cooled 214 L resonant cavity with a conventional grating monochromator. The argon plasma was contained in a 15 mm i.d. tube operating at a pressure of about 90 Torr. Sample introduction was achieved via an indirect nebulizer operated with argon (flow rate 4,3 l min^{-1}). Rectilinear calibration curves were obtained for each element and detection limits found were quite satisfactory as, for example, Zn 0.05 ppm, Hg 0,001 ppm, Cd 0,004 ppm, and Fe 1 ppm.

Runnels and Gibson (8) were the first to report the characteristics of an argon MIP for metal excitation, operating at atmospheric pressure. Using a 1 mm i.d. quartz tube, they determined that amounts of material in excess of 10^{-6} to 10^{-5} g/s were sufficient to extinguish the plasma. So, they desolvated and evaporated the sample in a platinum filament prior to introduction in the discharge. They determined Fe, Cu and Cr in metal acetylacetonates and metal trifluoroacetylacetonates.

The distribution of argon intensity inside the cavity was presented and afterwards was confirmed by other workers (9, 52). The maximum occurs about 0, 8-1cm on each side of the centre of the cavity. Also, as the microwave power increased, the size of the discharge increased too. The argon flow rate and heating rate of the sample plays an important role in the sensitivity of emission. If the sample is evaporated too fast the response of the amplifier and recorder appear as a limiting factor; if the rate of evaporation is too slow the curves become broad and the wings of the curve become indistinguishable from background noise. Some of the calibration graphs reported show a slope different from unity. As they suggest, this could mean a constant loss of sample through vaporisation or a self-enhancement as the total amount of sample increases. An increasing amount of chromium or iron acetylacetonate was added until the intensity of copper became constant. So, the addition of chromium not only alters the slope of the calibration curve of copper to unity but also increases the emission intensity of copper. Plotting copper in the chromium matrix vs. iron complex shows no effect of the iron on the determination of copper. So chromium acted as a buffer in the determination of copper. A plot of emission intensity of copper vs. position in the discharge when chromium matrix is present shows an increase of residence time of the sample in the plasma as well as an upward displacement of the maximum emission intensity. Increasing microwave power was found to increase background emission, although decreases the intensities of copper and argon lines. Detection limits provided by these workers were at least equal to AA, i.e., Cu 10^{-12}g, Fe 10^{-11}g and Ag 10^{-11}g.

Taylor et al. (35) determined trace amounts of sulphur by AA and AE using MIP, operating at atmospheric pressure. They report a single, intense and unidentified line which was proportional to the sulphur concentration at 216, 9 nm. The sample was introduced either by means of the thermal filament assembly or using a gas chromatographic system which separated and vaporized compounds prior to the discharge. Detection limits were dependent on the compound introduced and the support gas but in general, fractional microgram quantities of sulphur were determined either by emission or absorption. 0, 2 ppm of S can be determined in cast iron using a 1 g sample.

Sulphur-containing pesticides were determined via emission in an atmospheric pressure plasma evaporated by the electrically heated filament technique. Limits of detection were found to be of the order of fractions of a microgram of sulphur and the best results were found using AES, in a helium reduced pressure plasma (35). These workers also compared the performance of an atmospheric pressure argon plasma with low pressure argon and helium plasma when using different species, i.e. H_2S and SO_2 for sulphur determination. Although the influence of microwave power and pressure on the sulphur intensity for both species were similar, a marked difference in the degree of dissociation was observed when using low pressure plasmas. The degree of dissociation was the same for both H_2S and SO_2 when using argon plasma at atmospheric pressure. It was also reported that there was approximately ten-fold improvement in sensitivity for a helium supported discharge.

Dagnall et al. (53) used an atmospheric pressure argon plasma supported at the mouth of a quartz tube connected to a platinum or tungsten loop for the determination of trace metals using c a. 0.12 μl of aqueous solutions. They also described an amplifier/integrator system which is capable of following the weak and transient emission signal received from the photomultiplier. With the main body of the plasma formed above the orifice, no plating out and devitrification problems were encountered.

A calibration curve for cadmium at 228, 8 nm was reported showing unit slope. Spectral interference occurred with arsenic (228, 8 nm) but none was observed for cobalt (228, 78 nm) or antimony (228, 89 nm). The addition of phosphate, silicate and aluminium does not affect the cadmium signal although vanadium present as ammonium metavanadate gives a 40% reduction in the expected cadmium emission intensity. Detection limits for some elements, such as zinc ($8,0 \times 10^{-11}$ g), cadmium ($2,0 \times 10^{-10}$ g), iron ($3,0 \times 10^{-10}$ g), mercury ($1,6 \times 10^{-11}$ g) and others were determined. Mercury has been determined in blood, leaves and hair by reduction of its compounds to the metal followed by volatilization with an argon plasma operating at atmospheric pressure (54). A detection limit of 6×10^{-11} g was reported and a relative standard deviation of 5%.

A desolvation facility combined with an ultrasonic nebulizer to produce dry aerosol samples was reported (55) to introduce trace elements in solutions into a microwave induced plasma operating at atmospheric pressure. The efficiency of the sample introduction system was 41% using this system. Detection limits were determined for 14 elements, i.e. Ag (0,001 ppm), Al (1 ppm), Fe (1 ppm), Zn (0,01 ppm) Pb (0,1 ppm), Sb (1 ppm) and others. The standard deviation of the spectral intensities measured varies from 2-5%. Sodium or potassium was found to enhance calcium emission while aluminium depressed it. Sodium slightly affected zinc and boron emission. Phosphoric acid also depressed calcium emission.

Metal acetylacetonates eluted from a gas chromatograph were determined using an argon MIP (56) operating at atmospheric pressure. The detection limits for aluminium, beryllium and chromium were respectively 100 ng, 0,01 ng and 1 ng. The relative SD of the response were 10-15%.

Busch and Vickers (31) determined mercury using a MIP operating at 3 Torr and 25% full power in nanogram level, by depositing the mercury electrolycally on copper wires and heating it ohmically using the Brandenberger and Bader technique (57). Detection limits and standard deviation were not reported.

Arsenic has been determined in water, blood, leaves and hair using the Holak arsine generator system (58) coupled with a microwave induced plasma operating at atmospheric pressure (59). The detection limit is approximately 5 ng, limited by the reagent blank. Typically, relative standard deviations better than 5% were observed. Superiority over the colorimetric method normally used was reported, not only because the former used smaller samples but also because the detection limits found were better.

Kawaguchi and Vallee (9) determined the optimum operating conditions for excitation of metals in a low pressure microwave induced helium plasma coupled with a tantalum filament vaporization system. The analytical sequence including desolvation, vacuum control, microwave output, sample vaporization and display are programmed by an electronic controller. The fast rise time of the signal (2-10 msec) was followed by an electronic peak detector and a peak integrator. The process was discontinuous and only after desolvation and decomposition of the matrix, the system is evacuated. The whole duration of the process is 103 seconds. The peak maximum was chosen as a measure of concentration. Influence of tube diameter, microwave power and helium flow rate was studied. Interference of alkali salts on Ca, Pb, Mn, Mg, Cu, Co, Fe, Cd and Zn were studied. A great improvement in the detection limits of some elements adding potassium chloride were found as well as the conversion of calibration curves slope to unity for iron and cobalt. This effect is dependent on the element analysed. They determined zinc in enzymes and found the results in agreement with the ones formerly obtained by AA. Detection limits for the metals mentioned above were determined, i.e. Zn (0, 003 ng), Mn (0, 002 ng), Cu (0, 001 ng), Cd (0, 003 ng) and others.

The effect of potassium addition on the slope of calibration curves and detection limits of some elements has been the subject of further studies by Kawaguchi et al. (42) and a mechanism to explain these effects was suggested. This will be discussed later in Section 3. 2. 4.

A microwave sample atomizer coupled with an MIP operating at atmospheric pressure has been reported by Hieftje and Layman (44).

The high voltage, low current, pulsating d.c. discharge vaporizes predried discrete volumes of sample solutions. The plasmas were viewed axially and the sample volume was measured electronically. All the operation was controlled by computer.

The discharge described combines high temperature and ion sputtering to vaporize even refractory samples, so matrix interferences are minimized. Superiority of the axial view of the discharge over the radial view is claimed based on the improvement of signal to noise ratio, and because instabilities of the plasma are not as noticeable from the end of the plasma as from the side. Also light losses are minimized by placing the plasma far from the window to prevent fogging of it by etching or sample deposition. Detection limits for several elements such as B (33 pg), Cd (2.8 pg), Cu (1,6 pg), Zn (9,2 pg) are provided. The precision obtainable was about ± 5% relative standard deviation in a single determination. Most of the error was attributed to plasma variations caused by changes in the microwave generator output and in coupling the microwave plasma to the cavity. The linear range is from the detection limit to up to near one microgram. Overloading the plasma seems to be the limitation on the high concentrations range. Interference was found with aluminium causing a depression on magnesium emission. This effect is reduced by addition of lanthanum. Refractory matrices also delayed the emission signal.

No anionic and pH effect was noticeable and also no phosphate interference in calcium determination has been found. Ionization interference was found, but was overcome by addition of about 30 ppm of an easily ionizable element. Spectral interference was found with platinum and tungsten.

The severe limitation of the system reported was the quenching effect of large amounts of sample which disturbed the stability of the plasma and thus its excitation ability. This quenching effect depends on the element present in high quantities but no relation has been established between the foreign atoms and their effect on the plasma. On this system the maximum amount of material admissable is 3µg.

The injection of samples into plasmas as easily dissociable chlorides, which result in an improvement of signal has been reported (60). The process can be applied to more than 30 elements whose chloride boiling points are up to 1000°C. The standard deviation obtained was 10%or better. Using this method, lead, cadmium and molybdenum have been determined down to the nanogram level. Linear range was restricted to 1 or 2 decades.

Subnanogram quantities of mercury have been determined using a low pressure helium MIP (61). The mercury calibration curve was found linear from 10^{-10} to 10^{-12}g when H_20_2 2%v/v and 10mM MCl are added. It was suggested that H_20_2 prevents losses of Hg during the desolvation step. Potassium chloride as well as also preventing losses seems to alter the plasma conditions resulting in an increased excitation and/or atomization efficiency. Drying temperature is also important in preventing mercury losses during the desolvation step. Application to mercury-substituted carboxypeptidase was successful. The standard deviation obtained was 0, 002µg/ml or 0, 04µg/ml of mercury with a coefficient of variation of 6%. The detection limit attained was 2, 5 x 10^{-12}g Hg.

The same basic system used for mercury (61) was employed in the determination of nanograms of arsenic in arsenic-monoarsanilazo TYR-

248 carboxypeptidase (62). A temperature programmed discharge mode of sample vaporization was developed. In this system, the energy pulse applied to the filament is increased and the energy profile modified.

Alkali salts enhance arsenic emission several fold and shift the maximum emission towards the centre of the cavity. Results obtained using different filaments were compound and showed that sensitivity and linear dynamic range is dependent on the composition of filament material. A relative standard deviation of 5.4% was obtained when 7 ng of As was determined.

1.6.4. Multielement Analysis

The application of multielement MIP coupled to a vidicon detector for simultaneous determination of trace metals has been reported (45). A carbon cup was used as sampling device. The argon plasma was operated at atmospheric pressure and 45W microwave power. A comparison between detection limits of several elements such as Cd (0,004 ng), Zn (0,005 µg), Pb (0,08 ng), As (0,2 ng) and others using both carbon cup and tantalum strip vaporisation systems is reported. The lower limits obtained using the carbon cup are justified on the basis that the sample is restricted to a small area in this device instead of being spread on the large area of the tantalum strip, which seems to provide a greater analytical throughput per unit of time of analyte to the plasma. The standard deviation reported with the carbon cup is 4%.

An application of an oscillating mirror rapid scanning spectrometer to the simultaneous analysis using an argon microwave induced plasma was described (63). The Harrick Rapid Scan Spectrometer was employed coupled with the carbon cup vaporization system described before (45). The emission of metallic elements in solution excited by the argon MIP was recorded. Calibration curves for bismuth, magnesium, manganese and cadmium were presented. Sensitivities for the last three elements were at the nanogram level; bismuth is not as sensitive and its standards are 5-fold more concentrated than for the other metals. Although this was a preliminary study, it seems that the Harrick Model RSS-B Spectrometer has potential value as a detector for multi-element atomic emission spectrometry.

Skorgerboe et al. (64) evaluated an argon MIP operating at atmospheric pressure for multi-element emission spectrometric analysis. Interferences due to excess of sodium were reported and indium has been used as an internal standard in the determination of trace elements in food. The sample was introduced by means of a nebulizer coupled with a desolvation system. A comparison of the results obtained and obtained previously using a small monochromator having a high aperture, shows that the use of a large polychromator with a low aperture is not a limitation. In terms of detection capability, the results obtained using MIP and ICP show that the former can be competitive with the latter.

CHAPTER 2

Fundamental properties of a MIP as excitation source for spectroanalytical chemistry

2.1. General Considerations

2.1.1. Thermodynamic Equilibrium

The state of a plasma enclosed in a cavity with walls at a constant temperature equal to that of the gas can be described by a few parameters, i.e.: the temperature, the density and the concentrations of particles present. The temperature of the plasma is the most relevant parameter, although it is only significant when related to a definite equilibrium.

A monoatomic gas may be characterized by four temperatures (65):

a) the electron temperature

b) the gas temperature

c) the excitation temperature

d) the ionisation temperature

If all the temperatures are equal, the system is said to be in thermodynamic or thermal equilibrium. The properties of the system are those of a gas inside a blackbody furnace at an equal temperature and it can be described as follows:

a) the velocity distribution of the particles is Maxwellian

b) the relative population of different states for each particle obeys the Boltzmann Law distribution

c) the ionization equilibrium is described by the Saha equation

d) the chemical dissociation equilibrium is defined by the Law of Mass Action

e) the radiation density is given by Planck's Law f) a steady state occurs so that the rate of population of a state is balanced by the rate of depopulation following the same path in a converse way, e.g. absorption of radiation is exactly balanced by spontaneous and stimulated emission.

If the walls of the cavity are removed, energy is dissipated by radiation and heat conduction and to have a steady state, energy should be supplied to the plasma by heating. In order to describe this plasma, an infinite number of parameters should be known. However, the more interactions take place and the more frequently they occur, the more the plasma approaches the steady state prevailing in the black body cavity. The more intense the energy exchange between the degrees of freedom is, the nearer the distribution functions are described by the Boltzmann Law. However, if few interactions occur, the plasma is far away from thermodynamic equilibrium and the only way to describe the system is through microscopic processes. In such a system interaction processes and cross sections of interaction become important. In practice, no complete thermodynamic equilibrium is possible since energy losses by conduction, convection and radiation are not compensated by the existence of surroundings which are at the same temperature.

However, if the change in temperature along a mean free path, in a definite element of volume is small compared with the mean temperature of that element, the equilibrium is only slightly affected and the system is referred to be in a "local thermodynamic equilibrium".

2.1.2. Local Thermodynamic Equilibrium (LTE)

A system in LTE has a population of states exactly the same as that of a system in a complete thermodynamic equilibrium having the same total density temperature and chemical composition as the actual system (29). The equilibrium is said to be local because the plasma has a radial temperature distribution and therefore all parts of the source cannot be in complete equilibrium.

The term LTE was initially intended for the state of matter in the interior of stars with a nearly perfect blackbody radiation field. In stars, there always exists a temperature gradient and thus a flow of energy. However, the local state of matter is quite well described by thermodynamic equilibrium, thus the term LTE.

Griem (66), McWhirter (67) and Wilson (68) have independently derived a criterion for LTE in optically thin collision-dominated plasmas which is:

$$n_e \geqslant 10^{12}\ T_e^{\frac{1}{2}}\ (E_k - E_i)^3\ \mathrm{cm}^{-3} \qquad (2.1)$$

where

T_e : electron temperature in ^oK

$(E_k - E_i)$: electron energy between states i and k expressed in electron volts.

2.1.3. Partial Local Thermodynamic Equilibrium

The occupation numbers in an optically thin collison dominated plasma do not obey a Boltzmann distribution if the Griem criterion (66) is not fulfilled. McWhirter et al. (67) have shown that, in a large interval of electron densities below the critical density sufficient for LTE, detailed balancing of all collisional processes holds which do not involve atoms in the ground level. Such plasmas are said to be in partial LTE. Partial LTE is used sometimes because the equilibrium is only related to the electrons, which, because their higher velocities and high collision cross section compared to the other particles dominate the collision population of states. The temperature of the electrons in the plasma is derived from their kinetic energy (Maxwellian distribution), the population of a particular level is given by Boltzmann equation and the fraction of ionized species is given by the Saha equation (69).

2.1.4. Coronal Equilibrium

Another possible type of equilibrium is termed coronal, in which the population of states is controlled by radiative and collisional processes together.

In practice, an approach is to assume that some type of equilibrium exists, measure the temperature and electron density by different methods and apply a theoretical criterion to verify the assumptions.

An example of a system in LTE could be an arc, in air operating at atmospheric pressure (65). The electron concentration is high, and on average, electrons do not travel over a distance longer than the mean free path without colliding with other species, so the ionization, dissociation and recombination processes are collision dominated.

2.2. Determination of the MIP's Parameters

2.2.1. General Considerations

Simple kinetic theory establishes a relationship between temperature and the mean translational energy of the molecules of a gas. A plasma, however, consists of a mixture of positive and negative charged particles together with neutral atoms. The electrons being smaller than ions and molecules move faster in the electromagnetic field applied losing an average 2, 66 m/M of their energy (74) upon collision with ions and molecules (where m and M are the masses of electron and atom or ion respectively).

So, their temperature is much higher than that of ions and molecules. The ions also will tend to have temperatures higher than the neutral molecules because they can be accelerated by the field. Thus the constituents of the plasma have widely different temperatures.

Furthermore, there is no universal method for measuring temperatures and even applying basically the same method, different interpretation of results can be applied, leading to different results (31, 81).

It seems from all of this, as was stated earlier, that the concept of temperature applied to plasmas is meaningless, mainly for low pressure plasmas, which are even further from equilibrium than high pressure ones. Sometimes, however, the variation in the temperature with other parameters provides useful information about optimum conditions for excitation and is related in some way with emission intensity from both the constituent atoms and analyte species. It is worth mentioning that the order of magnitude of temperatures obtained by different methods and different authors agree to some extent.

The electron temperature, the electron concentration and their variation with pressure, flow rates and microwave power- measured by different workers are presented overleaf.

Some proposed excitation mechanisms based on these data and on the lines emitted in different plasmas will also be discussed.

2.2.2. Temperature Determination

A) Spectroscopic temperature using the relative intensity of two spectral lines

This method measured the intensity of two spectral lines and from:

(2,1)

$$\frac{I_m}{I_n} = \frac{g_{um} A_m \lambda_n}{g_{un} A_n \lambda_m} \exp \frac{E_{un} - E_{um}}{kT} \qquad (25)$$

where I_m - spectroscopic intensity of line m

g_{um} - statistical weight

A_m - Einstein transition probability for spontaneous emission

k - Boltzmann constant

$E_{un} - E_{um}$ - Energy difference between the two levels.

This equation is applicable to systems in LTE where there is no self-absorption, so for moderate temperatures, this equation is not applied to ground state atoms.

This method can also be applied for determining temperatures by measuring the relative intensities of a series of lines writing (2-1) as follows:

$$\log_{10} \frac{I \lambda}{g_u A} = - \frac{E_u}{2,303\, kT} - \log_{10} \frac{Q(T)}{hc\, N_o}$$

Applying this method to the 4s-4p argon series between 390-430 nm, Sharp (29) found a temperature of 5680 ± 480°K for an MIP, operating at atmospheric pressure.

Busch and Vickers (31) measured spectroscopic temperatures of a reduced pressure MIP from the relative intensities of argon lines of the same series and found 4150°K (3 Torr); 4285°K (12 Torr) and 4535°K (25 Torr).

For an argon plasma operating at atmospheric pressure, Winefordner et al. found a spectroscopic temperature of 4850°K (29). These authors did not take into account how these levels were populated that means, whether by a recombination process of argon ions with electrons or only by a Boltzmann distribution from the ground level of the argon atom, so these temperatures can only give an indication of the order of magnitude of the mean temperature of electrons in the plasma.

Avni and Winefordner (75) measured the spectroscopic temperatures of a reduced pressure MIP using the 535, 0 nm atomic line of the thallium atom. The upper level ($6^2P_{3/2}$) is at 3. 3. eV and is metastable, the lower level being at 0. 96 eV above the ground state. The line was reversed by emission from a calibrated tungsten ribbon lamp and the reversal temperature measured (76). Because the mean kinetic energy of electrons in a low pressure MIP is not much higher than 0, 96 eV, it was assumed that this level is preferentially populated as a result of the gas temperature i. e., by Boltzmann ian distribution. The reversal temperature for thallium was constant with pressure from 4 to 10 Torr and has a value of about 1700°K; for pressures below 4 Torr it increases up to about 2200°K. They assumed that this temperature represented that of the plasma gas. Since comparison with average random velocity of the electron and the electron drift velocities indicates that $\bar{\nu}e > (\nu e)$ drift so the microwave source results in a plasma which is more thermal than electric (75).

Using the relative line-continuum method Sharp (29) found a temperature of 13, 350 ± 1000°K. Errors in the experimental determination and even the assumption of LTE (which could be wrong) did not account for the big discrepancy in the temperature compared to that determined by the relativity intensities of the two argon lines.

The Probe Technique

The probe method measures electron temperature and electron concentration independently of spectroscopic measurements. Since double probes do not require an external electrode and also do not draw large currents from the plasma causing instability and error on measurements (77), they were chosen by most of the workers.

Sources of error caused by reaction of the probe material and plasma are numerous (78) so an inert material has to be chosen. The way the probes are inserted into the plasma, its shape and the pressure where the measurements are performed are also important.

Sharp (29) measured the electron temperature in an atmospheric pressure plasma and found a value of 24, 250^{0}K ± 1600^{0}K. The temperature is much higher than the spectroscopic temperature since only electrons with energy in excess of the sheath potential are sampled by this technique (78). He used platinum probes (the temperature of the gas was previously found to be 750^{0}C) and applied the method of the "characteristic curve" or equivalent resistance method (77).

Busch and Vickers (31) using the same method found a temperature of about $5,2 \times 10^{4}$ °K for helium at 3 Torr and $3,3 \times 10^{4}$ °K for argon at 25 Torr and 3 Torr. Virtually, no change in the electron temperature with argon pressure was noticed and also addition of $4,4 \times 10^{-2}$ atom per cent of mercury in argon does not affect it. However, the electron temperature was affected by the ionization potential of the support gas, i.e. it is much higher for helium than for argon.

Brassem and Maessen (79) measured the electron temperature of reduced pressure microwave helium, neon and argon plasmas using the double probe technique and the Johnson and Malter "logarithmic plot" method (78). For neon at a pressure of about 0,05 Torr, they found an electron temperature of 130,000 °K. For He and Ar at 0,2 Torr they found 100,000 °K and 26,000 °K respectively. In the region of 0,05 Torr up to 0,1 Torr the temperature decreases sharply and for further increases in pressure, it is almost constant. Also, the electron temperature remains constant for the three gases studied, at increasing microwave power. It is worth mentioning again that the probe method in this case also only samples the high energy low density electrons, which are below the thermal limit in the distribution, since only they have sufficient energy to overcome the potential of the probe. As could be predicted, electron temperatures are higher for gases having higher ionization potential.

A study of the influence of flow rate independently for two different pressures, (0,2 and 1,0 Torr) was also undertaken by Brassem and Maessen (80). The desired conditions were attained by repeated readjustment of a needle valve that controlled the flow rate and the pumping rate. The values obtained showed that increasing flow rate decreases the electron temperature and at equal flow rates the electron temperature is higher at 0,2 Torr than at 1,0 Torr. The influence of flow rate on the electron temperature is higher at low flow rates, and at lower pressures. At 1,0 Torr the electron temperature reaches a constant value at different rates for different gases.

Winefordner et al. (75) measured the electron temperature using the double probe technique and found that it is almost constant with pressure for values above 4 Torr and has a value of about 3, 5 x 10^4 °K. Below 4 Torr, it can attain values up to 5, 8 x 10^4 °K (at 0, 5 Torr). It was suggested that at lower pressures bombardment of argon ions with other species release high energy electrons; at higher pressure, these electrons suffer more interactions losing their energy. However, no evidence was given to sustain this mechanism.

The greater variation of electron temperature at higher pressure found by Winefordner et al. (75) was in contrast with the results obtained by Braessen et al. (79) where the variation of electron temperature was greater at pressures between 0, 05 and 0, 1 Torr; at 0, 6 Torr it becomes constant. Also the curve of variation of electron temperature with microwave power shows a significant dependence on both parameters; at 0, 2 Torr the curve shows a completely different tendency and also Busch and Vickers (31) found a quite different relationship between both parameters, although they varied the microwave power only up to 50 W.

The difference in the electron temperature obtained by different methods is a measure of how far from LTE is the system. These high energy electrons are in the tail of the distribution below the thermal limit. They are responsible for the ionization of the species in the model proposed by Schülter (71) which will be discussed in section 2. 3.

2. 2. 3. Electron Concentration

The electron concentration was determined by Busch and Vickers (31) for a reduced pressure microwave plasma using again the double probe technique and employing the Swift and Schwar relation (81).

$$I^{+} = 0,6\, N^{+} e\, A_{p} \left[\frac{k\, T_{e}}{m^{+}} \right]^{\frac{1}{2}} \qquad 2.2.$$

where

I^{+} is the saturation current to an individual probe

N^{+} is the number density for the positive ion

e is the charge on the electron

A_{p} is the probe area

k is the Boltzmann constant

T_{e} is the electron temperature

m^{+} is the mass of the positive ions

assuming that, in a neutral plasma, the positive ion concentration is equal to the electron concentration, the latter is directly proportional to the saturation positive ion current. By using this method, they found an electron concentration of $1,5 \times 10^{13}$ cm^{-3} for argon, at 3 Torr and 25% full power. This method for the determination of electron concentration samples the high energy and low energy groups. The pressure seems to alter slightly the electron concentration over the range of pressure studied (3-25 Torr).

The electron concentration seems to vary with power, more at lower applied power and also more at lower pressures (3 Torr) than at higher pressures (25 Torr). This can be understood bearing in mind the increasing number of collisions at higher pressure, so more recombination of electrons and ions are expected. Also, the electron concentration is greater for a gas of low ionization potential than for higher ones. This behaviour is opposite to electron temperature.

Bra ssem et al. (79) determined the electron concentration by the probe technique, using a relation derived by Bohm et al. (84).

$$I = 0{,}5\, N^{+} A_{p}\, e \left[\frac{kT_{e}}{M^{+}} \right]^{\frac{1}{2}} \qquad 2.3$$

(the terms are the same as in eqn. 2.2)

For argon at 3 Torr they found an electron concentration of $5{,}7 \times 10^{12}$ cm^{-3} and for helium at 0,2 Torr they found a concentration of $1{,}95 \times 10^{12}$ cm^{-3} with a relative standard deviation of 16%. The electron concentration was found to increase sharply with pressure at low pressures (less than 0,75 Torr) and then decrease for both argon and helium. The electron concentration increases with microwave power for both gases although this last variation is not significant.

Using the double probe technique, Avni (75) measured the electron concentration and found a value of about 5×10^{12} cm^{-3} for argon at 4 Torr and about 1×10^{12} cm^{-3} for helium at the same pressure. An increase in pressure was accompanied by an increase in electron density up to about 8 Torr. This was also observed by other workers (31,79). The addition of metals of low ionization potential, e.g. Cs or Tl increases the electron concentration in the plasma.

2.2.4. The Neutral Gas Temperature

Sharp (29), using a thermocouple, measured the temperature of the plasma gas and found a value of about 700°C. This was expected to be low since fused silica and quartz are normally used as plasma tubes. The low temperature of the gas reflects the low enthalpy of the plasma and consequently the main reason for the necessity of previously evaporating the sample. The reason for this low gas temperature is the inefficient exchange of energy between ions, electrons and neutral atoms of the support gas (29).

The neutral atoms cannot gain energy from the applied microwave power by being accelerated by the field as do charged particles. So, considering an electron of mass m travelling with velocity $\underline{v}$ colliding with an atom of mass M with V = 0. If an elastic collision occurs, the particles will have changed velocities v' and V

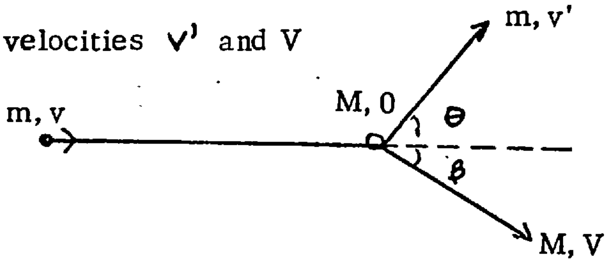

Fig. 2.1

Applying the law of conservation of energy and conservation of linear momentum it will give:

$$\frac{\Delta E}{E} = \frac{2m}{M} (1 - \cos \theta) \qquad (2.4)$$

So, due to the big difference in masses, collision with electrons is very inefficient. Ions have almost the same masses as neutral molecules so a large proportion of their energy is transferred to neutral atoms by collision.

From the measurements carried out by different authors, and the different temperatures obtained using different methods, some conclusions can be drawn.

a) The system is not in LTE and, as can be predicted, as the pressure decreases, the further it is from equilibrium.

b) The probe method gives temperatures at least 10 fold the ones found by spectroscopic measurements, so, a mechanism in which two groups of electrons with different distributions and consequently different temperatures, (different Maxwellian distribution) must be involved to explain excitation processes.

c) The spectroscopic temperature is in agreement with the one calculated by the Saha equation when using the electron concentration measured using the probe method (31). So, the density of these electrons is predominant over the high energy groups and in some ways, they determine the properties of the plasma.

d) The value of the flow rate beyond which the electron temperature and electron density do not vary with flow rate is the same from which the line intensity is also constant with flow rate (80). This suggests that the line intensity is in some way related to the temperature and the electron concentration, although, for a non-equilibrium system this relation is not straightforward.

It was also found (80) that, two lines of the same gas, with similar excitation potential can be affected in completely opposite ways by variations in pressure and flow rate, when excited under the same conditions.

e) Decreasing the pressure increases the electron temperature to some extent. It might be expected that because of the lower number of collisions, the electron energy is somewhat higher. Also the amount of collisional deactivation of excited states is lower, the probability of radiational deactivation is higher and then a high sensitivity might be expected.

Based on these experimental facts some mechanisms have been proposed by different authors for helium and argon microwave plasmas. These mechanisms were proposed also taking into account the lines observed in the spectrum.

2.3. Characteristics of the atmospheric pressure and the reduced pressure microwave plasma

2.3.1. General Considerations

To start the ionization of the gas, some electrons have to be "seeded" in the plasma, which is carried out using a Tesla coil. These electrons are accelerated by the field until an elastic collision occurs or the field changes direction. The energy transfer per collision is proportional to 2m/M (eqn. 2.4). So the electrons gain energy from the field and lose part of it by collisions until their energy is above the first excited state of the atom when an inelastic collision can occur. In this collision the electron will lose almost all its energy which will be radiated by emission of a photon from the atom. The plasma is sustained by these electrons being accelerated until they reach the ionization potential of the gas. Considering only the effect of the applied field, an electron when accelerated by the field, moves in a particular direction. Since both voltage and electron current are in phase, presenting a resistive load to the generator (83), the energy exhange between the field and the electron is almost 100% efficient. When the field changes direction, the force on the electron changes at once but the same does not happen with its direction of motion; the electron then acts as a generator, as it is decelerated, and its energy passes back to the field. After a few cycles a steady phase lag develops and for a voltage it can be represented by

$$e = E \sin wt$$

$$i = I \sin (wt + \phi)$$

where

e : instantaneous voltage

E : peak voltage

i : instantaneous current

I : peak current

w : the angular frequency of the field

t : the time

ϕ : the angular phase lag

The average power per cycle transferred to the electrons by the generator is given by

$$P = V_{rms} \, I_{rms} \, \cos \phi \qquad (2.5)$$

The electron atom collisions interrupt the out of phase motion with consequent increase in efficiency on the exchange of power. So, if there is no other effect it would appear that the maximum electron energies occur at high pressure because of the greater number of collisions, as at lower pressures the phase lag between voltage and current may approach 90^0 (in vacuum), leading to zero power transfer. However, as the pressure increases, the elastic collision damping effect becomes increasingly important. McDonald has shown (70) that the optimum breakdown pressure for argon at 2800 MHz is 4 Torr.

It has been shown that the effective field that the electrons experience is a function of the applied frequency and the collision frequency (70) in the form of:

$$\overline{E_e^{\,2}} = E^2 \; \frac{\nu_c^2}{\nu_c^2 + \nu^2} \qquad (2.6)$$

where

E_e is the effective field

E is the time field

ν_c is the collision frequency

From the kinetic theory, the collision frequency is given by

$$\nu_c = 2{,}1 \;\; 10^8 \, \upsilon^{\frac{1}{2}} p.Q \qquad (2.7)$$

where

υ = electron energy in electron volts

p = gas pressure in Torr

Q = the collision cross section in angstroms squared

Taking the temperature of the high energy group of electrons which are supposed to be responsible for ionisation (71) and comparing with the frequency of the applied field, Sharp (29) calculated that 378 collisions occur per cycle of the field, at atmospheric pressure and substituting this value in equation 2. 6, the result shows that the effective field is 0, 9997 of the actual field.

Using the same equations and assuming the electron temperature to be 3, 17 x 10^4 °K (31) at 3 Torr and using the data from MacDonald for the collision cross section for electrons, it has been calculated that about 13 collisions occur and also that the effective field is 0, 98 the applied field. The electron mean free path L can also be calculated from the relation (2. 8).

$$L = \frac{1}{p.2,81 \times 10^{-17} Q} \qquad (2.8)$$

For an argon plasma operating at atmospheric pressure, this yields a value of 9, 3 x 10^{-5} cm for the high energy group. For the reduced pressure plasma (10 Torr), the value is somewhat higher (about 0, 56 x 10^{-2} cm) but both values indicate that these electrons are lost mainly by diffusion. The same order of the electron temperature can be used over the range of 3 to 24 Torr, as the variation of this parameter with pressure is almost negligible (31).

The difference in the number of collisions and electrons mean free path between different plasma operating at different pressures should account for the differences in the operational characteristics of these plasmas as, e.g. tube diameter and flow rates, as well as the reason why some gases such as N_2, O_2, He only form microwave plasmas at low pressures. Also, a difference in emission intensity from the analyte atoms should be expected as different pressure as well as different gases are used.

2.4. Excitation Mechanism

2.4.1. Argon Plasma

A model was proposed for explaining the existence of different electron temperatures obtained by different methods (71). A radiative ionisation-recombination mechanism was suggested and it can be resumed by:

$$Ar^{o} + e \rightleftharpoons Ar^{+} + e + e$$

$$Ar^{+} + e \rightleftharpoons Ar^{*} + h\nu_{cont}$$

It was suggested that this equilibrium results in two distinct groups of electrons, a high energy low density group and a low energy high density group (71). These two groups were supposed to have different Maxwellian velocity distributions, characterized by different temperatures.

The high energy electrons are responsible for the ionization of the gas and are lost mainly by diffusion to the walls. The low energy electrons are responsible for the radiative recombination of ions with low energy electrons. A steady state plasma results from the balance between the ionization rate and the rate of ion-electron removal by diffusion to the walls (both free and ambipolar diffusion (72)) and radiative recombination.

Kenty (73) has shown that the radiative recombination cross section decreases with increasing energy, so the high density low energy electrons should be responsible for the radiative recombination while the high energy low density must be depleted mainly by diffusion.

The distribution of energies over the higher levels (bound states) is determined by the high density low energy electrons and extends from the continuum to the thermal limit. Below this limit, the probability for de-excitation by spontaneous emission exceeds the one by collisions with electrons. In these levels the equilibrium is controlled by a combination of collisional and radiational processes (29). Also, the argon atom has two metastable levels, one at 11,49 eV and the other at 11,66 eV. These levels can be responsible for the excitation of atoms introduced into the discharge by Penning ionization (85).

$$Ar_{meta} + M \rightarrow Ar + M^{+} + e$$

The condition for this reaction is:

$$E_{meta} > E_{ion}M$$

Another proposed mechanism was the excitation of metals by direct collision of the second kind with metastable atoms of the support gas

$$Ar_{meta} + M \rightarrow Ar + M^{*}$$

But, since the probability of this reaction decreases as the difference between E_{meta} and E_{exc} increases (31), this last mechanism is less probable. Also, the importance of the ionization by metastable argon atoms decreases as the pressure increases. Phelps and Molnar (82) found that argon metastable atoms were destroyed by two and three body collisions at pressures up to 16 Torr. However, when introducing 5% N_2 in an atmospheric pressure argon plasma, it was noticed (29) that there was a lack of bands from levels above 11,66 eV which suggests that the excitation was occurring by collisional energy exchange with metastable atoms. The increase in pressure decreases the emission intensity of the argon 696,5 nm line probably by collisions of excited atoms with ground state atoms, e.g.,

$$Ar^* + Ar \rightarrow Ar_2^+ + e$$

The dissociation of the molecule results in emission of vacuum ultraviolet radiation. If LTE does not exist, a radiative equilibrium could be important in the population of the lowest levels, e.g.

$$Ar^* \leftrightarrows Ar + h\nu$$

The introduction of 4, 4 x 10^{-2} atom % of mercury (ionization potential: 10, 43 V) did not affect the excitation conditions of the plasma (31) over the range of parameters studied. The emission intensity for mercury was found greater in argon than in helium at the same pressure, suggesting that the higher electron concentration is more important than higher electron temperature in excitation mechanisms.

Beenaker (51) shows that only atomic line emission was found in an argon MIP, for Cl_2, Br_2, I_2 S and P. These atoms emit ionic lines in a helium MIP operating at atmospheric pressure. The excitation energy of ionic levels of C, P, S and I in an argon MIP are above the argon metastable atoms energy. So, the ions of C, P, S and I formed by Penning ionization recombine with electrons giving emission at the atomic line. Direct electron impact could also fragment diatomic molecules because ionization energies of some fragments are above the energy of metastable states.

2. 4. 2. Helium Plasma

As in an argon plasma, the radiative ionization-recombination mechanism is supposed, the ionization process governed by the low density high energy electrons and the high density low energy electrons being responsible for the recombination. Helium also has two metastable states, having excitation energies of 19, 82 eV and 20, 96 eV, but since the latter is quickly converted to the former (51), only this will be considered.

So, the following processes are expected:

$$He + e \rightleftharpoons He^{+} + e + e \qquad \text{ionization}$$

$$He + X \rightarrow X^{*} + e \qquad \text{direct excitation}$$

$$X^{+} + e \rightarrow X^{*}$$

$$X^{+} + He + e \rightarrow He^{*} + h\nu_{cont} \quad \text{recombination}$$

Also, because of the existence of metastable atoms, Penning ionization is also probable:

$$He^{m} + X \rightarrow He + X^{+} + e$$

$$He^{m} + X^{+} \rightarrow He + X^{++*} + e$$

Beenakker(51), working with a helium MIP at atmospheric pressure found that the ionic lines observed for Cl_2, Bi_2, S, P and I_2, were in the range of energy between 12, 3 eV and 15, 9 eV which exclude the possibility of excitation by electron impact.

The range of energies observed suggested that excitation was <u>via</u> metastable helium molecules, <u>i.e.</u>,

$$He_2^{m} + X^{+} \rightarrow X^{+*} + He + He$$

They also explain the presence of ion line emission (190.0-800.0 nm) for S, P, Cl, Br and I, the limited range of energy involved in this ion line emission and the absence of ion line emission for C, N, O and F on terms of the predominant process being the excitation by impact with metastables (51).

So, as the concentration of metastable molecules increases with pressure and also the electron temperature, detection limits are expected to increase because of the enhancement of ion line emission and the increase of the sensitivity of atom lines produced by electron-ion recombination. This was justified on the basis of the better detection limits obtained for the atmospheric pressure helium MIP compared with those obtained at reduced pressures. The mechanism by which the excited species are produced in the atmospheric pressure and reduced pressure helium plasmas should be the same, since the spectrum is exactly the same, that means not only the lines emitted but also the relative intensities of the lines are the same. However, at higher pressure, the metastable molecules should predominate in the excitation process over the metastable atom, the contrary happening at lower pressure.

Houpt (10) suggested that a narrow tube discharge (2 mm i.d.) and higher pressure than was used before (10 - 100 Torr) were better than using wider tubes (3-8 mm i.d.) and pressures below 7 Torr (9) but no evidence was presented why these conditions were chosen. It seems that the optimum conditions vary according to other parameters of the system used, and not because the excitation conditions were modified significantly. The role of metastable atoms is important because their long life time and also their energy can only be dissipated by collisions of the second kind and not by emission of radiation (83). The concentration of metastable helium atoms 2^3S_1 was determined by atomic absorption at 388, 6 nm using an electrodeless helium discharge. They found that the intensity of helium atomic lines, 587, 6 nm and 388, 9 nm, decreases with pressure while the opposite happens with the molecular emission of He_2^* (vibronic transition) at 465, 0 nm.

The helium 388, 9 nm emission intensity shows a steep decrease with pressure up to about 15 Torr and from about 30 - 90 Torr a slight increase. The emission intensities of Cl 481, 0 nm, Hg 253, 7 n m and I 516, 1 nm were found to increase with pressure but correcting the values for particle density the opposite variation was verified.

The decrease in the intensity of emission of helium lines could be due to de-excitation of excited helium atoms with helium ground state atoms accompanied by the following reactions (10):

$$He^* + He \rightarrow He_2^+ + e$$

$$He + 2He \rightarrow He_2^* + He$$

He_2^* being a metastable state, has time enough to interact with impurity atoms in plasma at high pressure (at low pressure the probability of its formation is very low). Based on these results, a mechanism was proposed for high and low pressure:

low pressure - $M + He^*(\underline{ca.}\ 19.8\ eV) \rightarrow M^+ + He + e^-$

high pressure $\begin{cases} M + He_2^*(\underline{ca.}\ 17.5\ eV) \rightarrow M^+ + 2He + e^- \\ M + He_2^+(\underline{ca.}\ 21.5\ eV) \rightarrow M^+ + 2He \end{cases}$

and the recombination mechanism:

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

$$M^* \rightarrow M + h\nu$$

The decrease of intensity of measured lines at low pressure region coincides with the decrease of absorption of metastable atoms.

Kawaguchi et al. (42) proposed an excitation mechanism to explain the interferences found in a low pressure (4 Torr) MIP. They found enhancements of 6 - 1000 fold when KCl (2-10 mM) was added to the samples and also the slope for the log-log calibration curve is changed. The 10 mM KCl addition decreases the helium 194,5 nm line by 95% but other elements which also interfere do not seem to affect the excitation conditions. Also, KCl does not affect the neutral atom population. Measured by atomic absorption they found that the delay times of absorption and emission signals are not related and also that when KCl is added, the delay time for the signal of the analyte approaches the delay time for the K signal from both sides. These results show that another excitation mechanism not involving neutral atoms is expected. It was proposed that, in addition to the radiative ionization recombination mechanism proposed by Busch and Vickers (31) involving only neutral atoms, ionization of molecular species following its dissociation in the plasma is also possible.

So:

$$M + e \rightleftharpoons \underline{M}^{+} + e + e$$

$$M^{+} + e \rightarrow M^{*} + h\nu_{cont.}$$

Penning ionization $$Ar_{meta} + M \rightarrow Ar + M^{+} + e$$

also:

$$MCl + e \rightleftharpoons \underline{M}^{+} + Cl + e + e$$

$$He_{meta} + MCl \rightarrow He + \underline{M}^{+} + Cl + e$$

This mechanism was supported by the differences in emission and absorption delay time and the slope of calibration curves due to the volatilization process. When, after desolvation, the solute is evaporated, only a fraction of it is in contact with the filament. Increasing the concentration decreases this fraction. So, part of the solute will go into the plasma as molecular salt, and this fraction increases with concentration. As the ionization of the molecule after dissociation in the plasma is more efficient than the ionization of neutral atoms (56), the calibration curve increases sharply. The addition of a salt will occlude the analyte and homogenize its evaporation into the plasma, as well as prevent the dissociation of the chloride and formation of refractory oxides. Due to fractional volatilization of the salts, KCl is not suitable for all the elements. This proposed mechanism explains the influence of volatile salts, present in much higher concentrations than the analyte, but does not explain the effect of *e.g.* 2 ppm of Co on the calibration curve for iron. The effect of 12 ppm of barium on the detection limit of calcium could be explained in terms of ionization supression. It also did not take into account reactions that could occur on the filament and in the vapour phase over it when a different matrix is present together with the analyte. It was also suggested that, when amounts of different samples are present, the diffusion coefficient of the sample into the plasma changes and also the residence time of the analyte in the discharge (75).

2.5. Influence of Gas Impurities Added to the Support Gas

When the microwave induced plasma is used for analytical purposes, it consists not only of a support gas discharge but is a mixture of this gas plus the sample vapour. The main problem with metal solutions is that the actual amount of sample concentration in the plasma is unknown. Using the same equipment described before, Brassem *et al.* (84) studied the excitation conditions of a mixed-gas low pressure (0,1 - 0,5 Torr) MIP. The variation of the electron temperature and density on the line intensities with various gas mixtures were determined. The noble gas is considered the starting composition to which the impurity is added. The results obtained showed that up to the concentration of 1% v/v (10^{-3} Torr or 10^{13} impurity particle cm^{-3}) the electron temperature and electron concentrations maintain the values corresponding to the pure support gas. From 1 to 10% these parameters change significantly, approaching the values determined for the foreign gas added, if these differ from the support gas. From 10 to 100%, the excitation parameters either remain constant or change gradually until the value for the pure added impurity is reached. Zaitev and Miniskova (85) measured electron temperatures and concentrations in a helium d.c. discharge with and without mercury added and Vermey (86) observed a decrease in temperature and an increase in electron density when mercury was added to an argon d.c. discharge, if the partial pressure of mercury exceeds 0.6×10^{-3} Torr.

The variation of the emission intensities in MIP's of gas mixture is closely related to the variation in excitation conditions. At concentrations of impurity below 1%, the relation of the added component with the emission intensity is linear. At higher concentrations, the excitation conditions change toward the pure concomitant values, so line intensities of the added component start to change according to the variation of excitation conditions.

2.6. Conclusion

As for any system out of equilibrium, it is almost impossible to assert a definite mechanism which will enclose all the situations and even then the results would not be certain. Not only the plasma parameters themselves but also the peculiarities of each system makes the task of determination of optimum conditions even more hard. From the data collected in this chapter, it is almost impossible to foresee which conditions of *e.g.* pressure and microwave power will be the optimum for a particular system. For solutions deposited on filaments, the problem is even more difficult since the vapour cloud is introduced in the plasma for a few hundred milliseconds, so the possible variations in the excitation conditions during this short period are very hard to follow. Also, the transportation of the sample into the plasma can account for many of the interferences found.

As detection limits are not a reliable source for indication of the optimum parameters, since they are determined in different conditions for different systems, it seems that for a given system, all the parameters for optimization of the emission signal should be studied carefully.

So, for the work described in the present thesis, a set up was designed and the parameters optimized. The results will be presented in Chapter 3.

Chapter 3

Optimization of the Analytical Parameters

3.1. Introduction

In the determination of elements by any method, there are a number of conditions that have to be optimized in order to obtain a maximum signal for a given concentration of analyte. If the instrument is a commercial one, this optimization is limited by fixed parameters, characteristic of the particular apparatus. With research equipment, the limitations are the different pieces available, which are designed and adjusted to give maximum output signal for an amount of analyte. In this work, as in most others, certain parameters had to be chosen prior to the optimization of others, the initial conditions then being changed in the light of experience.

The most important parameter to be chosen is the pressure. Work at reduced pressure requires different equipment to that needed for work at atmospheric pressure. A study was undertaken to choose the pressure based on the theoretical measurements presented in Chapter 2 and on practical considerations. For reasons of simplicity, an atmospheric pressure plasma should be the choice since this system will not require vacuum pumps and all the instruments associated with vacuum work. Also, the leakage problem is not always easily solved, and this can introduce irreproducibility on the results. The sample introduction system is far more complicated as are the factors affecting reproducibility, since with the systems proposed before,the sample solutions were introduced and the cell evacuated with the plasma extinguished (9, 42, 56).

However, the high temperatures obtained (79, 80, 31) and also the smaller amount of collisional deactivation due to reduced particle concentration in the reduced pressure region, makes one expect a larger radiation output per particle than the atmospheric pressure range. Also, the variation of excitation conditions (79, 80) with pressure makes the low pressure region promising in terms of sensitivity with respect to higher pressures.

Some other factors, such as the amount of sample that can be introduced without quenching the plasma, and also the amount of molecular vapour that can be admitted without causing instability favour re-duced pressure. Busch and Vickers (31) showed that the concentration of argon metastable atoms decreases as pressure increases and since, because of their long life these atoms are supposed to play an important role in the excitation mechanism through Penning ionization, it also seems that the reduced pressure region could provide higher sensitivity than the atmospheric pressure region. Stability has not been compared for both reduced and atmospheric pressure plasmas, but since the reduced pressure region plasmas tend to occupy the whole tube from 2 mm i.d. to 10 mm i.d. and the atmospheric pressure plasmas only occupy a part of the 2 mm i.d. tube tending to wander (29, 87), the former could be better than the latter, as far as stability is concerned. The results obtained before for low pressure plasmas for the excitation of analytes in solution (9, 42) seemed promising so it was decided to undertake a study in this region.

3. 2. The Plasma Cell

As was mentioned in Section 3. 1, one of the drawbacks of working at low pressure is the difficulty encountered in the sample introduction systems. Most of the authors that have worked with solutions in reduced pressure MIP's (31, 42) overcome this problem by introducing the sample at atmospheric pressure, desolvating the solution and then evacuating the system. Only then is the plasma initiated, so some time has to be allowed for stabilization (42). This is not only wasteful of time but can also account for some irreproducibility of the results due to the lack of thermal equilibrium during the determinations and difficulty in reproducing all the conditions of operation.

In order to alleviate these problems, a cell design was sought whereby the plasma could be maintained at low pressure while the sample was being introduced at atmospheric pressure. One of the ways of achieving this was by moving the sample from a position where it was introduced at atmospheric pressure to an adjacent position while it was pre-treated and pre-evacuated. After this the sample is moved into the plasma chamber which has been maintained at low pressure, although some small variations in pressure were allowed. The plasma chamber was pumped using by-pass galleries all the time until the sample was underneath the plasma, ready for vaporisation and further excitation.

3.2.1. Vaporisation Chamber

The design of the vaporisation chamber had large effects on the sensitivity and reproducibility of the emission. Particular attention to the prevention of plating out was necessary (30). Kawaguchi et al. (9) and other workers (8) had noticed that the localisation of the emission maxima for most of the elements is at the leading edge of the discharge tube so that they were not carried further into the plasma. Some workers also outlined the importance between the place where the sample was vaporised and the discharge when working at atmospheric pressure (90).

So, it was borne in mind also to optimize this distance in the cell design.

3.2.2 Sample Introduction

As it was the purpose of this work to introduce elements in solution, some previous systems used for sample introduction were studied. It was stated before that, because of the low enthalpy of the gas, and its sensitivity to molecular species, the elements should be introduced as vapour, preferably atomic vapour, in order to get the maximum output per particle. For this purpose, several methods have been proposed, most of them using previous desolvation of the sample to prevent instability of the plasma and eventually its extinction (7-9, 31, 45, 55). Chemical generation included generation of arsine (59), reduction of mercury compounds (54), deposition of mercury on copper wires and evaporation of it by ohmically heating carbon or metallic filaments, (7-9, 42, 53, 56), ultrasonic nebulization (30) and desolvation facility coupled with a vaporisation chamber (7, 55). One of the limitations of using continuous sampling when using low pressure microwave induced plasmas is the gas flow rate, which is rather low to operate these systems efficiently. As one of the advantages of these plasma systems is the ability to give appreciable signals for small amounts of sample, it is the main reason why the most widely used method of sample introduction is electrically heated filaments or strips. Platinum filaments are mostly used due to their chemical inertness, with the only disadvantage of melting at relative low temperature (ca. 1700^{0}C) and its spectral interference with tungsten. Tantalum can be a possible alternative with the advantage of high melting point but it oxidises and breaks easily. Elements such as cobalt and nickel that react with Ta surface cannot be determined. Tungsten also can be used, although when heated at high temperatures (above 2200°C) its oxide evaporates and can eventually interfere with the relevant element. The main limitation of these filaments is therefore the temperature at which the atomizer support material can be used.

One alternative to these metallic filaments is the carbon filament. This filament has the main advantage of the higher temperature which can be attained (ca. 2800°C) without degradation and also the area of contact of analyte and filament is greater than using metallic filaments. Caruso et al. (45) compared the results obtained using a tantalum strip and a carbon cup device with noticeable advantages for the latter. They attribute this superiority to the small area where the sample was located on the carbon cup (about 3 mm) with the area of the tantalum strip (33 mm) which apparently provides a greater analytical throughput per unit of time of analyte to the plasma. Another advantage of the carbon filament is the reducing properties of carbon which should enable elements with moderately stable oxides to be atomized more efficiently. A disadvantage of using carbon filaments is when vaporising elements that form stable carbides at high temperature such as zirconium, titanium, boron and others. Another possible disadvantage of using the carbon filament together with microwave induced plasma isnot only the scatter due to carbon particles but also the formation of CO due to O_2 present in the argon as an impurity.

Some interelement interferences have also been found when using almost all types of filaments. Some of these interferences are due to changes in analyte volatilization efficiency due to different sample composition (87). Other workers have suggested that these interferences are due to combinations that occur in the vapour phase but this is more likely to occur when the analyte and interfering element have about the same boiling point (92). Another problem which arises when using filaments is the irreproducibility of sampling. The solutions are placed on the filaments normally by using a syringe or micro pipette. The volumes taken are of the order of microlitres. The precision of these pipettes is about 3%. Factors such as differences in viscosity and density of solutions can affect the precision. The place where the drop was left on the filament is also a relevant factor on the reproducibility of the results. The drop could spread over the surface and it can go to the cooler ends of the filament holders. This can be partially overcome by trying different filament shapes.

A micro arc system, also using discrete samples, was described by Hieftje (44). It is a high voltage low current atmospheric pressure d.c. discharge which atomizes discrete samples of metal salts. Many advantages were reported for this device but the most important seems to be the decrease of interelement interferences even when using a refractory matrix, due to the complete evaporation of the sample. For instance, aluminium matrix depresses only 15% of the magnesium signal compared with 50% suppression obtained in flames. No interference was found for PO_4^{3-} on calcium and a low detection limit was obtained for boron (3.3 pg). This system seems to produce the best results yet, as far as detection limits are concerned, although some of its advantages can be due to the automatic mode of sampling the solution and the microprocessor controlled system. Indeed, sample introduction was such a problem that microprocessor control was essential in order to obtain realistic reproducibility (44).

For the purpose of this work, the sample introduction process should be simple and able to handle discrete amounts of sample. It was decided to use the carbon filament because of the design advantages as well as those mentioned before rather than a system using wire filaments, although for future work the micro arc could be a tempting alternative.

3.2.3 Tube Position and Diameter

The tube material has to be clear fused silica because this material is transparent to microwave radiation, ultraviolet radiation and is thermally and chemically stable. Although some devitrification occurs after a time thus decreasing the transmitted emission, this is not a serious drawback as the same tube could be used for many days before it has to be changed. Another alternative is to use the tube in a horizontal position (so called axial viewing). This has been reported to allow a better signal to noise than radial viewing because instabilities of the plasma are not as noticeable from the end of the plasmas as from the side (44), but it has the disadvantage that radiation must pass through unexcited regions next to the discharge. Although no self absorption has been reported so far (44), De Galan (12), using the same conditions for both observations systems, found that using axial viewing a tenfold reduction in linear dynamic range and a twofold increase in detection limit compared with lateral observation.

In this work, for reasons of simplicity, on the design of the cell and because no major advantage was found with axial viewing, lateral observation was employed. The diameter of the tube is a point of disagreement between many authors; Kirkbright et al. (7) used 8 mm i.d. diameter; Kawaguchi et al. (9) reported that if the tube diameter is less than 2 mm, (at 30 W) using reduced pressure (4 Torr) the plasma is unstable, stability increasing as the diameter increases. Although the length of the plasma increased when increasing the i.d. of the tubes from 3-7 mm, the signal decreases. They adopted a tube of 3.2 mm i.d. and 4.3 i.d. as optimum. Houpt (10) reported a low pressure helium plasma using a 2 mm i.d. tube as optimum.

In the present work a 4 mm i.d. 6 mm o.d. was used as optimum. Tubes from 8 mm i.d. to 2 mm i.d. were tried. At 2 mm i.d. the plasma is easily quenched by small amounts of molecular vapour; between 8 mm to 4 mm the signal decreases although not appreciably. So, 4 mm was found a good compromise. The width of the tube, although not critical, was found to be important as far as devitrification and thermal stabilization are concerned and 4 mm i.d. again proved a reasonable compromise.

3.2.4. Microwave Frequency

The operating frequency for electrodeless discharge lamps has been subject of considerable work (87). The intensity of some lines in some lamps was found to increase with increasing the microwave frequency (89). The frequency of 2450 MHz (12.5 cm) is such that the coupling between the plasma and the power source is easily achieved using resonant cavities of reasonable dimensions. This frequency is used in diathermy units so the equipment is commercially available.

3.2.5. The Plasma Gas

Plasma gases have also been a subject of theoretical investigation by some authors. Busch and Vickers (31) studied the properties of an MIP argon and helium plasma at pressures in the range of 0 - 25 Torr; and compared the values obtained for both gases; Brassem and Maessen studied the electron temperature and electron concentrations in the pressure range of 0,05 - 2 Torr (81) and flow rate and pressure in the pressure range of 0,2 - 1 Torr (80) for plasmas sustained by monatomic and poli-atomic gases. Until some time ago, due to the inefficient transfer of energy to helium plasmas, these could only be sustained at low pressure (up to 200 Torr) whereas atmospheric pressure plasmas were sustained only in argon. At low pressure even nitrogen plasma can be sustained, although a good sensitivity might not be expected, in part because of the high background due to molecular species (see N_2 plasma spectra) and in part due to quenching effect of the molecules and molecular ions formed. No systematic work has been carried out employing helium and argon under the same conditions for excitation of metals. However, Skogerboe (35) found a 3 fold increase in sulphur determination in SO_2 and H_2S when using helium plasmas compared with argon plasmas under the same conditions.

In this work, both gases have been tried. No advantage was found in the use of helium; its background was higher possibly due to the impurities present and the high energy available to excite them and the signal to noise ratio was not better than that obtained with argon at the same pressure. Although it is a general consensus to use helium instead of argon for low pressure plasma due to the greater stability of the former (30), in this present work, the plasma stability with argon was comparable with that obtained with helium, for the same pressure. The analytical useful pressure range is greater for helium but with no advantage in the signal to noise over argon.

3.2.6. Flow Rate and Pressure

Most of the workers vary the pressure by varying the flow rate (9, 31). Bra ssemand Maessen studied the influence of flow rate and pressure in the excitation conditions of MIP varying both parameters independently over the low pressure range (0, 2 - 1 Torr) for He, H_2, N_2, O_2.

Ne, Ar. They reported that the influence of flow rate on parameters such as electron temperature and electron concentration is much more critical at 0,2 Torr than at 1 Torr. These parameters were measured using the double probe technique. At 1 Torr, the intensity of argon lines starts decreasing with the flow rate and then attains a constant value.

In this work, a plot of intensity of argon lines (420,0 nm, 415,9 nm) shows that these lines and also the background of the whole spectrum decreases slightly when the pressure is increased from 1 to 15 Torr, but from 15 Torr it is almost constant until 25 Torr when the discharge begins to behave erratically, probably due to turbulence of the gas in the tube. Varying the flow rate by altering the pump rate (using a more efficient pump) gives approximately the same variation of background intensity with pressure (Fig. 3.1)

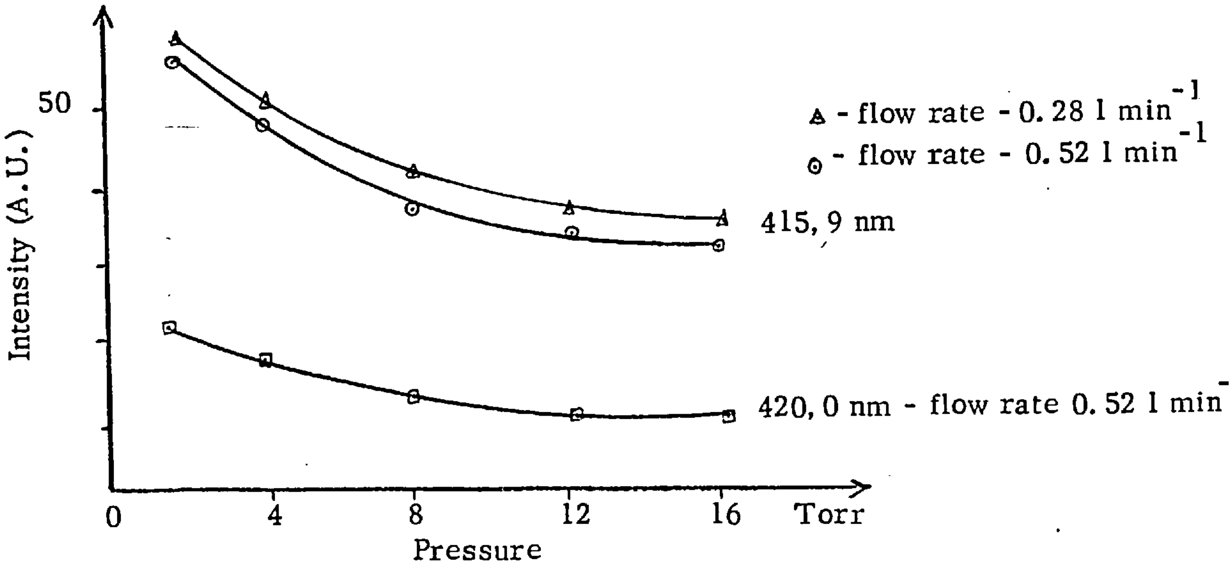

Fig. 3.1 - Variation of Intensity of Argon Lines with Pressure

On the other hand, when using very low pressure by using a low flow rate, the signal is smaller than when the pressure is increased by increasing the flow rate. At about 20 ± 1 Torr, the signal is only slightly affected by further increases in flow rate and consequent increase in pressure.

Using a more efficient pump which has a pumping capacity about 2 times the first one for a given pressure, the signal increased about 2,5 times for the same pressure but the shape of the curve of emission intensity vs. pressure remains the same for both pumping rates with the maximum signal being emitted at 17 ± 1 Torr.

From the results obtained for manganese, zinc, cadmium and copper, it seems that the influence of the flow rate on the emission signal is more likely to be due to transport mechanism of the sample vapours into the plasma rather than modifications in the excitation conditions of the plasma itself, on the range of pressure and flow rates studied. Low flow rates cause a bigger spread of the sample vapour inside the dead space of the cell, with higher condensation of them on the cool walls. The dead space could not be made very small due to difficulties in design. It was noticed also that, working at higher flow rates, the deposition of the sample on the leading edge of the tube also decreasedas well as deposition of the sample on the walls of vaporisation chamber. This suggests a more efficient transport of sample from the filament to the plasma tube. The decrease in the emission intensity of argon with pressure is probably due to collisional deactivation of the excited argon atoms or three body recombination (10).

So, based on these experimental data, at least for the system design used in this work, it was decided to work at 20 Torr. Most of the work was done employing the lower rate pump, as it was the only one available at the time and the flow rate using this pump at 20 Torr was 0,285 l/min., measured at atmospheric pressure. Bearing in mind these parameters, the following set-up was designed (Fig. 3.2):-

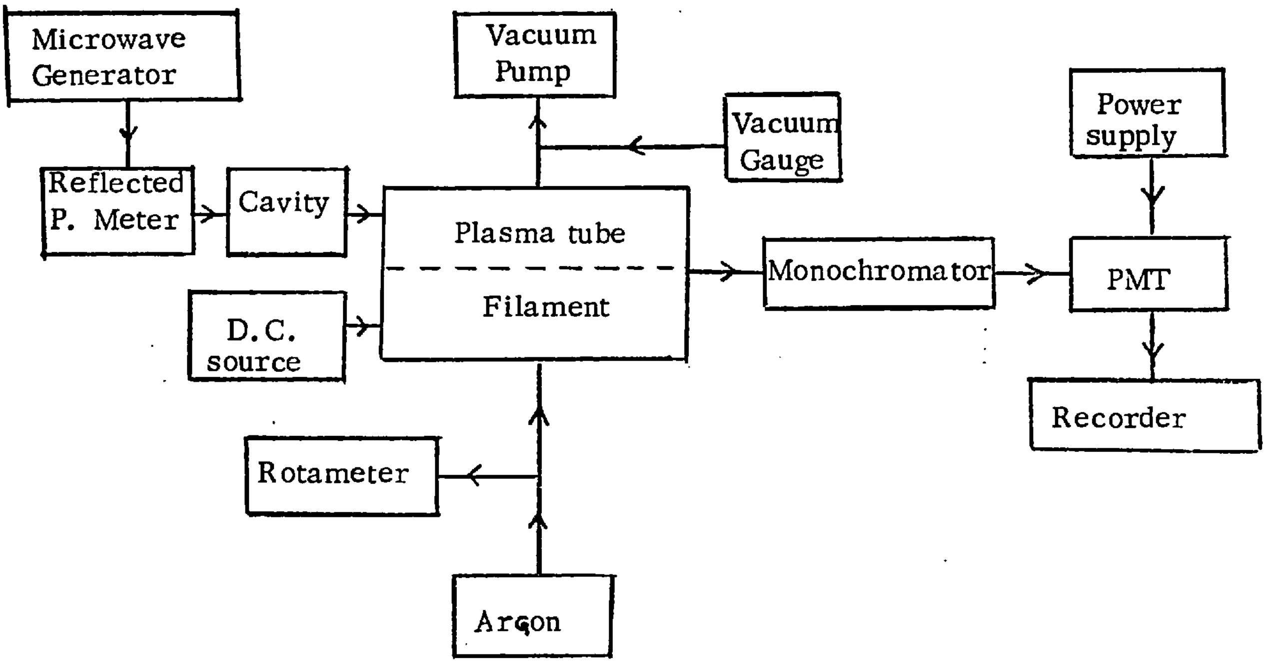

Fig. 3.2 Set-up

The equipment consists of:

1) Microwave generator (MicrotronModel 200 Mk 2 maximum power 200 W at 2450 MHz.
2) Evenson type $\frac{1}{4}$ wave cavity (22) (Electromedical supplies 214L)
3) Reflected power meter (EMS Model 1505)
4) Variac (Duratrak V6HM) Variable transformer
5) Vacuum meter (Speedivac C63)
6) Rotary vacuum pump (Speedivac Model 2SC 20A)
7) Argon rotameter
8) The sample introduction cell
9) Quartz focussing lens 30 mm dia. 50 mm focal length
10) Monochromator (Rank Hilger Model D330) Czerny-Turner mount, 1200 lines/mm grating. Resolution 15 μm
11) Photomultiplier tube (EMI 6256B)
12) Recorder (Oxford Series 3000) f.s.d. 250 ms.

The $\frac{1}{4}$-wave cavity couples the power from the microwave generator to the argon which flows into a vertically positioned quartz discharge tube (4 mm i.d., 6 mm o.d. 130 mm long) attached to the sample cell, where the argon plasma is generated. The rotary pump maintains a pressure between 1 and 20 Torr in the tube. This sample cell (Fig. 3. 3) consists of three solid parts, all made of brass, two of them are fixed and the middle part is able to turn horizontally around a central pin. A 3 mm diameter, 2 cm length carbon filament with a notch in the centre for placing the samples (Fig. 3. 4) is fixed on this middle part by carbon holders screwed into stainless steel supports, which are insulated from the bulk of the cell and to which ends the power is applied <u>via</u> a Variac connected to a stepdown

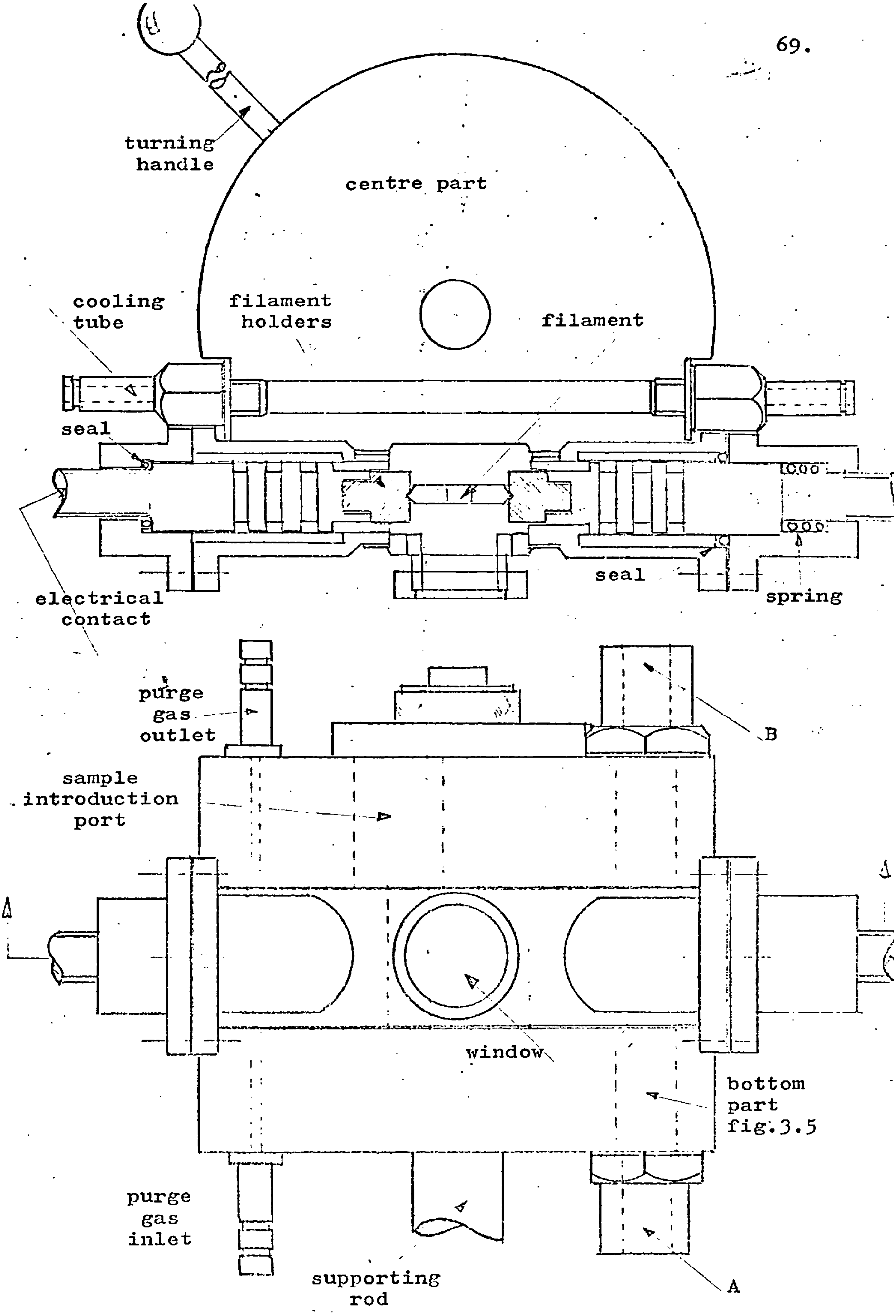

Fig. 3.3 The Plasma Cell (Scale 1:1).

transformer. Argon is introduced into the bottom tube (A) and the vacuum

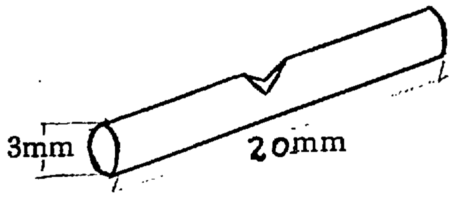

Fig. 3.4 The Filament

pump is connected to the top tube (B). The central part can be turned so the filament and the sample can be placed underneath the plasma tube and when heated, sample vapours enter into the plasma. All the surfaces are flat and the contact and vacuum is maintained using a silicone grease. Compressed air was used for cooling the filament. At low pressure (5 Torr) this system does not work ideally since the surfaces become very stiff and the grease spreads to the outer parts. This increases irreproducibility, as the pressure varies in each run, consequently the cell has to be dismantled after a few experiments. At 20 Torr this does not occur and the cell may be used continuously, producing more reproducible results. In the original design the sample was placed on the filament, the central part is then moved 45° clockwise where solvent and organic matter was removed by heating in a flow of argon; it was then moved to the plasma tube position while the sample is evaporated. All these steps are carried out with the plasma ignited all the time. This was achieved by channels in the cell so that argon is supplied to the plasma all the time and the vacuum is maintained (Fig.3.5). To maintain the vacuum during all the cycle, the surface has to be completely clean and homogeneously greased. The carbon filament always leaves some carbon residue which was transported all around the lower part; at low pressure (2-5 Torr), after some cycles, this carbon gets inside the small grooves and

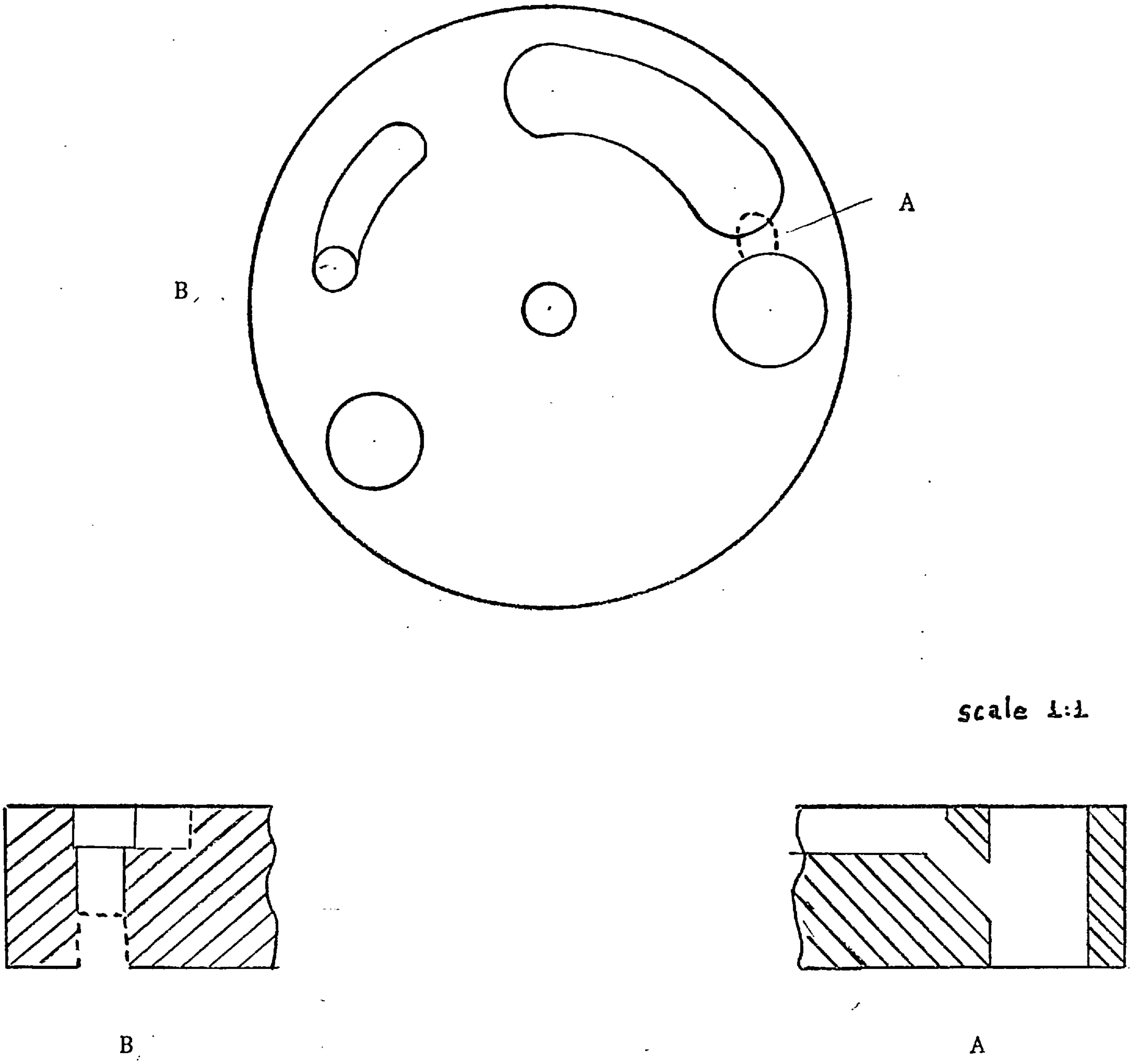

Fig. 3.5 Top View of the Bottom Part

has to be removed. The grease also seems to evaporate sometimes and was deposited on the filament and sometimes the drop creeps along the filament resulting in loss of sample. Working at higher pressure (15-20 Torr) less grease is used, and better reproducibility was attained.

After some attempts to optimize the parameters affecting the reproducbility of the results, it was found better to use only two positions. First, the sample is introduced, evaporated and then, instead of going all around, the filament is moved to 45° to be placed underneath the plasma. If this movement is done slowly, the plasma is not extinguished; an extra nozzle was placed between the sample introduction part and the plasma tube to pre-evacuated the sample; this keeps the plasma going and as long as an efficient pump is used, the plasma is not dramatically disturbed.

With the system working in this way, one can achieve a reproducibility in the 6% - 10% standard deviation range.

The radiation emitted from the plasma tube is focused into the entrance slit of the monochromator using a quartz lens attached to the optical bar. The photomultiplier tube operating at 1200 V anode voltage is attached to the exit slit of the monochromator. The photomultiplier output is then connected across the potentiometric recorder. It has been observed from the oscilloscope that the rise time of the signal for zinc evaporated by the carbon filament and excited in the plasma is about 100 ms. For elements such as manganese and copper, it is slower, so it was found that the recorder which has a f. s. d. response of 350 ms was rapid enough to follow the signal. Both slit widths were 50μ for all elements analysed and the effective slit height is 18 mm, except when experiments to determine the influence of pressure and flow rate in the signal and background intensities where the slit height was fixed at 2 mm. All the system has been optimized to produce maximum intensity, for the argon line, 415, 9 nm. The plasma region focussed in the entrance slit was from the center of the cavity 1 cm towards the bottom of the tube. This was the place where the maximum emission was found for the argon line and also the maximum signal to noise ratio for the emission intensity of the analyte.

The Influence of Microwave Power

The influence of microwave power on the intensity of the lines is not quite understood. For argon lines, (425, 9 nm, 420, 6 nm) increasing power increasesthe intensity until ca. 50W where an increase of power is accompanied by only a small increase in intensity (Fig.3. 6).

Temperature of the Filament

A study of the voltage applied to the filament in the vaporization step was carried out for each element and will be discussed in the next chapter. The voltage applied during the desolvation step was chosen so that in about 30 seconds the sample is dried. For mercury, however, it was determined experimentally that a low voltage applied for longer time, (about 60 seconds) decreases the losses in this step. For other elements such as Zn, Cd, Cu and Mn, if the drying is too quick, the sample creeps on the filament, and some losses were observed; if the voltage applied is too small, the sample is not dried completely in 30 seconds, and more time should be allowed for the stabilization of the plasma. Since allowing more than 30 seconds for desolvation did not produce any advantage, this time was chosen as optimum. The stabilization of the plasma can be checked by the attainment of constant background emission and also by the shape of the plasma. When

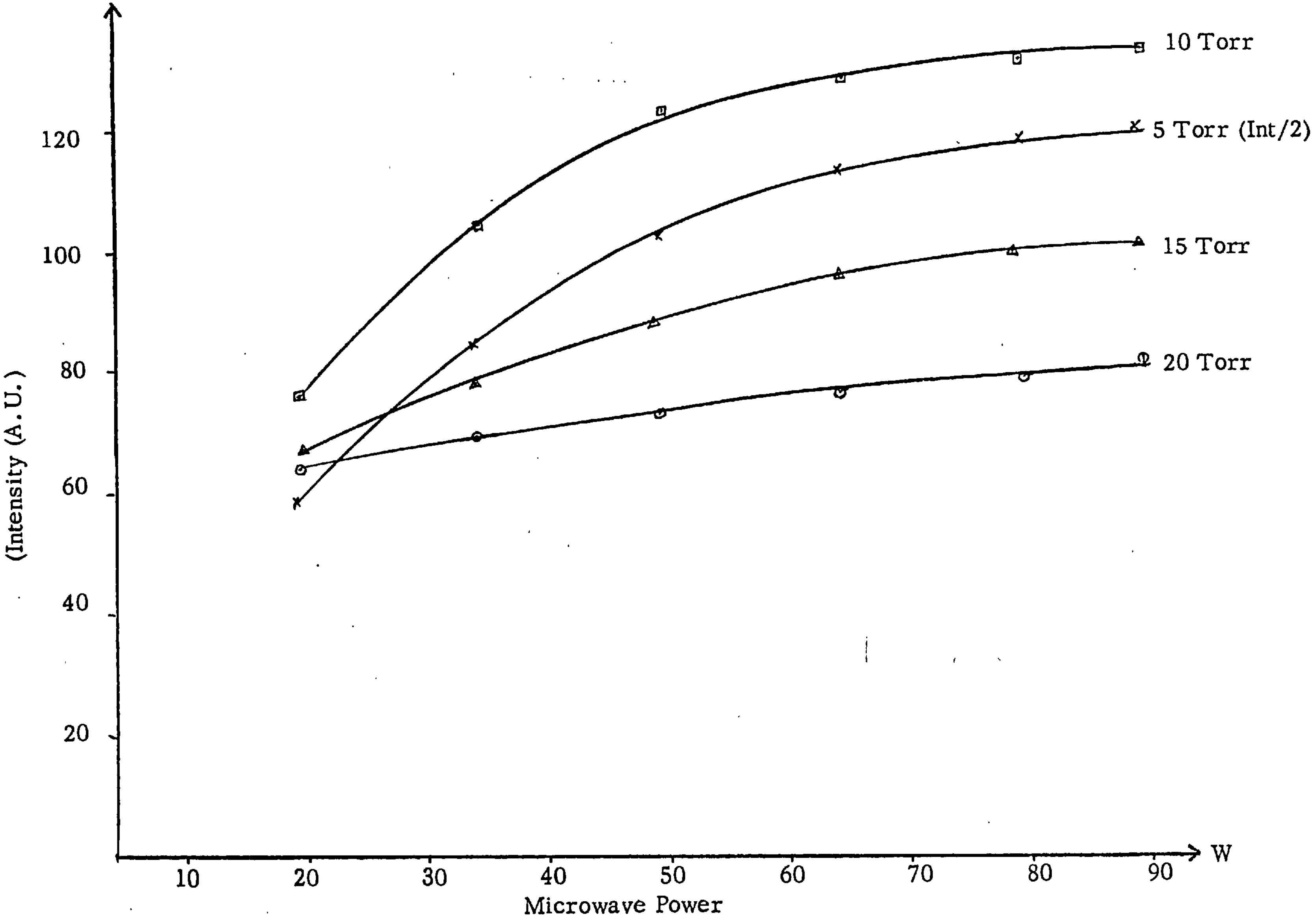

Fig. 3.6 - Variation of Argon Intensity with Pressure and Microwave Power

water is still present on the filament, the background is higher and the plasma is smaller (probably due to quenching effects of the molecular vapour). When there is almost no water vapour (except the amount present in argon, which can be checked by using the 308, 6 nm OH band), the plasma is more transparent, longer and pink (instead of almost red).

CHAPTER 4

4.1. Factors Affecting the Emission Signal

The results obtained are given by element since each analyte has its characteristic behaviour, not only in the plasma but alsoon the filament.

When using a complex system such as in this work, it is very difficult to separate the effects of the sample introduction system and the behaviour in the plasma.

On the filament, many parameters contribute to the analytical signal. Such parameters are not always a function of the properties of the filament, but also a function of the analyte, e.g.,

a) Vapour pressure of the metal oxide or metal compound

b) Degree of dissociation of the metal oxide

c) Reduction of the metal oxide by the material forming the filament

d) In the case of carbon filaments, carbide formation or compounds formed with metallic filaments and the analyte.

All these parameters are governed by thermodynamic constants which are a function of the temperature of the filament. Along with these, the design of the filament, the position of the sample, the flow rates used also can account for different results obtained with different equipment and also, the reproducibility of the measurements. The interferences found on these systems have been the subject of study (90). One aspect is to investigate whether the matrix is affecting the signal by affecting the rate of formation of metal atoms in the atomizer, or by affecting the atomization efficiency, that means the proportion of the element in the atomizer that is vaporized to metal atoms relative to the vaporization of molecular species.

The rate of removal of metal atoms from the atomizer is also important for the absorption profile. All these effects studied for atomic absorption (90) can also be applied for sample introduction into the MIP since it involves the formation of neutral atoms. In this case, however, when the atoms go into the plasma, they are subject to a series of effects, such as diffusion in the electromagnetic field, reactions with electrons, ions and molecules, giving rise to excitation of atoms and molecular species, so, these kinds of effects and parameters affect the recovery of the signal. The excitation conditions of the plasma itself change by addition of different amounts of gases (84) so it is also expected to change its characteristics by addition of analyte vapour. Different kinds of interferences might be expected, and ideal conditions for each analyte should be studied.

4.2. The Determination of Metals by MIP Excitation

4.2.1. General Considerations

In the determination of metals, argon 99,99% purity grade was used, without purification. The spectrum of argon in Fig. 4.1 shows that the main impurity is nitrogen, which can come from the argon itself or from leakage in the vacuum system. The tubes were all made from nylon with copper fittings and only in some places where the use of nylon was not possible, rubber tubing was used. Drying the argon was not found necessary, since the system was designed to work with aqueous solutions, but if gas analysis is the aim, this can easily be achieved by using a molecular sieve or silica gel column.

The desired flow rate was adjusted using a needle valve, and the desired pressure was attained by adjusting the flow rate. The experimental conditions used for all the elements determined are presented in Table 4.1.

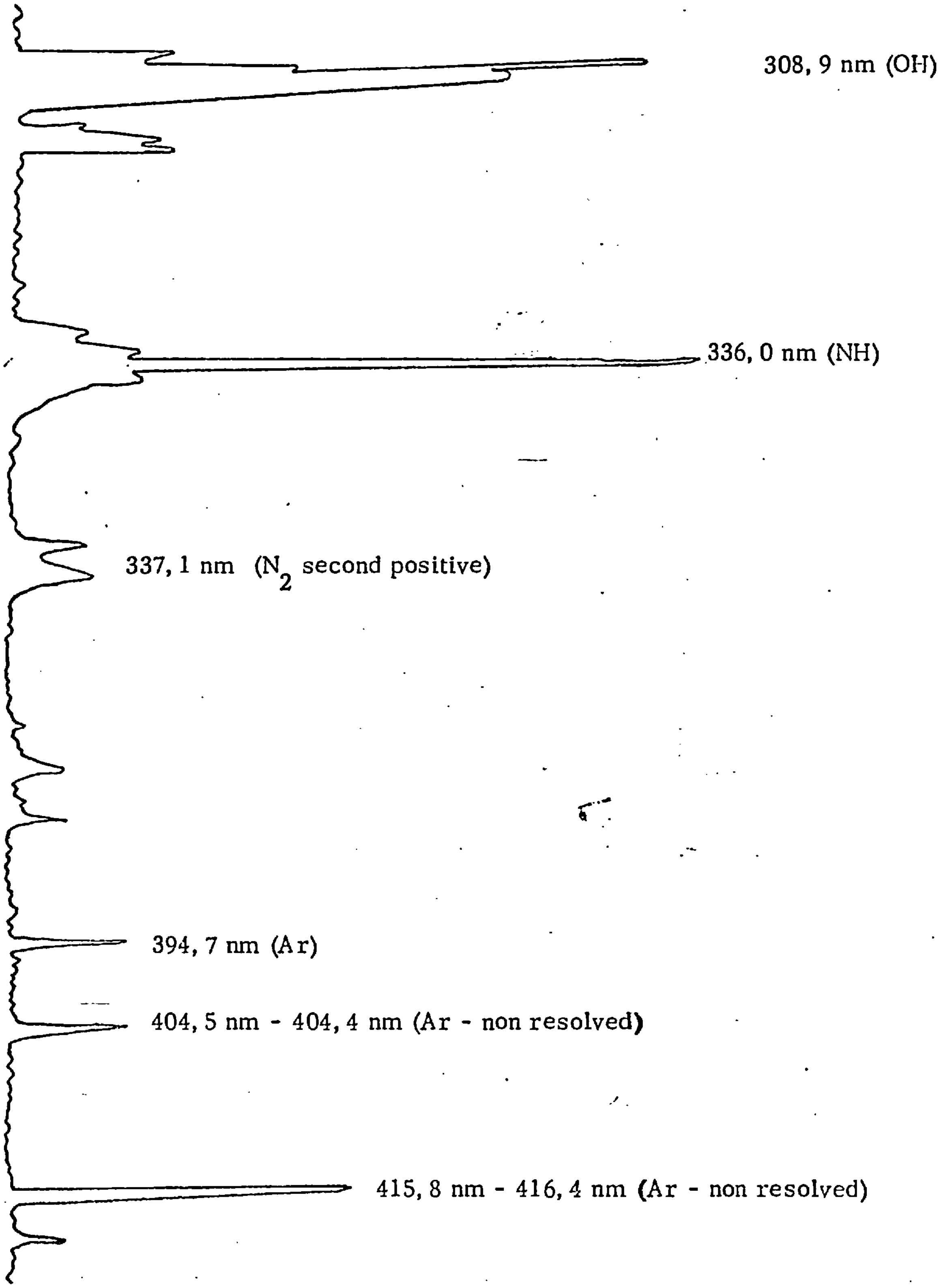

Fig. 4. 1

The Argon Spectrum

The parameters which are different for each elements are presented in separate tables.

Table 4. 1

Gas used : argon

Photomultiplier voltage : 1200 volts

Entrance slit width : 50μ

Exit slit width : 50μ

Sampling technique : carbon filament

Plasma tube diameter : 4 mm i.d.; 6 mm o.d.

All these parameters are found to be optimum for the elements studied.

4.2.2. Calibration Curves

The basis of quantitative spectrochemical analysis is the empirical relationship between the emission intensity and the number of atoms of the emitting species.

This relationship is usually expressed by (65)

$$I = KN^m$$

where -- I is the emitted intensity

K is a constant

N is the number of emitting species

m is the emission factor

This expression becomes

$$\log I = \log K + m \log N$$

The plot of log I *versus* log N is the working (or calibration) curve. In ideal cases, where there is no self absorption and background radiation, *m* is equal to unity; in other cases, m is varied to maintain the equality.

4.2.3. Precision

Precision (or reproducibility) refers to the random fluctuations in the results due to the inability of carrying out all the experiments under exactly the same conditions.

The precision was calculated by taking 10 different solutions of 0,1 ppm of cadmium and making 5 determinationsfor each solution.

The precision expressed as relative standard deviation was calculated using the expression:

$$r.s.d = \frac{r}{m} \times 100$$

where r is the standard deviation

m is the mean of the readings

4.2.4. Detection Limits

Normally, detection limits are defined as the concentration at which the signal peak height is twice the magnitude of the random fluctuation in the base line. In the present thesis, the detection limit was assessed as the concentration which gives a peak height twice the standard deviation of the signal obtained when a blank was put into the plasma.

4.3. The Elements

4.3.1. Cadmium

In the cadmium analysis, the 228,8 nm resonance line was used. The solutions were made from cadmium nitrate in distilled water. A study of the influence of the microwave power, filament voltage and pressure on the cadmium signal was carried out for optimization of experimental conditions and the results are presented in Figs. 42, 43, 44.

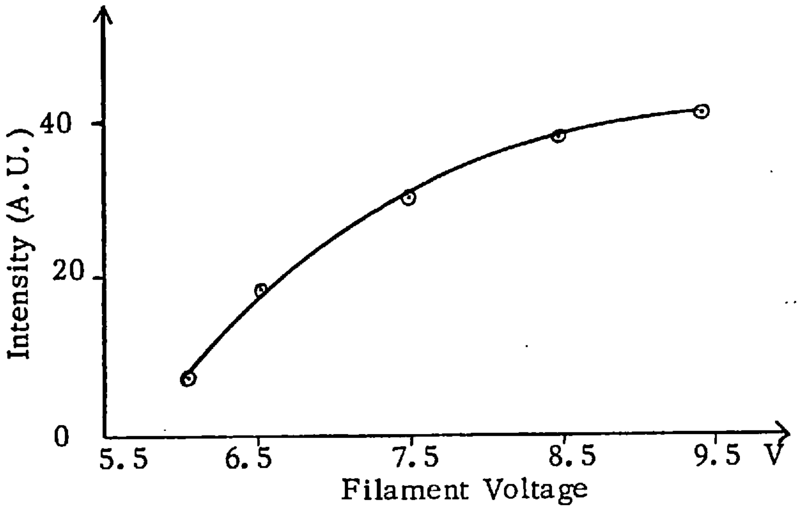

Fig. 4.2 Variation of the intensity with the filament voltage

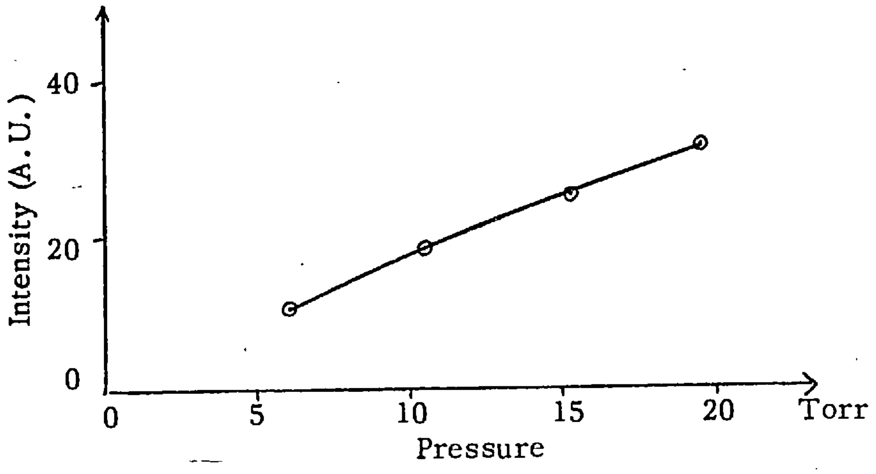

Fig. 4.3 Variation of intensity with pressure

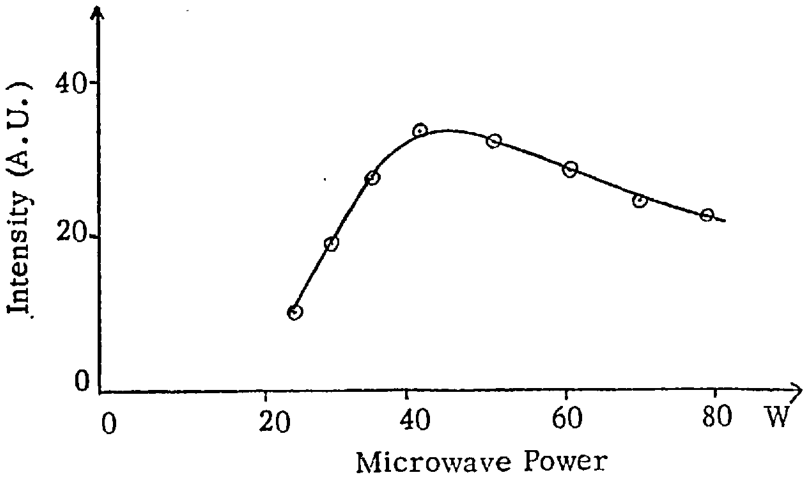

Fig. 4.4 Variation of intensity with microwave power

Based on these results, the experimental conditions for the analysis of cadmium are presented in Table 4.2.

Table 4.2.

Pressure : 20 Torr

Microwave power : 40 W

Variac voltage : 140 V

Drying voltage : 20 V

Concentration range : 0, 01 ppm to 100 ppm

Using these conditions, a calibration graph of log intensity vs. log concentration was carried out. The curve has a slope of 0.98 and is linear from 0, 01 to about 30 ppm (Fig. 4.5). The detection limit for cadmium was 1, 3 x 10^{-11}g. and the coefficient of variation was 7%.

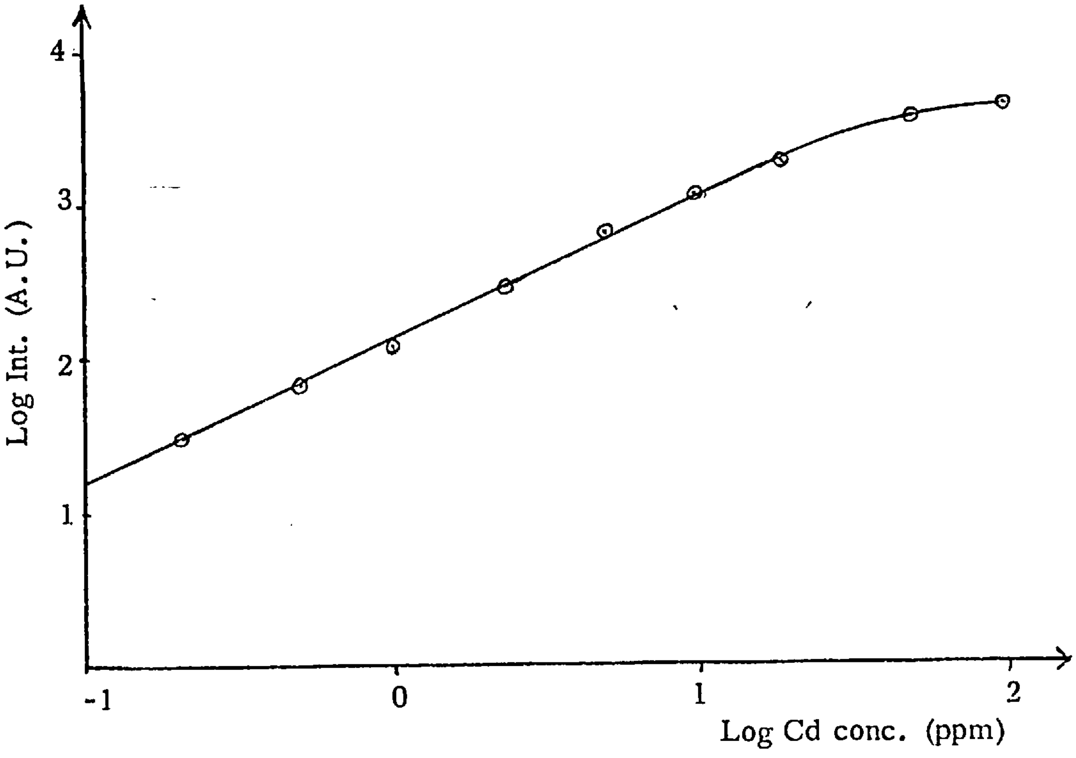

Fig. 4.5 Calibration curve for cadmium

Detection limits in an atmospheric pressure plasma vary from, *e.g.* 1 x 10^{-4}ppm (87) using a tantalum filament, 2.8 x 10^{-4}ppm (44) using the micro arc technique and 4 x 10^{-12}g (45) using the carbon cup technique. In a low pressure plasma a detection limit of 3 x 10^{-12}g was obtained with addition of potassium in the range of 1-5 mM (9).

It was reported that higher concentrations required long clean-up procedures (87). In this present work, no memory effect was found when using concentrations up to 100 ppm of cadmium, if the filament was heated between atomizations at these high concentrations. However, if these high concentrations are used for a whole day, some white deposit appeared, about 5 mm up from the cavity, which is probably due to plating out of the analyte. No interference was found from iron, copper and manganese. Potassium increases the signal by 10% and at high concentrations of cadmium (50 ppm), the addition of 100 ppm of zinc causes multiple peaks with less intensity. This could be due to some kind of excitation interference in the plasma, although the mechanism is not understood and the addition of 100 ppm of zinc did not affect the intensity of the argon lines. It is thought possible that the interference effect lies in the sample volatilisation stage rather than the excitation.

4.3.2 Zinc

The zinc was introduced on to the filament as the nitrate (A.R. grade). The lines studied were the resonance line of Zn (I) at 213.8 nm and the Zn (II) line at 206.2 nm. Optimization of the experimental parameters was carried out and the results are plotted in Figs. 4.6, 4.7, 4.8.

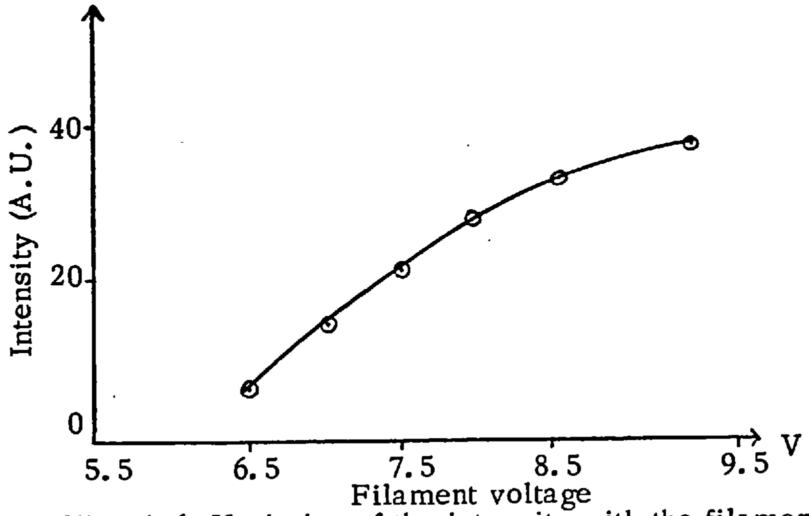

Fig. 4.6 Variation of the intensity with the filament voltage

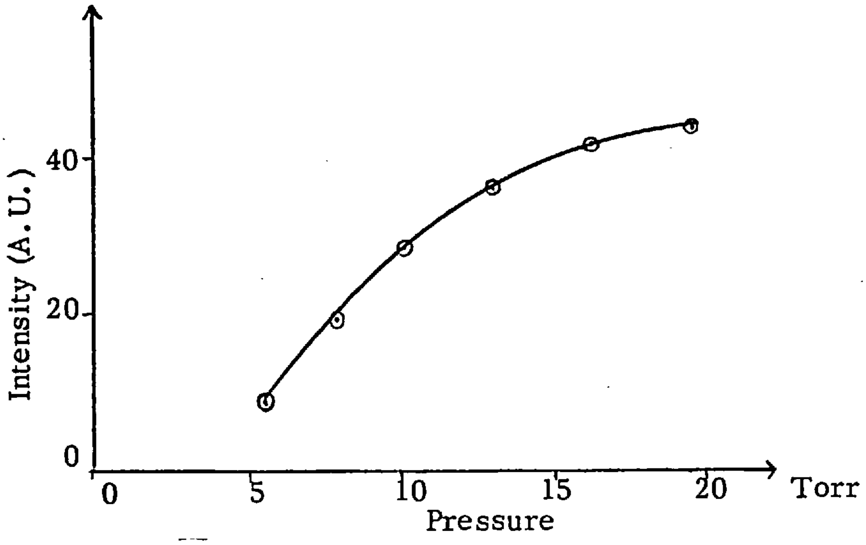

Fig. 4.7 Variation of the intensity with the pressure

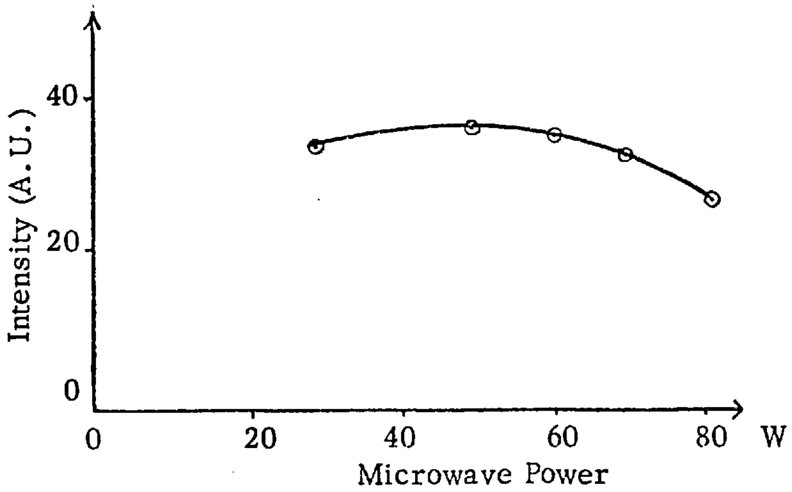

Fig. 4.8 Variation of the intensity with microwave power

From these plots, the optimum conditions for zinc were chosen (Table 4. 3):

Table 4. 3

Pressure : 17 Torr

Microwave power : 40 W

Variac voltage : 160 V

Drying voltage : 20 V

Concentration range studied : 0. 1 - 100 ppm

Using these conditions, the following calibration curve was achieved (Fig. 4. 9):

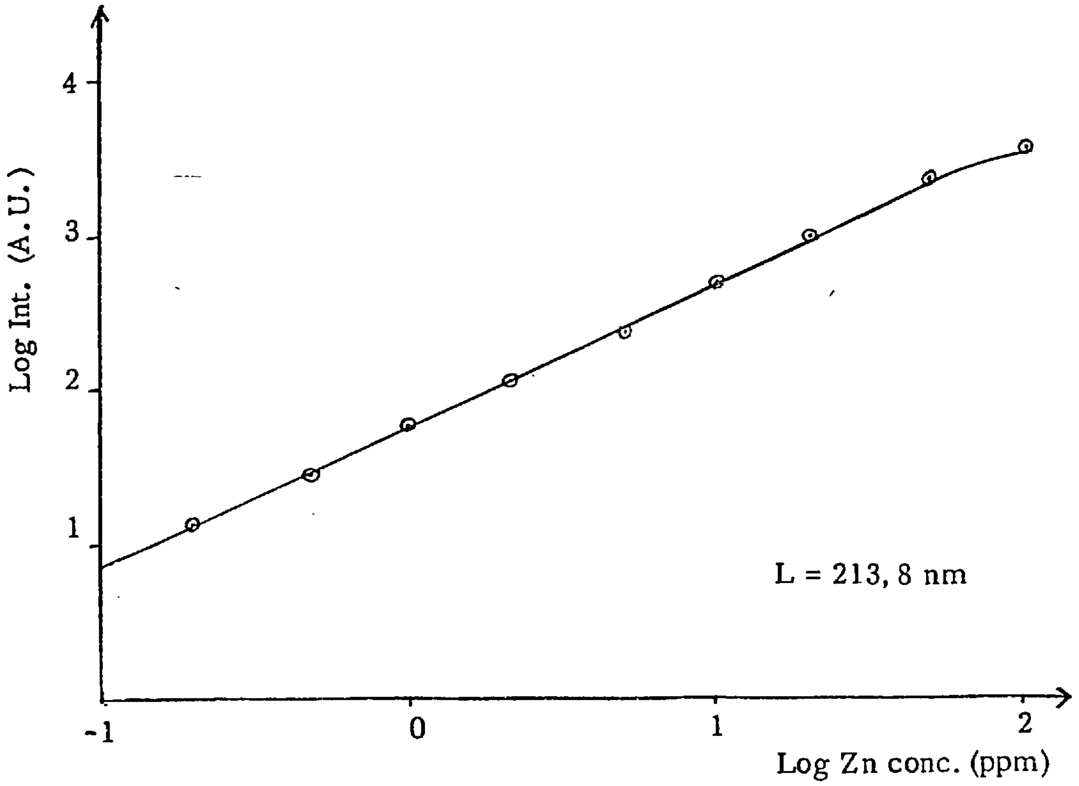

Fig. 4. 9

The curve is linear from 0.1 to 50 ppm. The detection limit found was 5×10^{-11} g. The ionic line was also investigated with respect to the variation of the emitted signal with microwave power and pressure. The results obtained using this line (Figs. 4.10, 4.11) were similar to those obtained using the resonance line 213,8 nm, that is, the parameters affecting the emission intensity of the former are the same for the latter.

The detection limit obtained using Zn(II) 206.2 nm line was 2×10^{-10}g. No interference was found from iron, copper, manganese and aluminium when present 100 Fold in excess of the zinc concentration. Potassium increases the emission intensity about 50% when present in amounts over 100 ppm. However, at high zinc concentration (50-100ppm) in the presence of potassium, the peak is broad and its peak height is less than the one expected for the zinc concentration. When quantities over 50 ppm of cadmium are added to concentrations about 100 ppm of zinc a double peak is observed, with a peak height half of the one expected to the same quantity of zinc. This was observed also in mixed EDL's (91), but no further real explanation can be found to explain these effects.

Zinc has been determined by using a low pressure (4 Torr) MIP and a tantalum filament (9). The detection limit found was 2×10^{-12}g (three times the SD of the background) and addition of KCl in the range of 2-10 mM increases 6 times the zinc intensity. Hieftje (44), using the micro arc technique in an atmospheric pressure MIP, found for zinc a detection limit of 0,92 $\times 10^{-3}$ppm. Caruso et al. (45) using a carbon cup found a detection limit of 5×10^{-12}g for zinc.

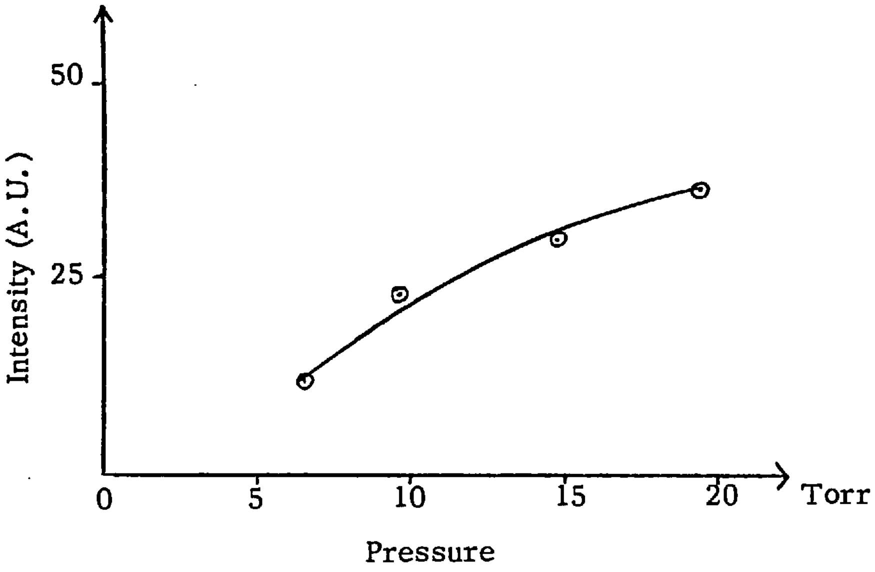

Fig. 4.10 Variation of the intensity with the pressure for Zn(II) 206, 2 nm

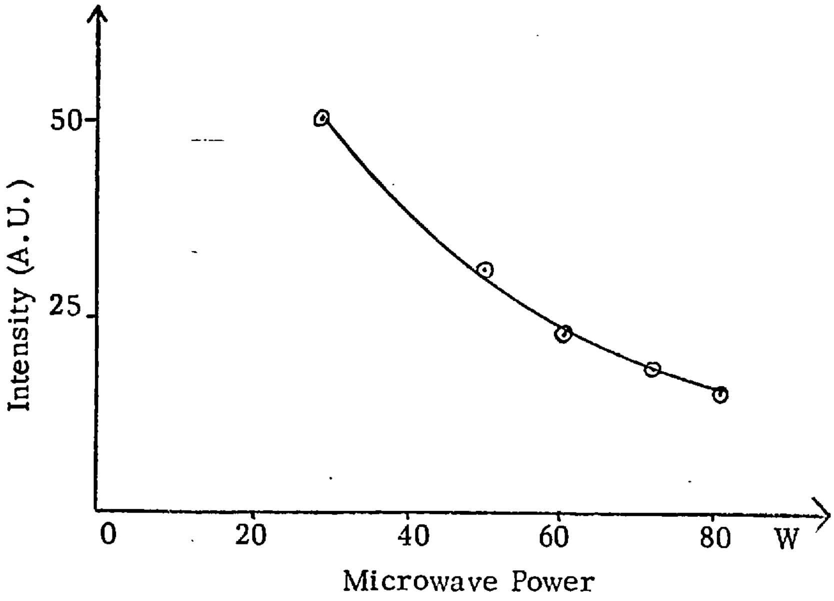

Fig. 4.11 Variation of the intensity with the microwave power for Zn(II) 206, 2 nm line

4.3.3 Mercury

In the mercury analysis, the resonance line 253,6 nm was used. A solution of mercuric nitrate in 1% HNO_3 was used since the addition of the acid decreases the losses in the desolvation stage (90). The influence of flow rate, pressure, microwave power and filament power has been studied (Fig. 4.12, 4.13, 4.14).

From the figures the optimum conditions for mercury were chosen (Table 4.4).

Table 4.4

Pressure : 20 Torr

Microwave power : 60W

Variac voltage : 160 V

Drying voltage : 10 V (1 minute)

Concentration range : 0,01 - 20 ppm

Under these conditions, a calibration curve was obtained (Fig. 4.15A). The curve was not a straight line, the reproducibility of 10 samples gave about 12% r.s.d. It was thought that some analyte was lost in the desolvation stage due to the high volatility of the metal and that this loss was not constant. It was proposed that mercury losses in the pyrolysis stage can be reduced by the addition of ammonium sulphide. This was not tried since the decomposition products could alter the excitation conditions in the plasma so another alternative was chosen. Some authors (93) have shown that a gold plated carbon atomizer also reduces the problem. So, 5 μl of 1000 ppm of gold was placed on the carbon filament and atomized several times at 160 V (which gives a temperature of about 2400°C measured with an optical pyrometer) After this, mercury was added to the filament and atomized at 140 V.

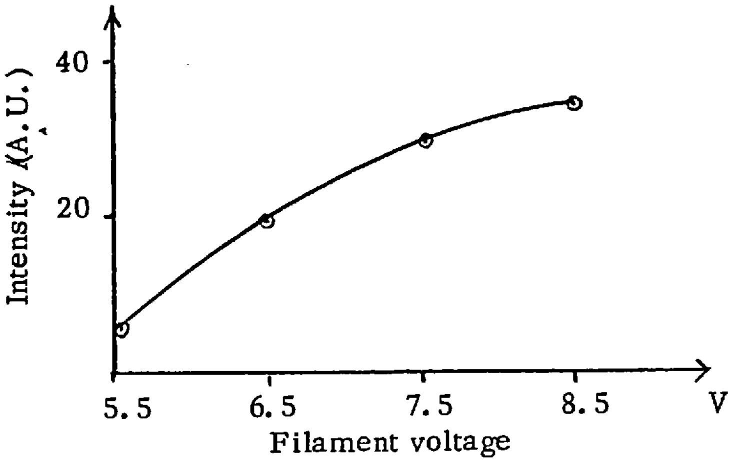

Fig. 4.12 Variation of the intensity with the filament voltage

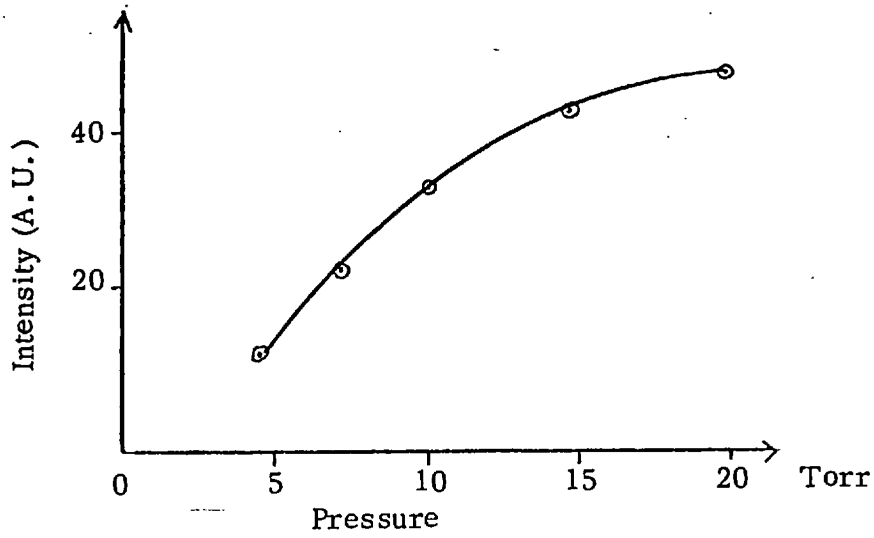

Fig. 4.13 Variation of the intensity with the pressure

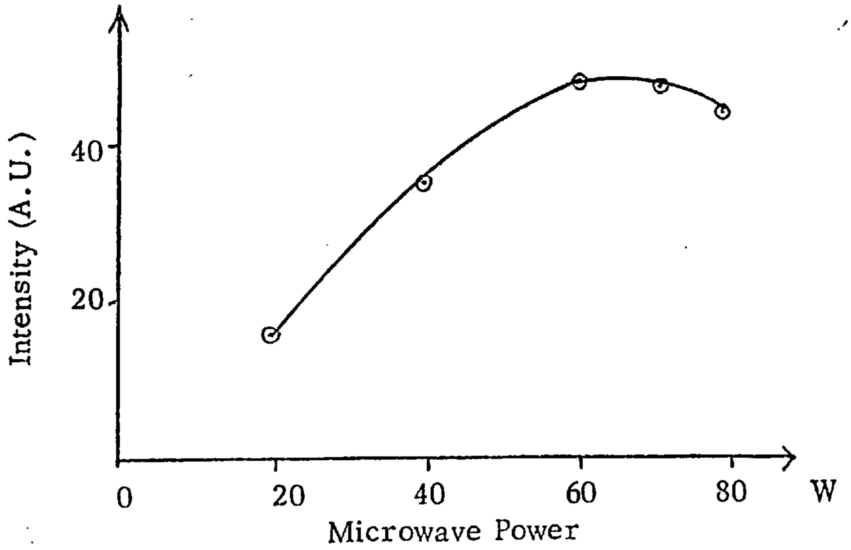

Fig. 4.14 Variation of the intensity with microwave power

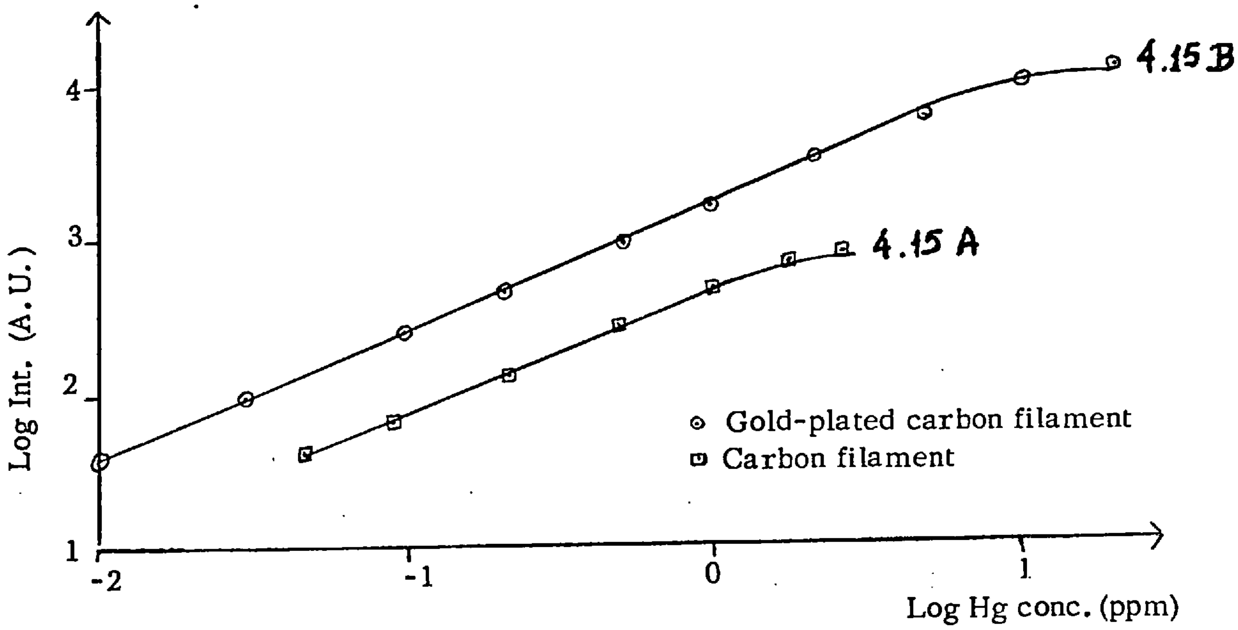

Fig. 4.15 Calibration curve for mercury

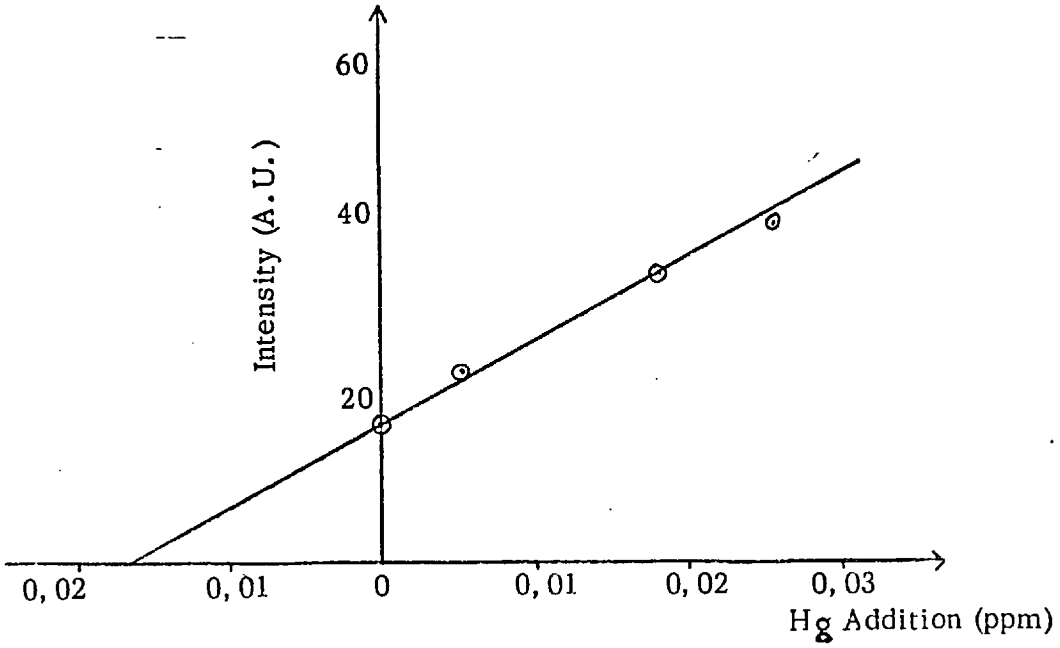

Fig. 4.16 Determination of the mercury content in water by the standard additions method

The calibration curve in Fig. 4.15B was obtained. The addition of gold not only increases the sensitivity for mercury but also increases the linear range of the calibration curve. Also, gold did not show any signal at the mercury resonance line after a few atomizations, nor did it affect the intensity of the argon lines. The detection limit found was 3×10^{-11} g. A mercury signal was obtained when evaporating water, probably due to contamination. If the method of standard addition was applied to the water, a value of 0,02ppm was found. No blank was observed when the filament alone was heated. The addition of 100 ppm of potassium chloride slightly increases the mercury signal but the reproducibility of the signal was worse. With the addition of gold, the reproducibility found was better than 6% r.s.d. Mercury was analysed using an atmospheric pressure MIP and the detection limit obtained was $3,8 \times 10^{-12}$ g (87). Contamination from the ambient atmosphere was avoided by flushing the system overnight with nitrogen and also heating the platinum loop. Trace amounts of mercury were also determined using an atmospheric pressure plasma with previous reduction of the salts to mercury; the detection limit found was 6×10^{-11} g.

4.3.4 Copper

For copper analysis, the resonance line 324,7 nm was employed. At first, the stock solution used for atomic absorption was used (copper metal dissolved in perchloric acid). The results obtained with this solution were not only irreproducible (r.s.d. up to 12%) but also two peaks were observed, whose relationship was not constant. The first peak is not reproducible at all (r.s.d. up to 44%). It was thought that these two peaks were due to different compounds of copper with different degrees of oxidation being present, but since Cu_2O is decomposed giving CuO, which is the compound more likely to be the result of the reduction, this should not account for the two peaks observed. On the other hand, a solution of $CuSO_4$ gives only one peak, which comes almost at the same time as the second peak obtained with the previous solution. Since copper sulphate was found to decompose at $650^{o}C$ at atmospheric pressure to CuO, this peak should correspond to the emission intensity of the atomized copper from the oxide. So, the two peaks obtained using the first solutions could be due to the emission firstly of the $CuCl_2$ present as molecular vapour when the drop was heated. The surface of the drop in direct contact with the filament is reduced, but the outer part of it is evaporated as molecular vapour when the sample is heated. This was also reinforced by the fact that the second peak increases with the concentration. As the concentration increases the percentage of analyte in contact with the filament decreases. A calibration graph was drawn (Fig. 4.17) with this solution using only the second peak and a $CuCl_2$ solution.

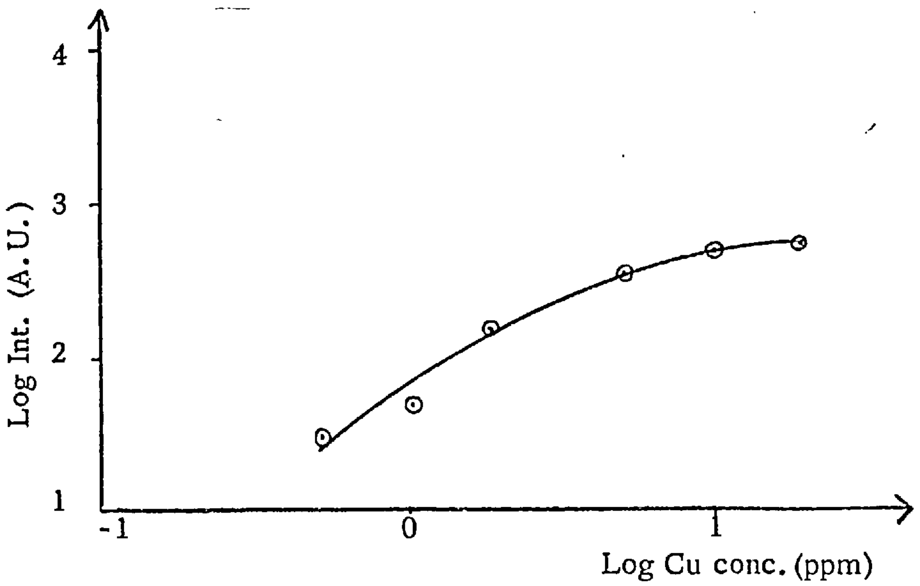

Fig. 4.17 Calibration curve for copper using a $CuCl_2$ solution

The curve was not a straight line, curving at much lower concentration than with using a $CuSO_4$ solution. A solution of $CuSO_4.5\ H_2O$ in distilled water was chosen for the calibration curve and the results obtained were found reproducible.

A study of the influence of the microwave power, flow rate and filament power on copper emission was carried out and the results are plotted (Figs. 4.18, 4.19, 4.20). From these results the optimum conditions for copper were chosen.

Table 4.5

Pressure : 20 Torr

Microwave power : 40 W

Variac voltage: 220 V

Drying voltage : 20 V

Concentration range : 0,1 - 100 ppm

A calibration curve was obtained (Fig. 4.21) with a gradient of 1.14. A detection limit of $1,5 \times 10^{-11}$g was obtained and a linear range of three orders of magnitude can be attained. Addition of potassium chloride increases the emission of copper by 25%. The addition of 100 ppm iron to 10 ppm of copper increases the copper emission 1.6 fold; the effect of iron on copper was therefore investigated more carefully. The ionization potential of iron is 7,87 V compared with 7,72 V for copper; so this small difference should not account for such interference by ionization suppression.

The addition of iron increases the argon emission intensity at 425,1 nm, 425,9 nm and 426,6 nm by less than 30%, but it also increases the background by the same amounts (Fig. 4.22).

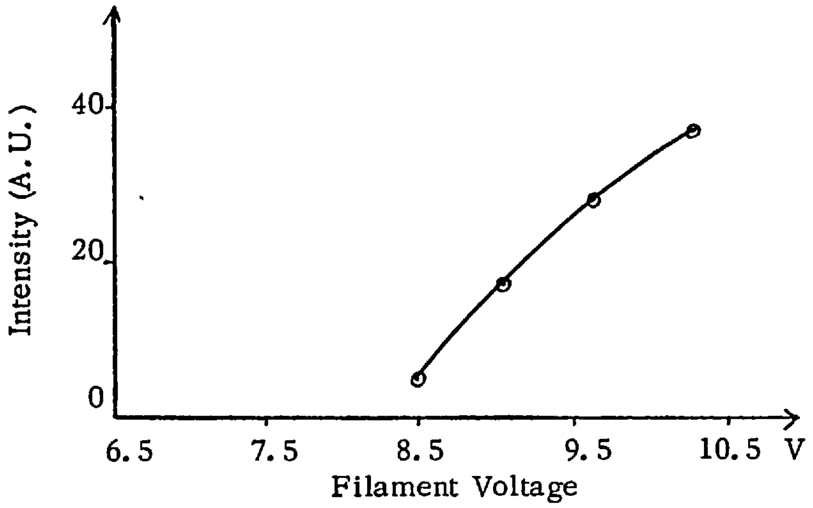

Fig. 4.18 Variation of the intensity with the filament voltage

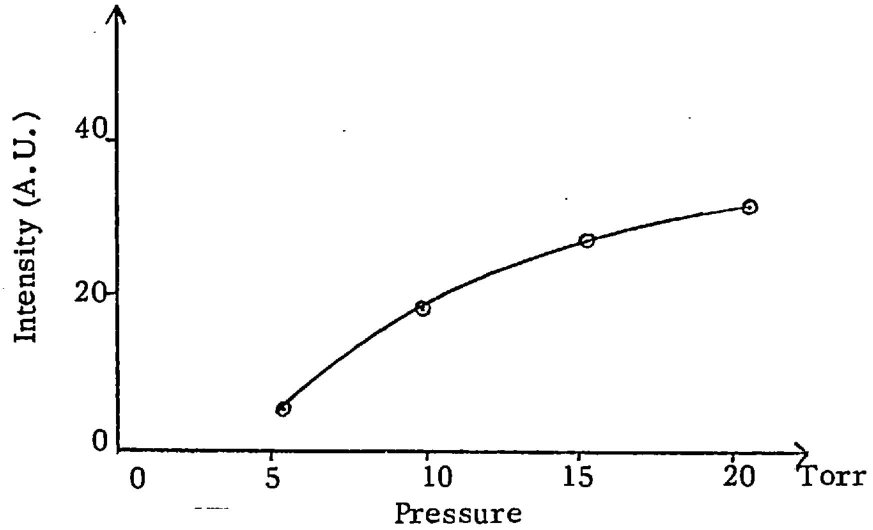

Fig. 4.19 Variation of intensity with the pressure

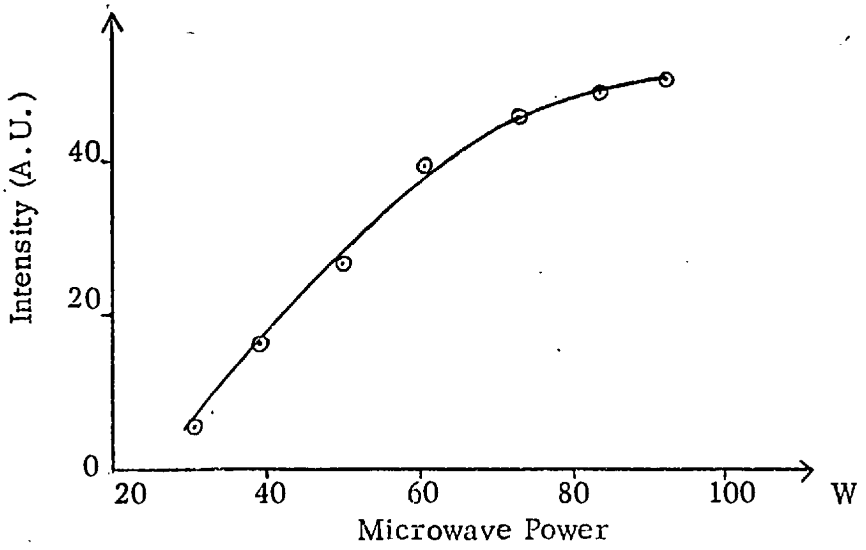

Fig. 4.20 Variation of the intensity with microwave power

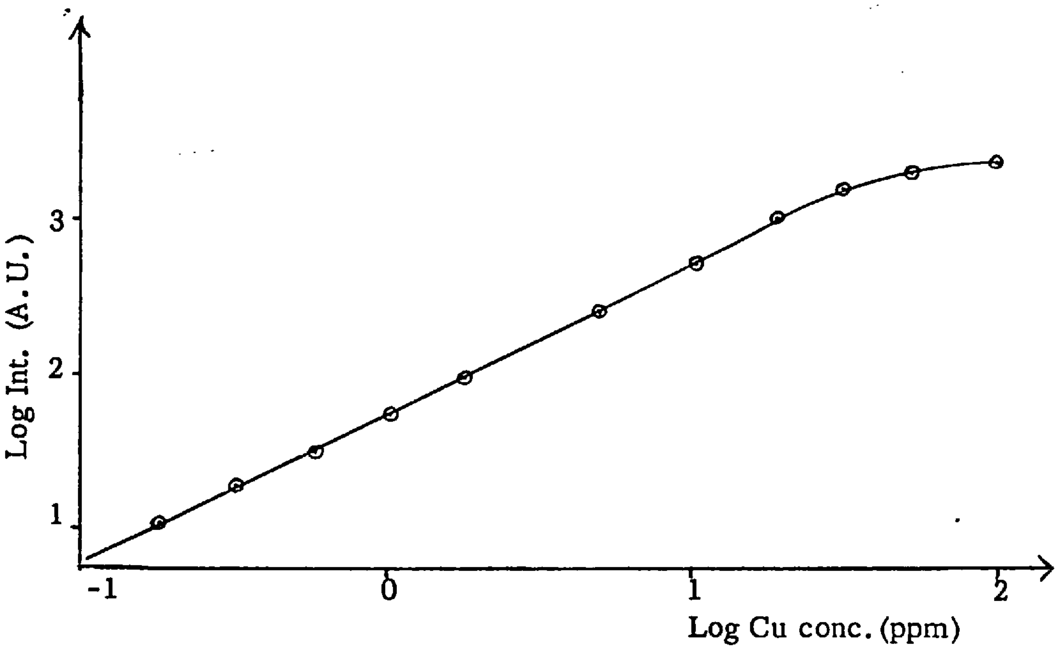

Fig. 4.21 Calibration curve for copper

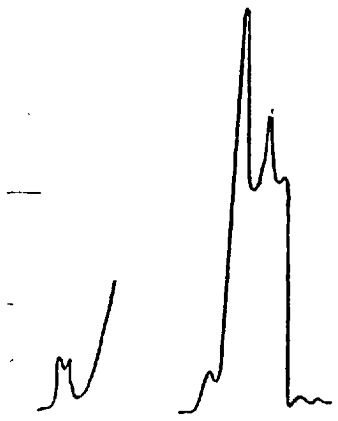

Fig. 4.22 Emission signal at argon line 425, 9 nm with addition of 200 ppm of iron

Runnels and Gibson (8) working with an atmospheric pressure MIP using a tantalum filament and working with acetylacetonates found that the addition of iron to copper not only increased the latter emission but also altered the slope of the calibration curve to unity. The amount beyond which the copper emission was constant was 10^{-7}g of interferent. In the present work, the copper signal increased with the iron addition to values of about 10^{-6}g of interferent from which the copper signal is not only constant, but addition of other metals such as potassium and manganese does not affect the intensity. Also, the addition of iron affects the copper intensity more when using the atomic absorption stock solution ($HClO_4$) than when using copper sulphate.

It was decided to investigate the influence of iron in the transport of the vapour to the plasma and the subsequent atomisation. A two hole filament was used so that there was no communication between the iron and copper except by vapour phase diffusion (Fig. 4.23). A copper solution was placed in one hole, and the 10^{-6}g of iron was placed in the other. The influence of the iron was smaller than before, that is, almost no increase was observed for the $CuSO_4$, but a big increase was found when using the copper/perchloric acid solution as before. Another interesting aspect was that, when using the atomic absorption solution, the addition of increasing

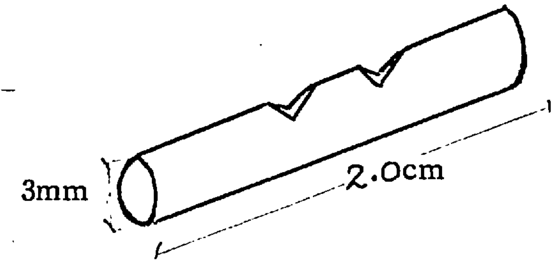

Fig. 4.23

quantities of iron, reduces the first peak, increasing the second and the total peak was much greater than the one obtained by addition of iron to $CuSO_4$ solution.

Kawaguchi et al. (42) proposed a mechanism for explaining the interference of potassium in manganese (1000 fold increase) based on the ionization and dissociation of molecular vapour direct in the plasma which can also be applied in this case.

The copper sulphate solution gives the oxide by reduction and some vapour of CuO possibly, but these are less easily dissociated than, e.g. $CuCl_2$. If iron (sulphate) is added to $CuCl_2$ when the latter is atomized, it seems that the $CuCl_2$ is held by the iron vapour and then all the compound is carried by the excess of iron into the plasma as chlorides by association with iron. Since the bonding of the copper in this sort of CuFe matrix should be weaker than the CuO bond, these compounds are easily dissociated. So the iron acts not only as a carrier but also as a buffer, since it avoids the selective volatilization of the different compounds but also avoids the interference of other elements on the atomization stage because it is present in much larger quantities than others.

One can suggest also that, iron in this case can act like a buffer in the excitation conditions of the plasma "protecting" the analyte from other interfering elements. An important observation is that this effect cannot prevent or explain all the interferences, since some of them are caused by elements present in rather small quantities (42).

Copper was determined in a low pressure MIP (4 Torr) (9) and a detection limit of 1×10^{-12} g was found. The enhancement factor by addition of 4-12 mM of potassium was 1000 fold. This also can reinforce the mechanism proposed (42) for the excitation of species in the plasma. These workers (42) used a V shaped filament of 0,25 mm diameter tantalum wire, 14 mm high with a round bottom of 2 mm diameter and used 5μl samples. The area of contact of the sample with the filament is much smaller than the area of the carbon filament used in this work. According to the mechanism proposed (42), the more easily dissociable molecular vapour is present in the plasma, the more intense is the emission obtained. This can account for the differences on the results obtained with the different atomizers.

A plot of emission intensity vs. position in the cavity was also carried out with and without the addition of iron. The iron changes the maximum emission of the copper towards the centre of the cavity (Fig. 4.24).

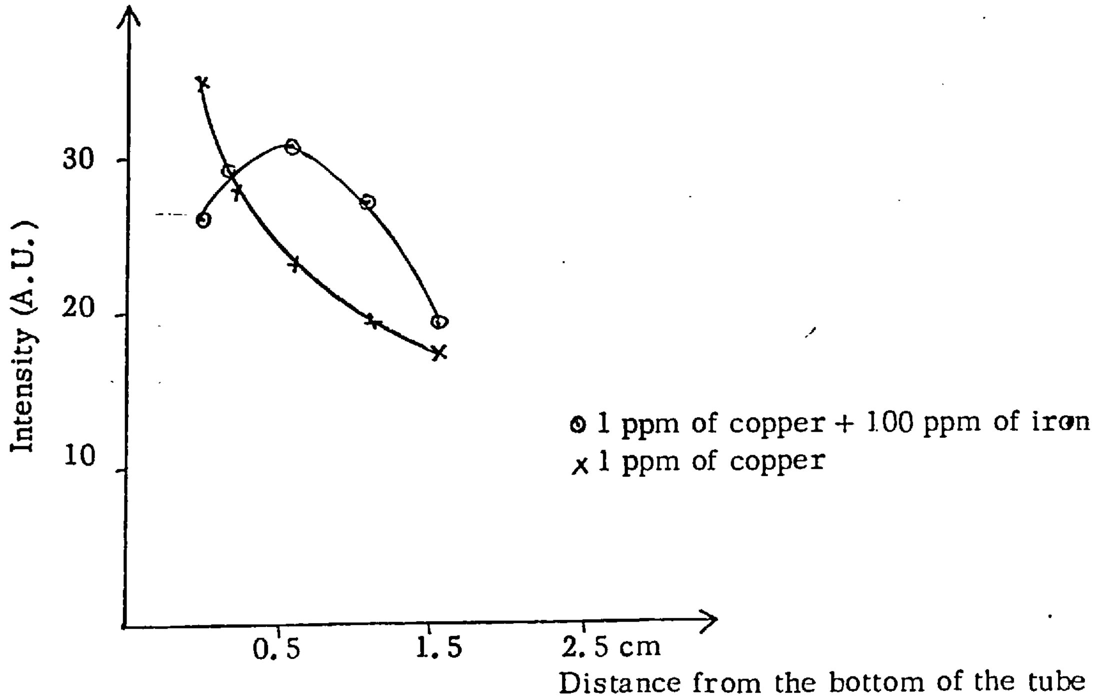

Fig. 4.24 Distribution of copper emission intensity along the discharge.

This effect was found also when potassium was added to some elements (9).

4.3.5. Manganese

In the manganese analysis the resonance line 403,0 nm was used. Some effects at the manganese (II) 275,6 nm line were also investigated. A manganous sulphate solution in distilled water was used. The effect of microwave power, flow rate and filament power on both manganese lines was studied (Figs. 4.25, 4.26, 4.27). Based on these figures, the optimum conditions for manganese determination were chosen (Table 4.6)

Table 4.6

Pressure : 20 Torr

Microwave power : 30 W

Variac voltage : 220 V

Drying voltage : 20V

Concentration range : 0,1 - 100 ppm

The calibration curve of log intensity vs. log manganese concentration was obtained (Fig. 4.28) with a slope 1.18 and linear range 0.1 to 50 ppm manganese the detection limit being 9.2 x 10^{-12}g and the coefficient of variation was 6.5%.

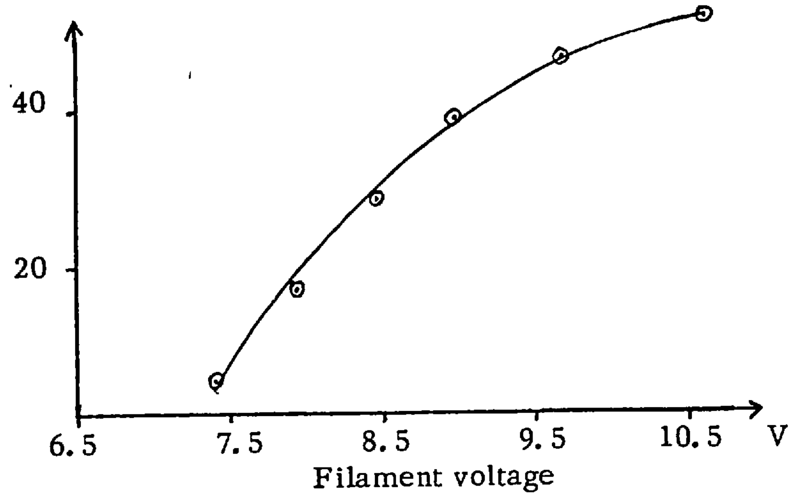

Fig. 4.25 Variation of the intensity with the filament voltage

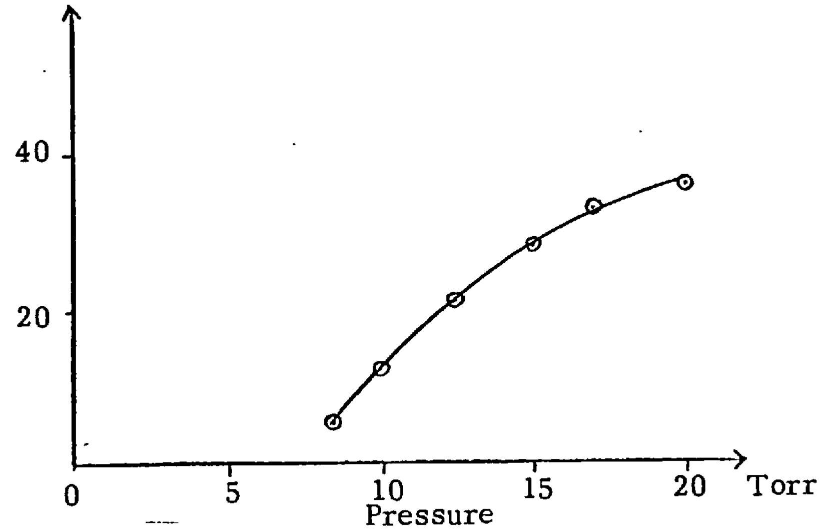

Fig. 4.26 Variation of the intensity with the pressure

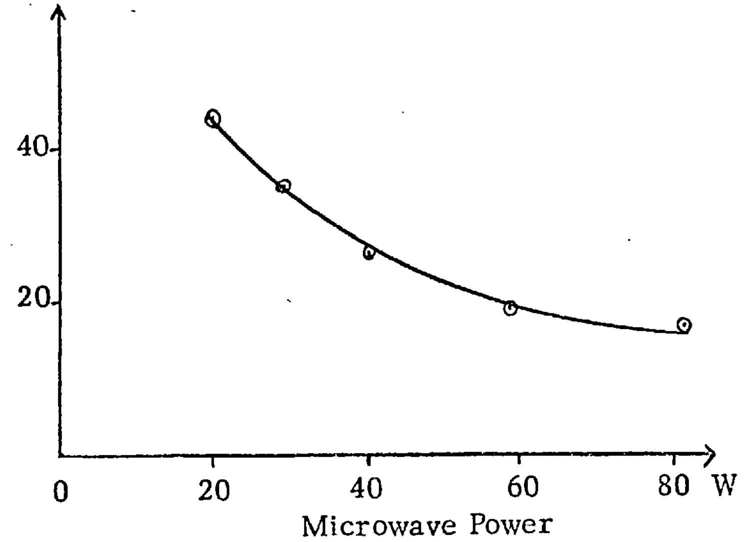

Fig. 4.27 Variation of intensity with microwave power

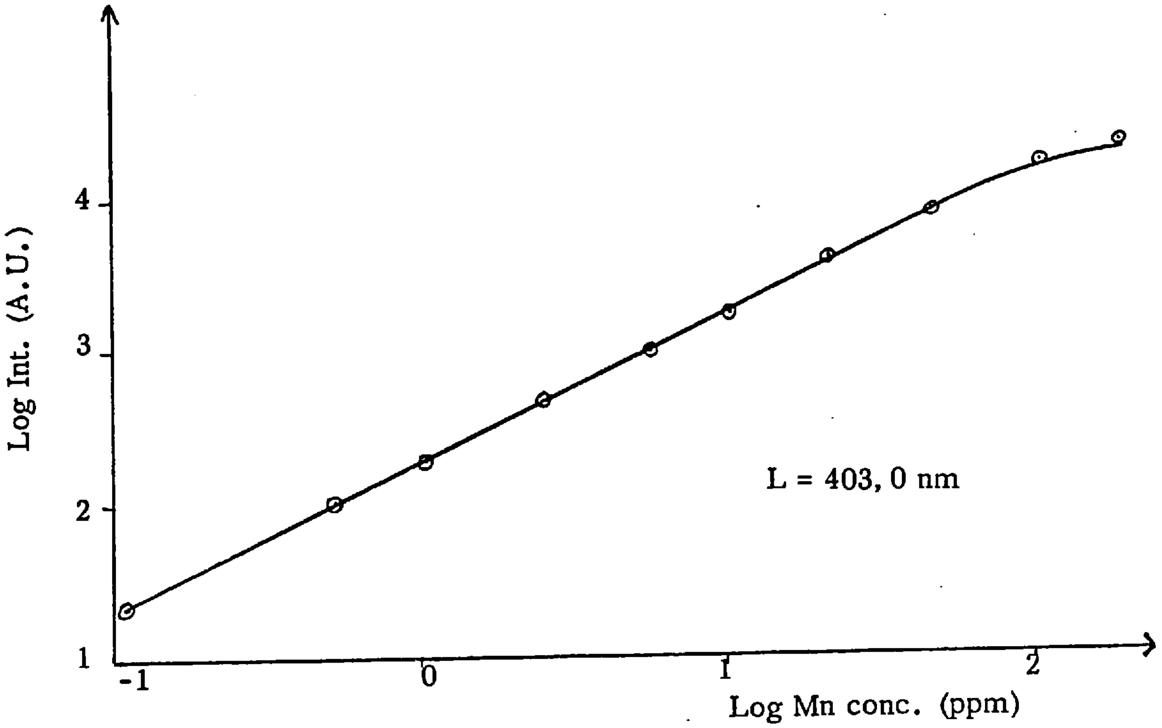

Fig. 4.28 Calibration curve for manganese

Two peaks were also observed in the manganese work. Since manganese has different degrees of oxidation, it was investigated if this can account for the two peaks observed. Using different salts, nitrate and permanganate, the two peaks were observed for both the salts used. The influence of the heating rate on the two peaks was investigated, but both of them increased as the atomisation voltage (and hence temperature) increased, although the second peak increased more dramatically than the first one. The addition of other elements was investigated. The addition of potassium chloride increases the manganese emission by 2.7 times but also increases the first peak by 13, 0 times (Fig. 4.29). Increasing amounts of iron

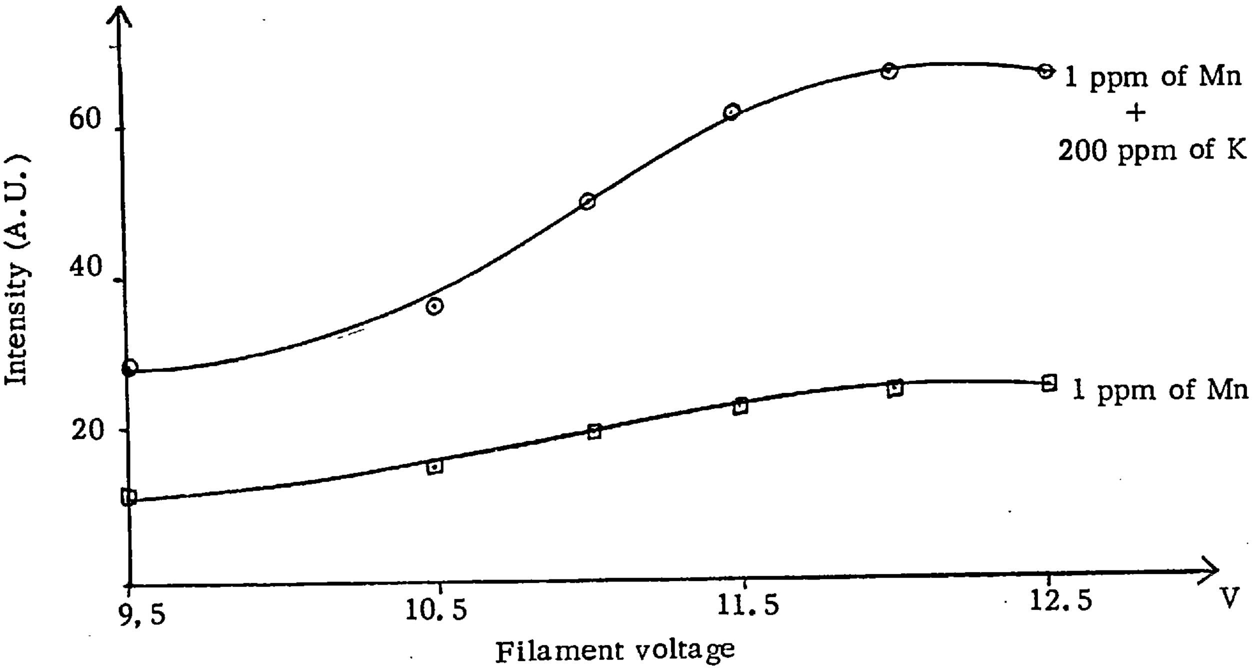

Fig. 4.29 Variation of manganese intensity with the heating rate with and without KCl.

chloride almost eliminates the first peak, giving an increase in emission of about 2, 5 times over the emission produced by the excitation of manganese alone. The peak also comes a few milliseconds later than the second peak of manganese with interferent. This is quite consistent not only with the mechanism proposed by Kawaguchi et al. (42), but also with the effects found for copper. The addition of potassium affects the same way both manganese atomic and ionic lines (Fig. 4.30). Also, a linear calibration curve for manganese with 200 ppm of iron was found, with a slope of 0, 94 (Fig. 4.31).

A steel sample containing 147 ppm of manganese was analysed. The sample was dissolved in a sulphuric-nitric acid mixture

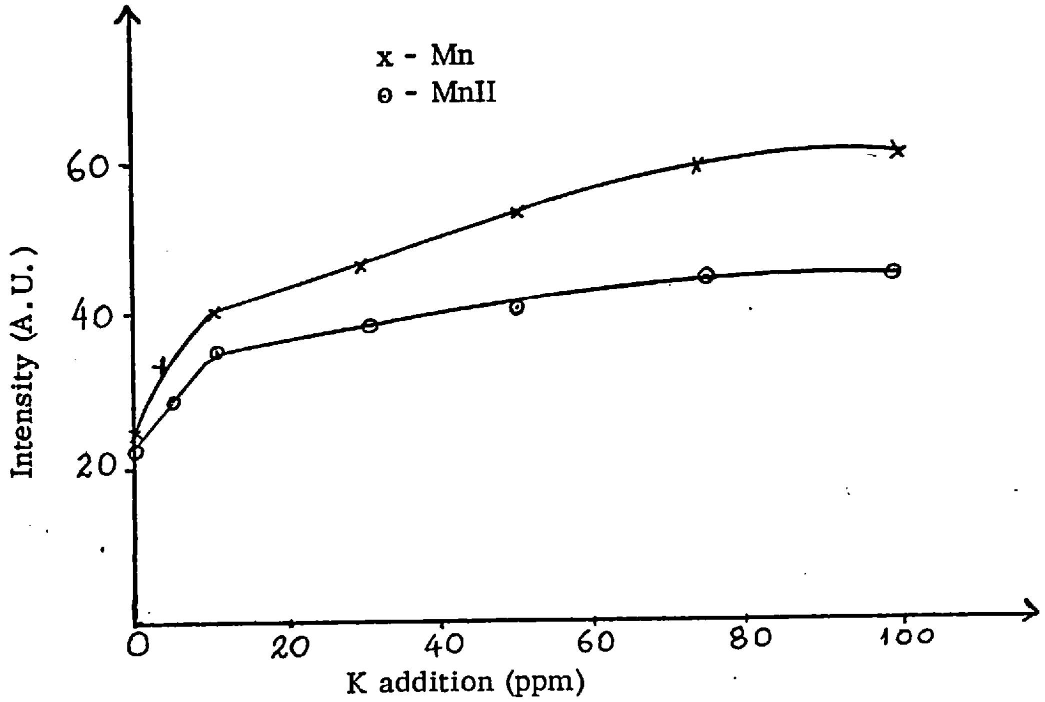

Fig. 4.30 Effect of potassium addition in the emission intensity of MnI (403, 0 nm) and MnII (275, 6 nm) lines

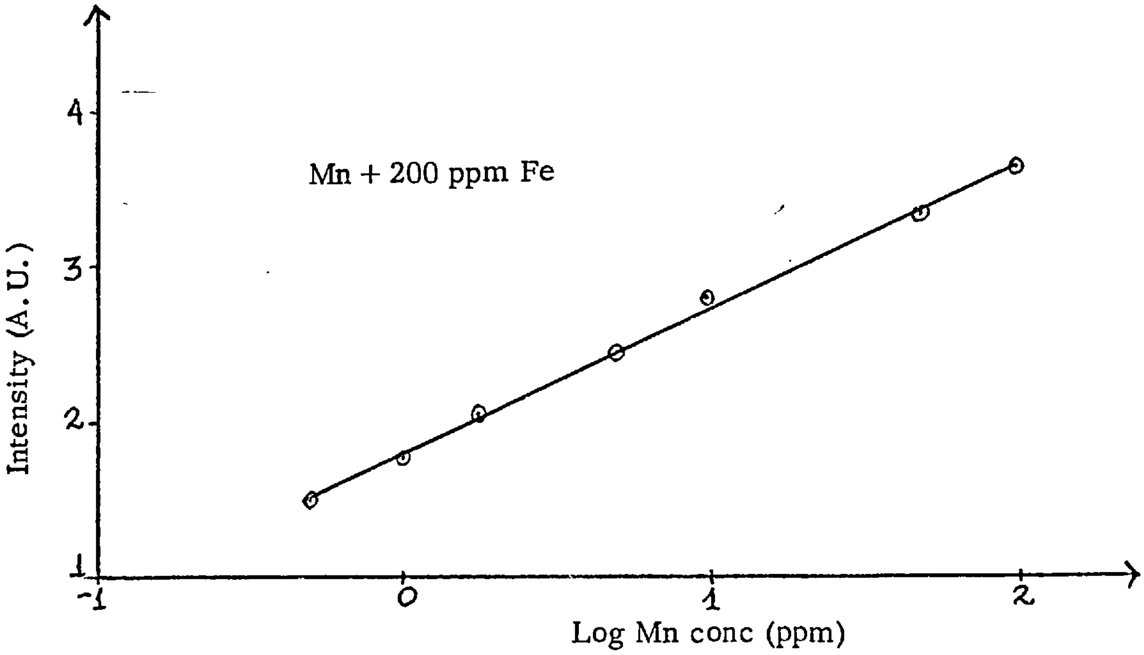

Fig. 4.31 Calibration curve for manganese with 200 ppm of iron

and diluted with distilled water. Using aqueous manganese standards, the concentration obtained for manganese was more than 2 times greater than the one expected. Addition of 200 ppm of iron to the standards gives an error of 5, 5% on the determination. Applying the standard addition method, using aqueous standards, the error was 1% on the nominal value (Fig. 4. 32).

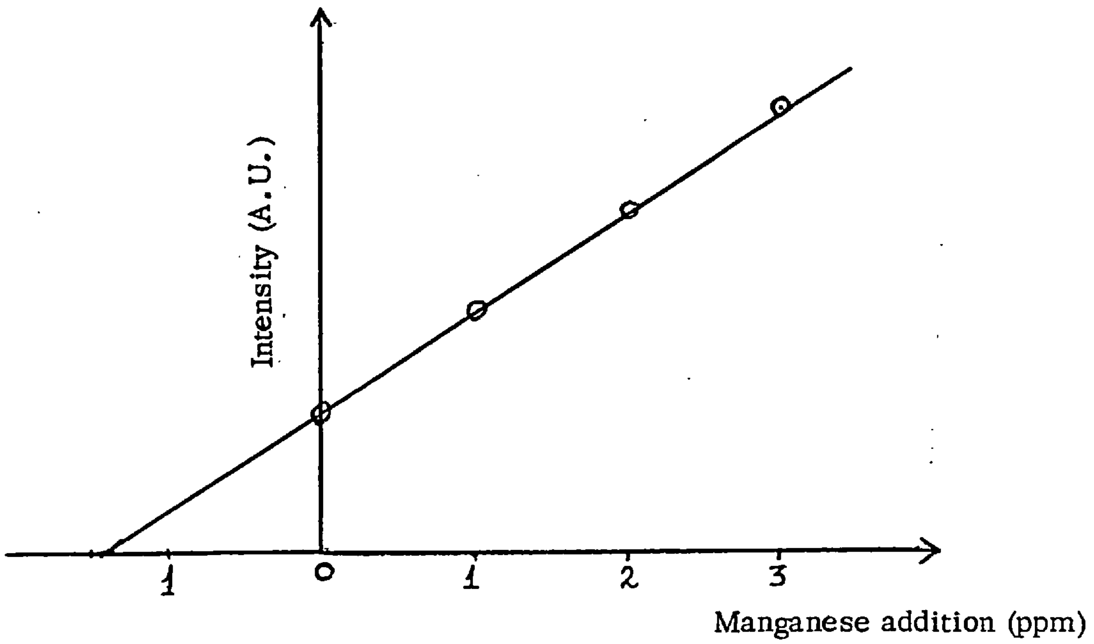

Fig. 4. 32 Determination of manganese in steel by the standard additions method

Addition of 200 ppm of potassium to a manganese solution containing 200 ppm of iron does not alter the emission intensity of the analyte. Manganese has been determined by Kawaguchi et al. (9). An enhancement of 1000 fold was found by addition of potassium and a detection limit of 2 x 10^{-12} g was found.

4.4. The use of Nitrogen Plasma

The spectral plot for argon (Fig. 4.1) shows that the main impurities present in the support gas were nitrogen and water. Nitrogen has an extensive spectrum of band emission, corresponding to a wide range of photon energies. A nitrogen plasma cannot be sustained at atmospheric pressure, since the structure of the molecule makes it an efficient quencher. When the level of nitrogen reaches 5% of the total flow, the atmospheric argon-nitrogen MIP is quenched (29). At low pressures, because the electrons suffer few collisions, their energy is higher, so that greater ionization and dissociation of the nitrogen molecule can occur, so that a nitrogen plasma can be sustained at low pressure. It was decided to make a study of the excitation of metals on the nitrogen plasma.

Brassem et al. (79) measured the electron temperature and electron concentration of a nitrogen plasma. The electron temperature was of the order of 5×10^4 °K(decreasing with pressure) and the electron concentration was about $2 \times 10^{12} cm^{-3}$ and is almost constant with pressure. Comparing this with an argon plasma, the electron temperatures for argon is somewhat lower (about 2.0×10^4 °K) but the electron concentration is 4 times higher. The addition of nitrogen to the argon plasma increases the background (possibly due to the band spectrum of molecular species) and tends to decrease the plasma size. This can be due to the quenching effect of the molecular nitrogen, which can absorb the electron energy and convert it into the internal energy of the molecule.

The operational characteristics of the nitrogen plasma are also different from that of the argon plasma. The argon plasma length increases when increasing the pressure up to a certain limit (Fig. 4.33); the nitrogen

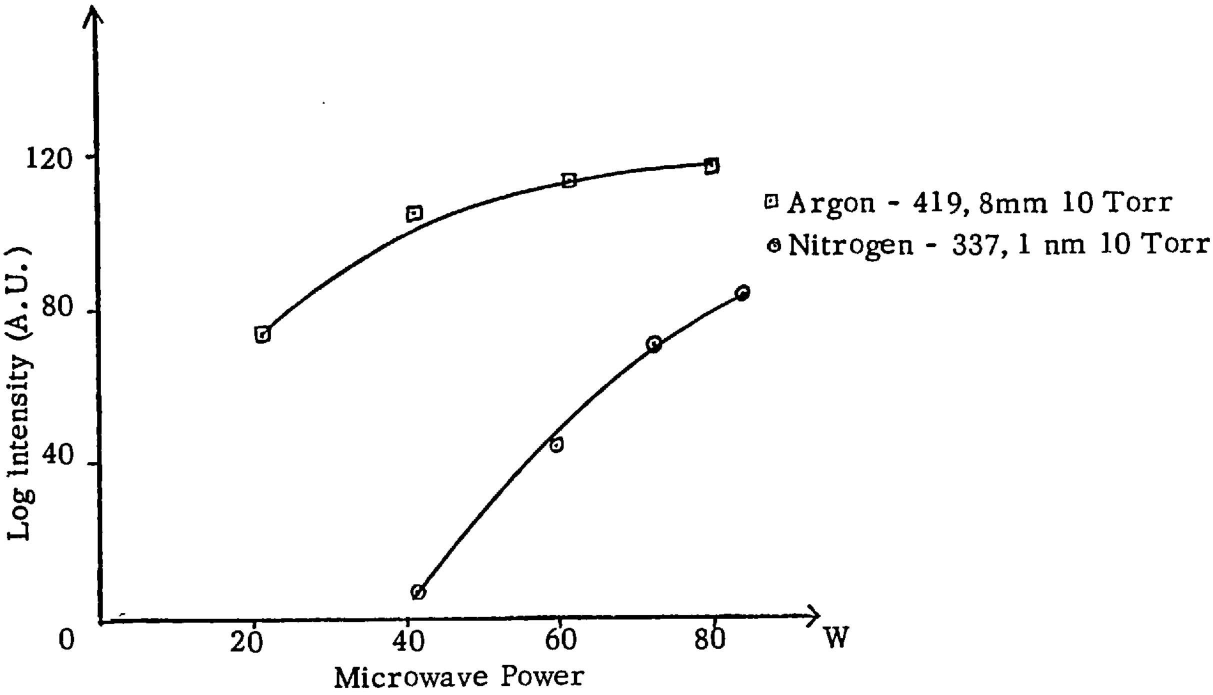

Fig. 4. 34 Variation of the emission intensity of argon (419, 8 nm) and nitrogen (337, 1 nm) with microwave power

A calibration curve was carried out for zinc in a nitrogen plasma (Fig. 4. 35) using the conditions in Table 4. 7.

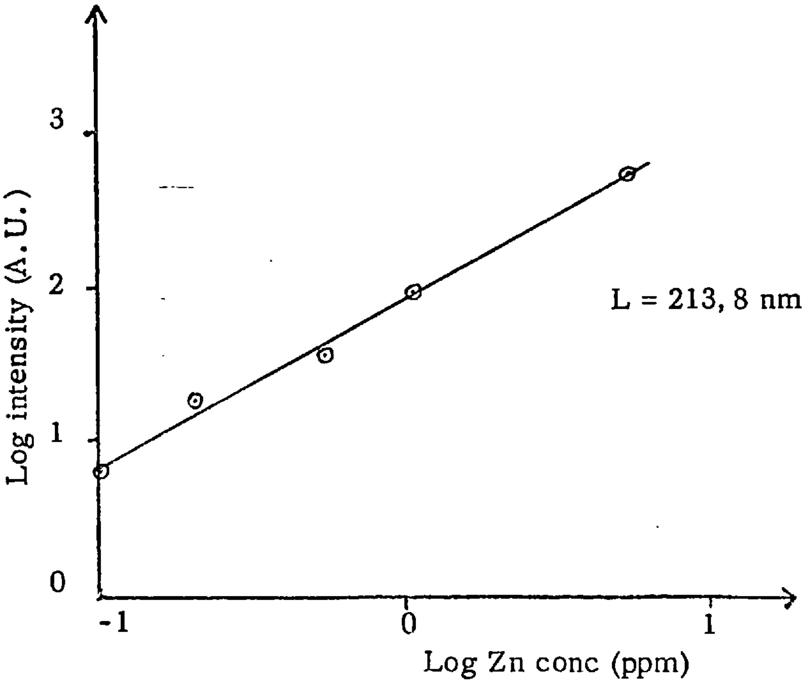

Fig. 4. 35 Calibration curve for zinc (213, 8 nm) in a nitrogen plasma

Table 4.7

Pressure : 16 Torr

Microwave power : 50 W

Slit : 25 μ

Filament voltage : 160 V

Concentration range : 1 to 5 ppm

The curve was linear over the range studied but the detection limit was poor (1,5 x 10^{-9}g) and the relative standard deviation was 7%. No further studies were carried out.

.4.5 Oxygen

The addition of oxygen to the plasma was reported to improve the detection limits for chromium in an helium MIP, operating at low pressure and so this idea was investigated.

In the present system, when introducing oxygen the carbon filament is burned very quickly, giving rise to a band emission due to carbon-oxygen compounds and also scattering, so no further studied were carried out. The background of the argon plasma decreases when the oxygen concentration is increased and also the transparency of the plasma. Increasing the amount of oxygen decreases the plasma length and eventually quenches it. The improvement obtained in the reported work could be due to the more efficient oxidation of the compounds eluted from the gas chromatograph.

.4.6 The Helium Plasma

At low pressure, helium was the most widely used plasma gas. This is probably due to its higher ionization potential and higher electron

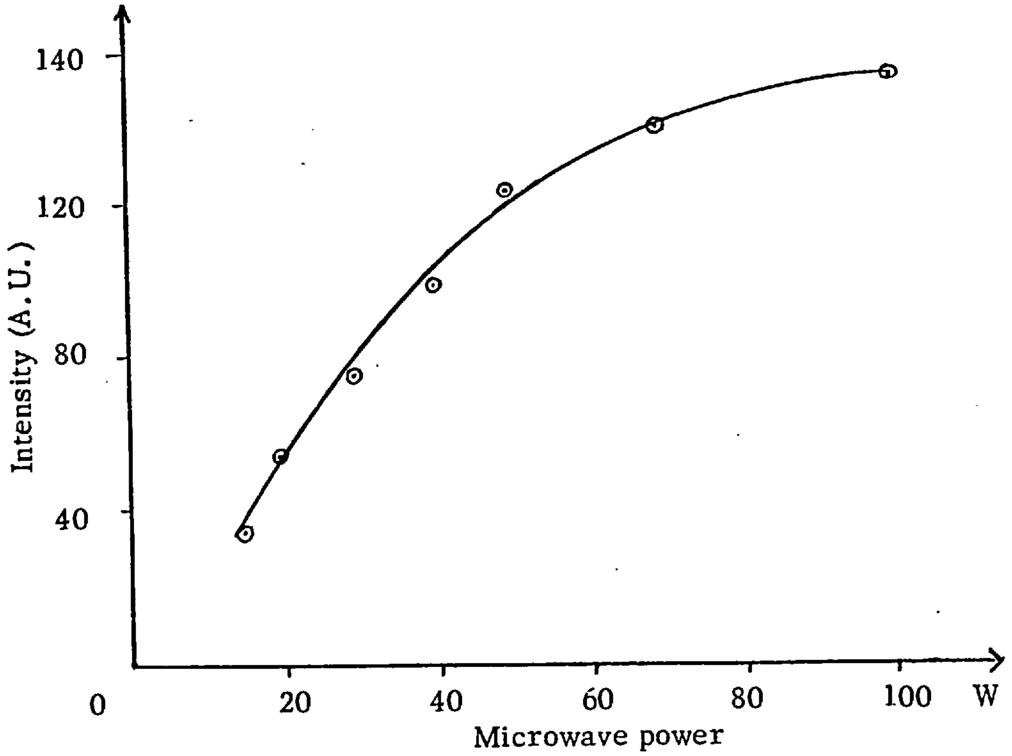

Fig. 4.36 Variation of the intensity of the 388, 6 nm helium line with microwave power

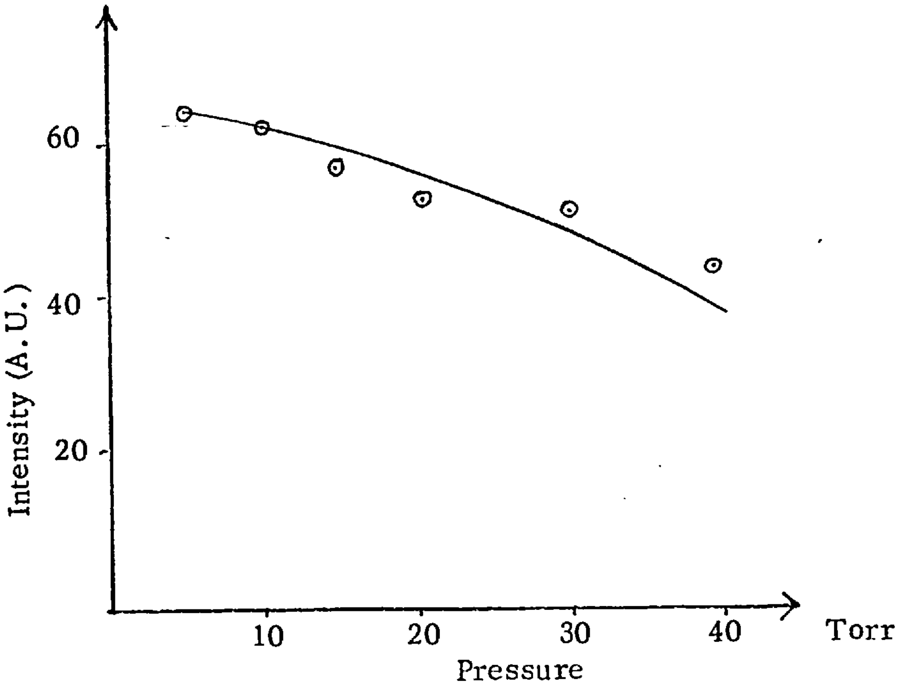

Fig. 4.37 Variation of the intensity of the 388, 6 nm helium line with pressure

temperature, which allows a much more efficient dissociation and excitation of species, such as the effluent of a gas chromatograph, in which it is mostly used. Also, it is a general consensus that it is more stable than the argon plasma (30). Recently, with a new cavity design, a helium MIP can be sustained at atmospheric pressure, probably due to a more efficient power transfer to the plasma gas.

In terms of stability in this system, no advantage was noticed when using helium as plasma gas. as far as reproducibility is concerned but the helium plasma can be submitted to higher variations in pressure without being extinguished than the argon plasma. Also higher pressures can be used with helium before the discharge begins to behave erratically. The helium plasma also alters only slightly its length on increasing the pressure. The helium background is also higher than for argon at the same pressure, although the signal for zinc was smaller. This was also reported by Busch and Vickers (31) when analyzing mercury.

If the pressure is increased by increasing the flow rate up to 30 Torr, the detection limit obtained for zinc was about the same obtained when using argon at 20 Torr. So, the decrease in intensity observed when using helium plasmas can be due to variations in the flow rate when changing gases. The intensity of the helium line 388, 6 nm increases with microwave power up to 100 W and decreases with pressure (Figs. 4. 36 and 4. 37).

A calibration curve was carried out for the zinc 213, 8 nm and copper 324, 7 nm resonance lines and the same conditions as used for the determination of these elements using an argon plasma (Figs. 4. 38 and 4. 39). The detection limits were $1,7 \times 10^{-10}$ g for zinc and $2,3 \times 10^{-10}$ g for copper.

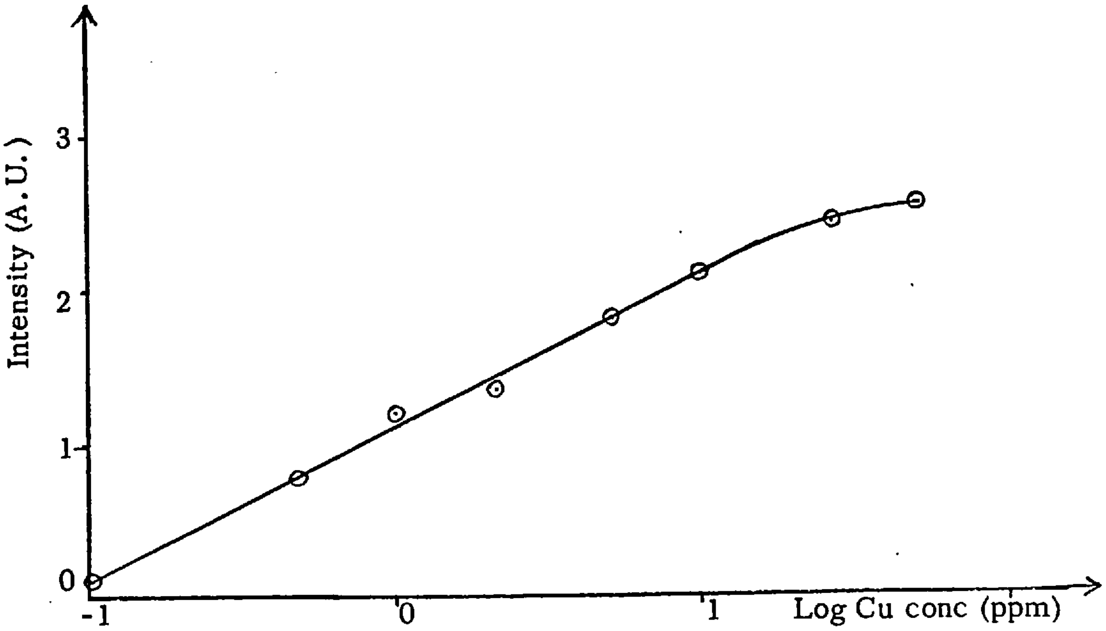

Fig. 4. 38 Calibration curve for copper in a helium plasma

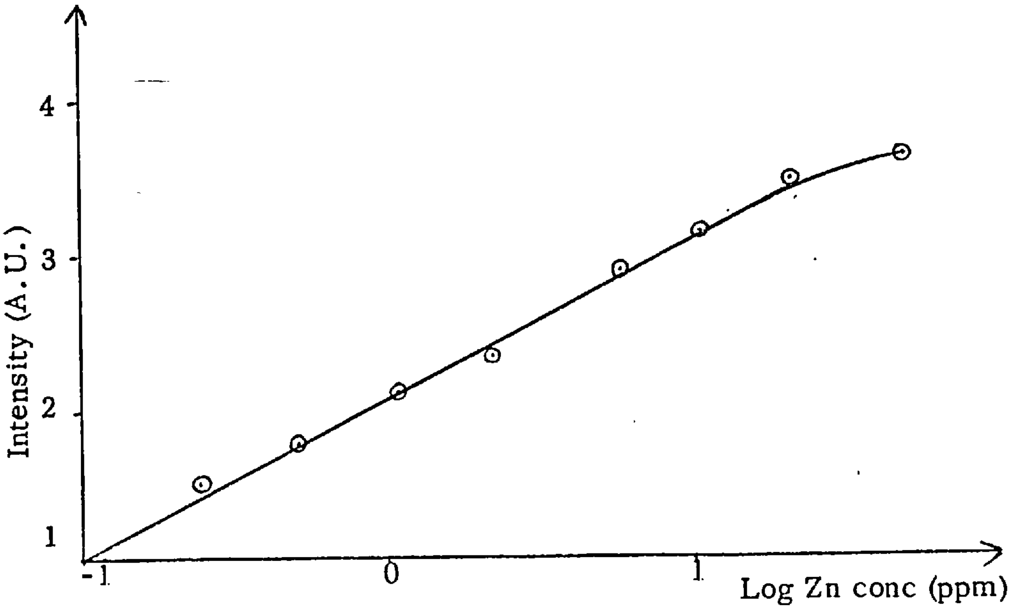

Fig. 4. 39 Calibration curve for zinc in a helium plasma

CHAPTER 5

Discussion and Conclusions

It is a well known fact that the microwave induced plasma is efficient in exciting atomic species (30). The low pressure MIP has been used by a number of authors with some advantages, mainly when using helium which seems more efficient in breaking down compounds in gas chromatography systems, where the advantages are more noticeable (9, 10, 35, 37). Theoretically it was suggested that because of the higher electron concentration and temperature it should have more energy (79, 80) for exciting species and because of less collisional deactivation, more intrinsic sensitivity is expected. However, in order to get to the low pressure region where these advantages are more noticeable, very low flow rates have to be used. Brassen and Maessen used a flow rate of about 0, 08 l/mm to attain a maximum pressure of 0, 9 Torr (79). In a real system, the transport of the sample to the plasma presents a problem when very low flow rates are used and this is a limitation when low pressures are the main point. Using the system proposed in this thesis it was found that increasing the flow rate increases the emission signal for all the elements studied. The emission of argon lines decreases when increasing the flow rate (or pressure), (Fig. 5. 1), probably due to reactions of the argon excited atoms with ground state atoms and this effect is more noticeable at lower pressures. So, if some improvement in sensitivity could be achieved by using low pressures, this is limited by the necessity of transporting the sample into the plasma.

At atmospheric pressure the electron concentration and temperature are not so high, but much higher flow rates can be used, so for the same system, the sample is more efficiently introduced into the excitation region. The influence of microwave power is not understood. The argon line intensitiesin general increase with microwave power, but more dramatically at low values of microwave power. This can be due to the decrease of excited species by three-body collisions, as the electron concentration increases. This can account also for the decrease of emission intensity with power for all the elements studied, although some self-absorption also can account for the effect.

The temperature of the filament seems also to increase the emission signal for all the elements studied. This can be due to the method used for recording the signal, since the height of the peaks are well affected by the rate of formation of the atoms in the filament. This can be overcome by integrating the intensities of the peaks instead of using peak height.

The maximum power available cannot be used for all the elements, since for the very volatile elements the recorder response was the limitation and also, because of the signal emitted when the carbon filament is heated at very high rates, probably due to the scattering of carbon particles and also to the CO and CO_2 bands emitted by combination of carbon with O_2 present in the argon as impurity. This signal always comes after the analyte signal but does not seem to interfere with rather volatile metals (Fig. 5.2). However, if metals such as aluminium, molybdenum, vanadium and others, which form refractory oxides are atomized, a long time is necessary to produce an analytical signal. In this case, both signals come together and it is impossible to distinguish between them. This is also valid for elements forming refractory carbides such as boron, titanium and zirconium, Unless more volatile compounds are formed, these elements cannot be analysed in this system, which presents its main limitation.

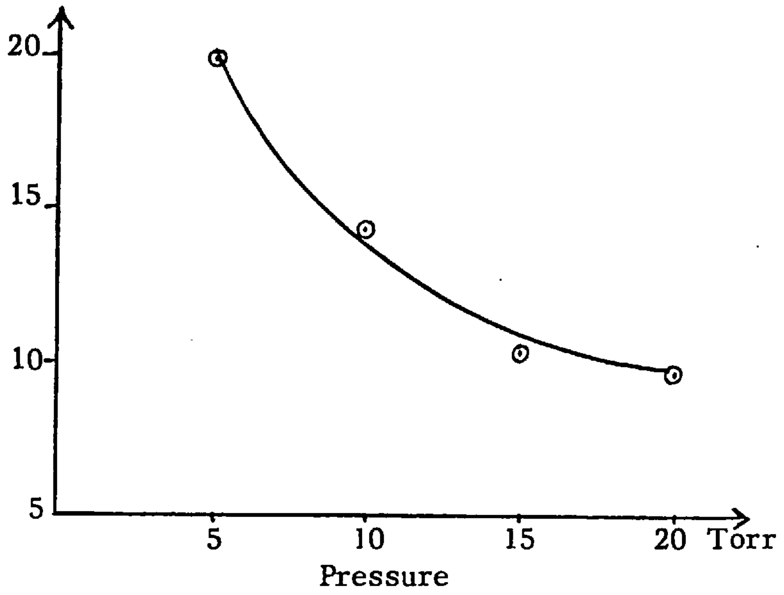

Fig. 5.1 Variation of the intensity of argon 415, 9 nm line with pressure

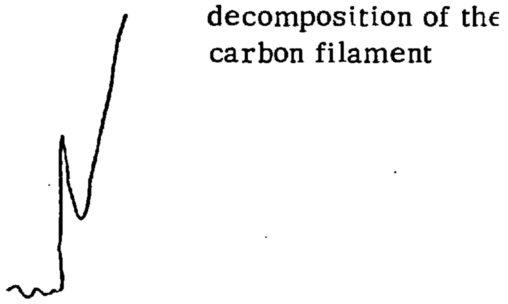

Fig. 5.2 The analytical signal

An attempt to decrease the distance of the filament to the plasma, increases the effect of scattering by the carbon from the filament (see appendix).

The use of metallic filaments instead of a carbon filament will avoid this effect but will bring other limitations, as discussed before. As far as sample introduction is concerned, the best method designed is the micro arc technique, although it could not be foreseen which influence it will have in the plasma conditions if a design like the one used in this work is employed. Although detection limits are not entirely reliable to compare results, at least for the range of pressures used in this work, low pressures do not seem to give any advantage over the atmospheric pressure system. Vacuum systems are always a problem since they introduce more variables, and consequently, more sources of error., as variation in pumping rates, leakages on the system which sometimes are so small that they cannot be easily detected, causing however high irreproducibility due to the presence of higher concentrations of nitrogen and oxygen than that present in "pure" argon.

In the present system, another problem is the grease that was used to maintain the vacuum and allow the movement of the surfaces. Excess of the grease, even if it is used in small amounts, sometimes deposits on the filament. This not only makes the sample creep on the surface but also gives big signals due to the decomposition of the organic material. The grease tends to go to the outside of the cell, making the surfaces hard to move. This is not a serious drawback when higher pressures are used.

The precision and accuracy achieved with low pressure systems is no better than atmospheric pressure. The main source of error for both plasmas is the tuning of the cavity, which is affected by changes in temperature, frequency drip of magnetron valve and composition of the gas and by the position of the tube inside the cavity. The latter can be maintained constant, and the other factors are minimized by working in a region where the signal is not too dramatically affected by small changes in microwave power. Other sources of error, apart from leakages from the system which can be detected by changes in the shape, colo· . and also background of the plasma, are the instability in the microwave power supply (which can be as high as 10%) at 50 W, variations in pressure (up to 5% at 20 Torr) and sample introduction (3-5%).

At the present moment, the only advantage seems to be the upper limit of the concentration linear range. Since the method was proposed to analyse low concentrations of materials, this advantage is not very useful, since other methods such as atomic absorption will give the same results with more simplicity and probably more precision.

Apart from the effects mentioned before, that is factors that affect the introduction of the sample into the plasma, the matrix should also affect the plasma itself. Brassem et al. (84) studied the variations in the plasma excitation conditions when gases such as hydrogen, helium and argon are added to the support gas. They found that at concentrations up to 1% of the interferent, the plasma shows the characteristic excitation conditions of the support gas and the intensity of the emitting lines for the interferent is proportional to the amount added; from 1% to 10% the excitation conditions of the plasma such as temperature and electron concentration change towards the ones found for the interferent and the proportionality between intensity and concentration is no more valid. So, if a matrix is added such as sodium, potassium, iron or any other element for that matter in high concentration, the plasma would be expected to change its excitation conditions towards the one of a mixed plasma, where the principal constituents will be a mixture of the support gas and vapour of the matrix elements. It is known that when an easily ionized element is added to a plasma its temperature decreases and the electron concentration increases. In the real case, the vapour is not only atomic species but also molecular species. In such cases, it is even more complicated to foresee what kind of effect these vapours will have in the plasma. It is to be noted that 5 μl of a 1000 ppm metal solution introduced into the plasma would result in a particle concentration of about 0.3% of the total gas particles present in the plasma. This is considerably higher than that for atmospheric MIP's and r.f. plasmas. In atmospheric pressure MIP's as well as in other plasmas, the flow rates of the gases are higher so the dilution of the sample is higher and then the excitation conditions are less prone to suffer dramatic changes. This seems to be the biggest drawback to the analytical use of low pressure plasmas, since the sensitivity is bound to be affected by the matrix. This also is supported by the change in the maximum emission in the plasma, when high concentrations of analyte are added (42).

The excitation mechanism proposed by Schlüter, based on the model of a radiative recombination mechanism (71) is well supported by the results obtained in this work. The fact that different temperatures are obtained by different methods seems to lead to supposition of the existence of two groups of electrons with different maxwellian distribution or a group of electrons with non-maxwellian distribution, but much more has to be done to explain the excitation mechanism of different species added to the plasma gas. This is not easily achieved where the sample is a vapour which stays in the plasma for few milliseconds. Measurements of electron concentration and electron temperatures seem impossible, although a proper furnace working at high temperature and continuously introducing the analyte vapours may possibly help to estimate the variations in excitation conditions and by this means, explain some unknown facts.

The excitation of molecular vapours proposed by Kawaguchi et al. (42) can be accepted in the light of the experiments and results found also in this thesis but more evidence will have to be obtained to accept this as a definite basis for the interferences found.

The use of the low pressure MIP for analytical use does not seem to be competitive with other methods for routine analysis of solutions, although it provides good sensitivity and acceptable detection limits. Using lower pressures, lower detection limits can be expected but higher interferences problems and manipulative difficulties will come together with higher sensitivity.

APPENDIX

Other Cell Designs

In an attempt to overcome the problems encountered with the first cell, a second one was designed and constructed.

The main problems with the first one were:

A-1 The distance between the filament and the plasma -

This distance was 6 cm and could not be less because of the design of the channels whose purpose was to maintain the plasma during all the steps. Since, after some experiments it was found that if one minute is allowed for stabilization, reproducible results could be obtained, it was decided to sacrifice the advantages of maintaining the plasma,in order to have a smaller distance between the sample introduction and the plasma itself. This new design reduces the dead space also, so should improve the sample introduction efficiency at the low flow rates used, as well as reduce the plating out of the vapour on the cool walls of the cavity.

A-2 The grease -

Vacuum grease was used, not only to maintain the vacuum but also to allow the middle part of the cell to slide on the flat surfaces of the others. This grease sometimes accumulates in the holes, dropping onto the carbon filament and on the filament holders, decomposing and producing spurious signals. It also gets onto the outside of the surfaces, and after some time, they stick together. Different greases have been tried, but the ones that show good lubricant properties did not maintain the vacuum so well. The one that proves to have a reasonable compromise between the two properties was the silicone grease "Apiezon".

In order to avoid this problem, a system with two positions was designed. In the first position, the sample was introduced and desolvated; then the top part of the cell was lifted by means of four balls set into recesses in the lower part. As the upper part was rotated, the balls rolled out of the recesses and lifted it up against a spring. This design has two major advantages. Rubber 'O'-ring seals can be used to maintain a vacuum seal. This is why the "lifting" design is necessary, as ring seals cannot be used between slipping parts under pressure, particularly if the rings have to pass over holes. The use of ring seals means also that grease is not required, which therefore removes all the problems associated with its use.

In the second position the plasma tube was placed over the sample filament. The system was then evacuated and the plasma initiated (Fig. A-1).

The main problem encountered with this system was due to the use of the carbon filament. Decreasing the distance between the filament and the plasma not only allows the sample to be introduced more efficiently but also increases the scattering signal of the carbon particles from the filament. So, it was observed that even for the low temperatures used to evaporate very volatile elements such as zinc and cadmium, the analytical signal came almost at the same time as the signal due to emission caused by the carbon. The evaporated carbon also was deposited on the flat surfaces and after few atomizations the pressure was no longer reproducible. Also, the vacuum obtained with this design was 2 Torr, which was much worse than that obtained with the previous cell, probably due to leakage across the ring seals. The screws below the cavity were tightened so that maximum pressure was exerted on the 'O'-rings, and consequently in the surfaces, but only a slight

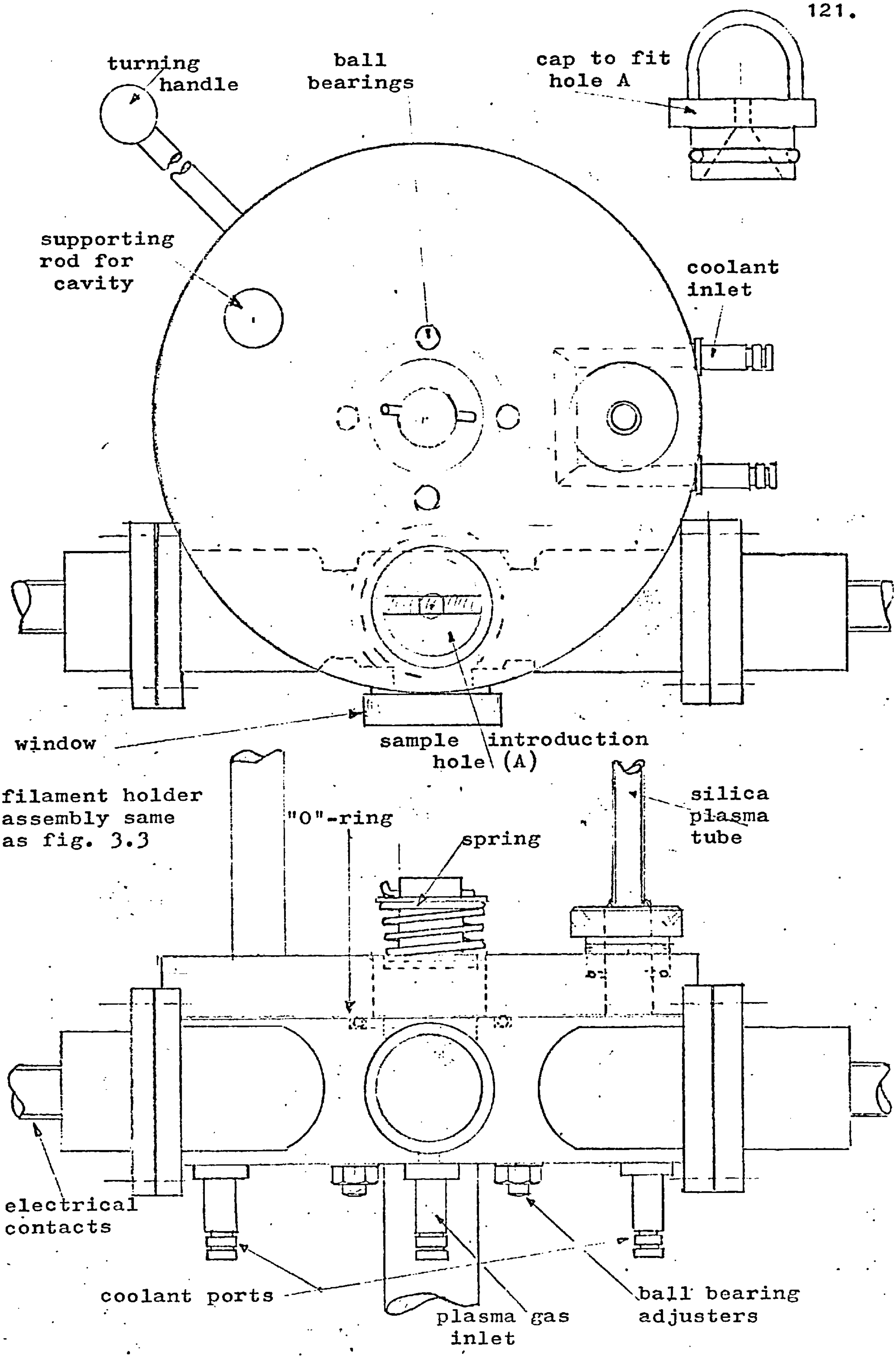

Figure A-1 (scale 1:1)

improvement in pressure was observed.

A suggestion for further work could be the use of this cell with a metallic filament and with atmospheric pressure plasma, although it is considered that further refinements in the cell design would result in a workable system even for low pressures.

SUGGESTIONS FOR FURTHER WORK

As far as the study of the low pressure range is concerned, studies should be directed to an improvement in design of the sample introduction systems, since interferences, detection limits and precision are closely related to this. The use of sealed sample cells could provide useful results, although it is not very practical for routine analysis.

In the present system, modifications that can improve the performance is the improvement of the cooling system, and a more adequate method of fixing the cavity with respect to the tube.

Not only should other cell designs be investigated more deeply, but also the facts concerning the excitation mechanism of the processes occurring in the plasma, so interferences between elements could be anticipated and avoided. Also a better knowledge of the conditions will help to optimize the conditions for determination of the elements.

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