

ERRATA

p.18 line 16 asymmetrical should read asymmetrical.

p.62 equation 15 should read 
$$I_{qp} = \frac{e}{4\pi} A_{qp} \lambda_{aq} n g_2 \frac{\exp(-E_i/kT)}{Z}$$

p.173 line 23 Poisselle should read Poiseuille.

ANALYTICAL STUDIES OF A DC TRANSFERRED PLASMA

by

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ABSTRACT

The historical development and analytical applications of various types of plasma are described. In particular, plasmas generated by dc arc discharges are discussed together with several applications.

A short chapter of general atomic emission theory discusses the origin and intensity of atomic spectral lines.

A Capillary Arc Plasma (CAP) is described and investigated for its analytical potential as an atomisation and excitation source for solution spectrochemical analysis. The tail-flame region provides the best signal/background ratios and hence the best detection limits. However, the detection limits are poor because the sample does not experience the high temperature zones of the plasma.

The CAP is used as a high temperature atomisation and fragmentation source for a low wattage microwave plasma contained in various diameter quartz tubes. The plasma formed inside a 2 mm i.d. tube gives the best detection limits.

The construction and operation parameters of nebulisers/desolvating systems used in conjunction with the CAP are described.

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# THE DEVELOPMENT OF PLASMAS FOR OPTICAL EMISSION

## DETERMINATION OF TRACE ELEMENTS

### CHAPTER 1

## 1.1 INTRODUCTION

Plasmas possess physical and spectroscopic properties that make them useful as atom generators and excitation sources for elemental trace analysis. In this chapter, the development and analytical applications of various types of plasma are discussed.

### Definition of a plasma

A plasma may be defined as any luminous gas in which a fraction of the atoms or molecules are ionized. This definition covers a wide range of hot gases, in which the energy is high enough to cause significant ionization and emission of radiation.

### Classification of plasmas

Plasmas used for trace analysis may be classified into two main groups: (i) non'flame-like' plasmas and (ii) 'flame-like' plasmas. The former are plasmas generated by conventional dc arc discharges, high voltage ac arc and spark plasmas. These have had a long history of successful analytical applications, however as the work reported in this thesis is concerned with the type (ii) plasmas, type (i) will only be dealt with briefly in this review. The type (ii) plasmas can be further sub-divided according to the mode by which power is coupled to them.

DC transferred plasmas

Single electrode high frequency plasmas

Plasma/combustion flames

Inductively coupled plasmas (RF plasma torch)

Low wattage microwave plasmas

## 1.2 (i) NON 'FLAME-LIKE' PLASMAS

### 1.2.1 (a) the dc carbon arc

The carbon arc consists of two rod electrodes arranged vertically and coaxially and separated by a small gap. The electrode material is usually graphite but sometimes copper

or silver is used. The arc operates either in air, or in an inert gas, or mixture of gases normally at atmospheric pressure. When a voltage is applied to the electrodes and the gas is ionized to make it conducting, current flows across the gap, heating the electrode tips and gas to a high temperature. Commonly the arc has a current capacity of 12 to 15 amps with a potential drop of about 50 volts across the plasma. The dc arc is analytically more sensitive than other arcs or sparks, but its precision is generally poorer than that obtainable in other plasmas, 5% being typical for ideal samples. Either electrode can carry the sample, but the anode is usually chosen because of the greater heat energy available, which results in more rapid volatilization. The dc arc burning in air, emits strong CN bands which mask a large and valuable portion of the spectrum. This difficulty has been overcome<sup>(1)</sup> by enclosing the electrodes in a chamber purged with argon. These arc chambers have come into widespread use and are commercially available.

### 1.2.2 (b) The electric spark

The electric spark is distinguished from the dc arc by its intermittency, by the fact that it is not self-sustaining, and by much higher voltage and current requirements at breakdown. The spectrum is similar to that obtained with the dc arc, but shows more ion lines. The electrodes can be made from any conducting material and the gap between the electrodes must be small enough for the gas to break down under the applied voltage. Normally voltages in the region of 500-30,000 are used with electrode separations of 2-5 mm. The spark is produced by repeatedly charging and then discharging a capacitor across the analytical gap. The sample for spark analysis must be conducting, or made to conduct by briquetting with a suitable

conducting powder such as graphite. Solution samples are usually analysed by the rotating disk method. In this technique a small disk of graphite is rotated slowly by means of a motor while its edge dips into the sample solution contained in an ignition boat. A counter electrode is mounted a few mm above the surface of the disk which is the sparking surface. Baer and Hodge<sup>(2)</sup>, have published detection limits for several elements analysed by this technique (see Table 1.1).

TABLE 1.1 - DETECTION LIMITS FOR SEVERAL ELEMENTS, USING  
THE ROTATING DISK ELECTRODE<sup>(2)</sup>

| <u>Element</u> | <u>Wavelength</u><br><u>(mm)</u> | <u>Detection</u><br><u>limit (ppm)</u> |
|----------------|----------------------------------|----------------------------------------|
| Ag             | 328.0                            | 0.1                                    |
| Al             | 309.2                            | 0.3                                    |
| Ba             | 455.4                            | 0.05                                   |
| Bi             | 306.7                            | 2.5                                    |
| Cd             | 228.8                            | 0.5                                    |
| Cr             | 283.5                            | 0.5                                    |
| Fe             | 259.9                            | 0.5                                    |
| Mg             | 279.5                            | 0.005                                  |
| Mn             | 257.6                            | 0.1                                    |
| Ni             | 341.4                            | 0.5                                    |
| Pb             | 283.3                            | 5                                      |
| Sb             | 259.8                            | 2.5                                    |
| V              | 309.3                            | 0.25                                   |
| Zn             | 334.5                            | 5                                      |
| Zr             | 339.2                            | 0.25                                   |

### 1.3 (ii) FLAME-LIKE PLASMAS

Atmospheric flame-like plasmas may be generated in a variety of ways, and possess similar physical and spectroscopic properties. They are usually supported by nitrogen or inert gases and are characterised by high electronic excitation and gas temperatures. Many of these sources exist in local thermodynamic equilibrium (LTE), where the population density of the excited states, the distribution and dissociation products of molecules, the distribution of atoms and their ions can be described by a single temperature.

The use of combustion flames for trace analysis has been an important technique for the last forty years. The technique of flame photometry has been applied to the determination of trace constituents in aqueous and non-aqueous solutions. However, the flame as an atomisation and excitation source has its limitations. Flames such as the premixed air-acetylene and air-hydrogen do not have sufficiently high temperatures to atomise and excite some of the more refractory elements. Many elements form chemical compounds in the flame environment and this leads to a loss in analytical sensitivity. Plasmas possess temperatures that are sufficiently high to atomise and excite most of the elements in the periodic table, and when supported in inert gases yield a chemically inert environment which precludes the formation of non-volatile chemical compounds.

If plasmas are to be used for trace analysis, the sample should experience the high temperature of the source, with a residence time long enough for complete atomisation and excitation. Thus, the sample must be injected into the plasma and remain in this environment as long as possible. This condition is often difficult to achieve. In the plasmas

described in this thesis, the gases are heated internally, they expand and accelerate in a direction perpendicular to the exterior plasma surface. These high surface-temperature gradients develop an aerodynamic barrier to the aerosol particles. High injection velocities are often needed to overcome the rejection problem, although this can create instability or extinguish the plasma.

### Detection limits

The detection limit obtainable is a useful figure of merit in any analytical trace technique. The scientific value of experimentally determined detection limits is often questioned, because the values obtained depend upon the experimental conditions under which they are measured. Most are measured on solutions containing only the analyte elements; when a matrix is added the power of detection is often reduced. A notable example is the determination of tin by atomic absorption spectrometry. A reducing air-hydrogen flame gives a higher sensitivity than the air-acetylene or the nitrous oxide-acetylene systems. However, serious interferences are obtained in an air-hydrogen flame from most metals. With the less sensitive but hotter nitrous oxide-acetylene flame, interferences are much less pronounced. It is often advantageous, for the determination of tin alloys, ores etc. to utilize the hotter but less sensitive flame system.

If detection limits are made under carefully controlled experimental conditions which can be duplicated, and if the statistical basis for the detection limit is stated, then the values obtained are of real use. The detection limit provides the analyst with a numerical basis for comparing analytical techniques.

### 1.3.1 Transferred plasmas

Transferred plasmas encompass those generated by dc arc discharges which are then transferred away from the arc column. It is thus possible to view a 'flame-like' plasma without viewing the region of high emission background. Margoshes and Scribner<sup>(3)</sup>, Korolev and Vainshtein<sup>(4)</sup> independently developed methods for introducing aerosols of solutions into a 'plasma-jet' which was generated by the techniques originally described by Gerdien and Lotz<sup>(5)</sup> and Giannini<sup>(6)</sup>. In these plasmas, a dc arc was struck in a chamber between a graphite anode and a ring cathode. Figure 1.1 shows the type of electrode arrangement used. The arc was thermally compressed by cooling its surface with a tangential stream of inert gas or nitrogen. Thermal compression, or 'pinch' effect, restricted the current flow to an arc column of smaller cross section, thus increasing the current density and energy available per unit volume. The arc plasma formed was then transferred from the arc column zone, through the ring cathode by the tangential vortex coolant flow.

The original Margoshes and Scribner adaptation of the 'plasma-jet' can be seen in Figure 1.2. An argon-operated concentric nebuliser, was held within a water cooled chamber, and the nebuliser tip was surrounded and protected by a graphite anode. The cathode was a graphite disk, with an internal diameter of 5.5 mm, and was held by a water cooled brass ring. Helium was used as the coolant and was introduced tangentially through the hard-rubber 'plasma-jet' case. To prevent the arc from striking on the nebuliser, the nebuliser body and capillary tube were electrically insulated. The plasma was operated in the current range 10-25 amps, which gave the best stability and operating conditions. Solution was nebulised at an uptake rate

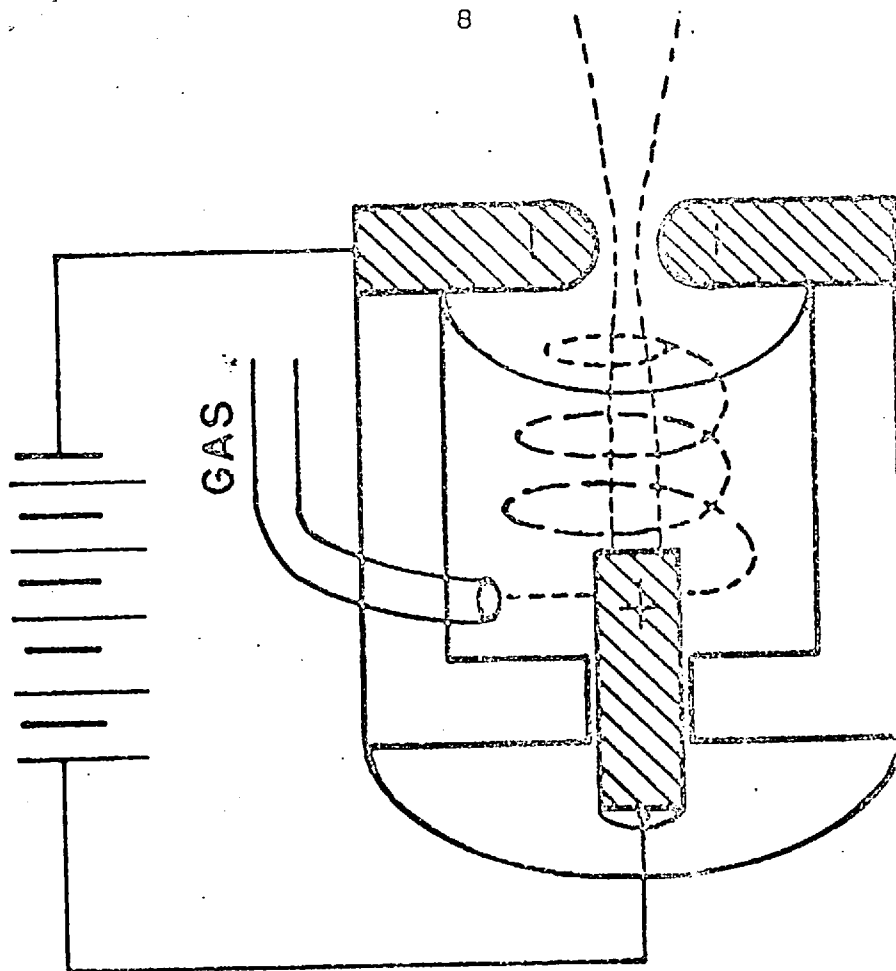


Figure 1.1 .  
Schematic diagram of a 'plasma-jet'

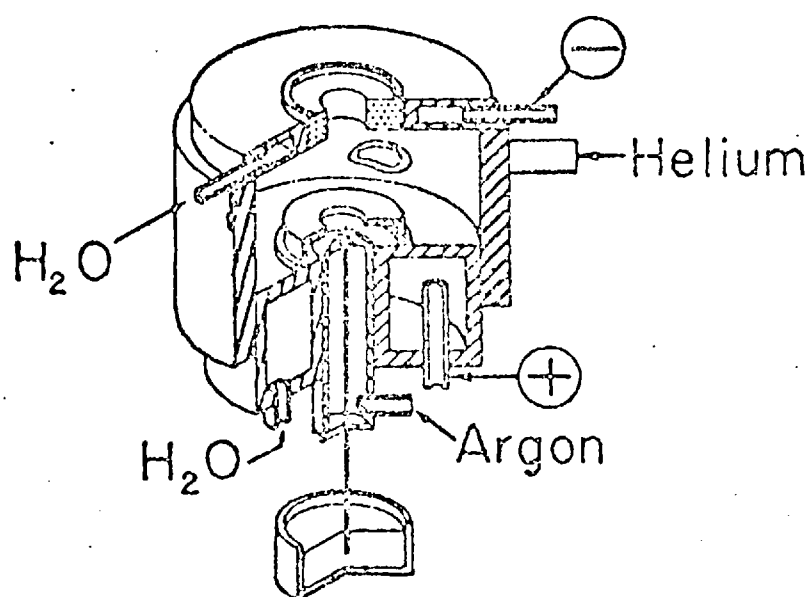


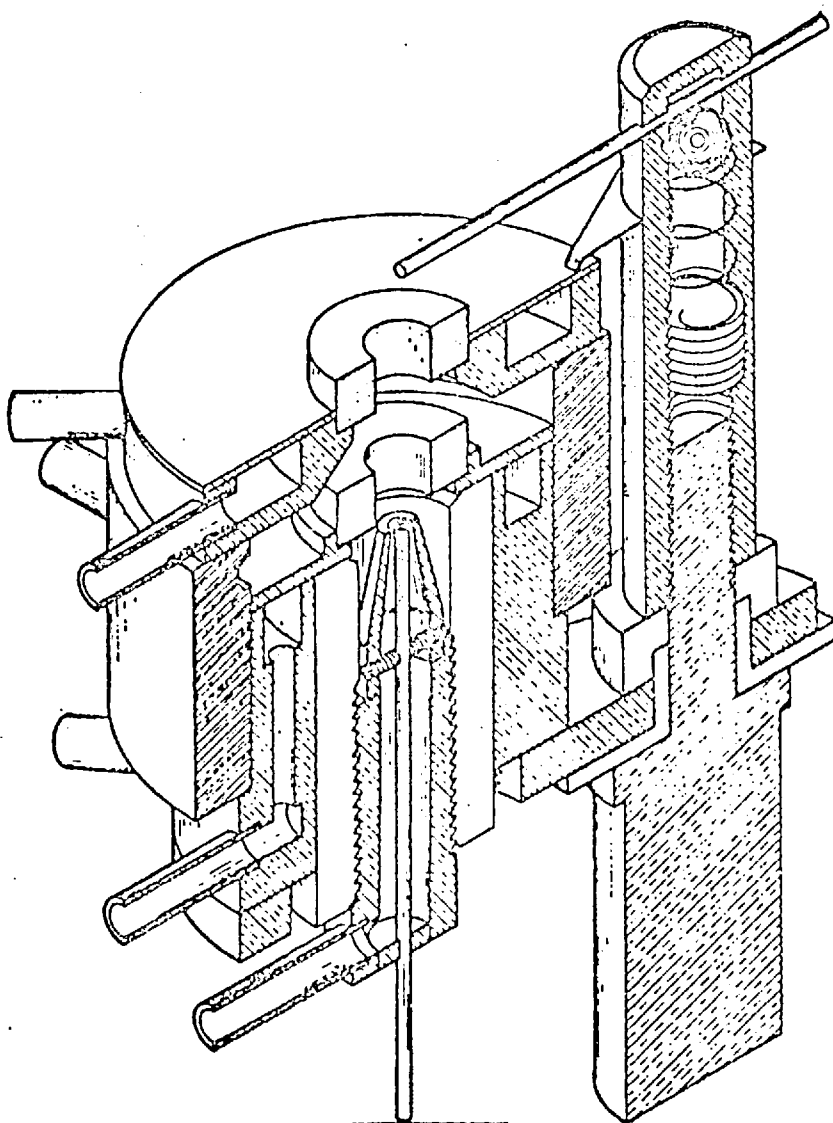
Figure 1.2. The original Margoshes and Scribner 'plasma-jet'

of  $1 \text{ ml. min}^{-1}$  using argon gas at  $3 \text{ l.min}^{-1}$ . A helium coolant flow rate of about  $20 \text{ l min}^{-1}$  was used to create the thermal 'pinch'. Under these conditions the 'plasma-jet' produced a flame approximately 1 cm high and roughly conical in shape. The arc contacted the cathode by a streamer from the jet 'flame' to the top of this electrode; an extremely bright spot marked the contact point. The point moved around the ring cathode, and since the streamer had a resulting magnetic field, the plasma 'flame' moved as the streamer wandered over the surface of the cathode.

In 1961 Owen<sup>(7)</sup> published a paper which showed that a considerable improvement in stability could be achieved if the plasma was transferred to another electrode. Owen constructed a consumable graphite electrode which was fed into the jet about 5 mm above the cathode surface. Discharge stability resulted from the elimination of the arc streamer. This consumable graphite rod was replaced by a more durable tungsten electrode which was electrically connected to the cathode ring. Owen's modification can be seen in Figure 1.3.

Margoshes and Scribner<sup>(8)</sup> subsequently modified the Owen design (see Figure 1.4). The upper cathode was placed axially and was water cooled. The ring electrode, originally the cathode, was allowed to assume its own potential, thus it floated electrically and was identified as the control ring. This plasma was renamed a gas-stabilised arc discharge and was used to determine the nickel and chromium content of stainless steels. Precisions in the range 1-2% being obtained.

Other workers have used these discharges, notably Maecker<sup>(9)</sup>, Riemann<sup>(10)</sup>, Heemstra et al<sup>(11)</sup> and Muntz<sup>(12)</sup>. Marinkovic et al<sup>(13)</sup> have reported detection limits for several elements, with a gas stabilised arc discharge. The plasma was



Sectional drawing of Owen's gas stabilised arc plasma.

Figure 1.3.

operated at low current ca. 3 amps, with a potential drop of 80 volts between the electrodes. Potassium chloride solution was used to reduce the high background emitted by the plasma; Ar, H, and O lines in the spectrum disappeared when a 0.25 M solution was nebulised into the discharge. Temperature measurements showed the arc to be about 4000 K and this was reduced to 3100-3300 K when potassium chloride was sprayed. Table 1.2 shows the detection limits for several elements, with and without the addition of potassium chloride.

TABLE 1.2 - Detection limits for a gas stabilised arc discharge<sup>(13)</sup>,  
with and without potassium chloride

| <u>Element</u> | <u>Wave-length<br/>(nm)</u> | <u>Det.lim.<br/>Water<br/>(ppm)</u> | <u>Det.lim.<br/>0.25M<br/>KCl (ppm)</u> | <u>Det.lim.<br/>0.5M<br/>KCl (ppm)</u> | <u>Det.lim.<br/>1M<br/>KCl (ppm)</u> |
|----------------|-----------------------------|-------------------------------------|-----------------------------------------|----------------------------------------|--------------------------------------|
| Al             | 396.2                       | 0.35                                | 0.005                                   | 0.014                                  | 0.05                                 |
| Ca             | 422.7                       | 0.03                                | 0.0001                                  | 0.0002                                 | 0.0004                               |
| Cr             | 425.4                       | 0.08                                | 0.004                                   | 0.006                                  | 0.01                                 |
| Cu             | 510.6                       | 1.0                                 | 0.4                                     | 0.6                                    | 1.6                                  |
| Li             | 670.8                       | 0.0012                              | 0.00003                                 | 0.0006                                 | 0.00012                              |
| Mn             | 403.1                       | 0.08                                | 0.004                                   | 0.007                                  | 0.013                                |
| Mo             | 390.3                       | 0.2                                 | 0.04                                    | 0.12                                   | 0.8                                  |
| Nb             | 405.9                       | 1.0                                 | 0.3                                     | 2.1                                    | 5.0                                  |
| Sr             | 460.7                       | 0.1                                 | 0.0004                                  | 0.0006                                 | 0.001                                |
| Ti             | 399.9                       | 1.1                                 | 0.2                                     | 0.7                                    | 2.4                                  |
| V              | 437.9                       | 0.27                                | 0.07                                    | 0.04                                   | 0.3                                  |
| W              | 400.9                       | 1.2                                 | 1.1                                     | 2.4                                    | 6.0                                  |

A similar arrangement to the gas stabilised arc was described by Elliott<sup>(14)</sup>. This design (see Figure 1.5) showed the cathode positioned toward the side of the central plasma column axis. The dc arc was bent at right angles and a 'flame-like' plasma was formed above the bent primary zone. Again, the plasma was generated in a similar manner to Owen's arc

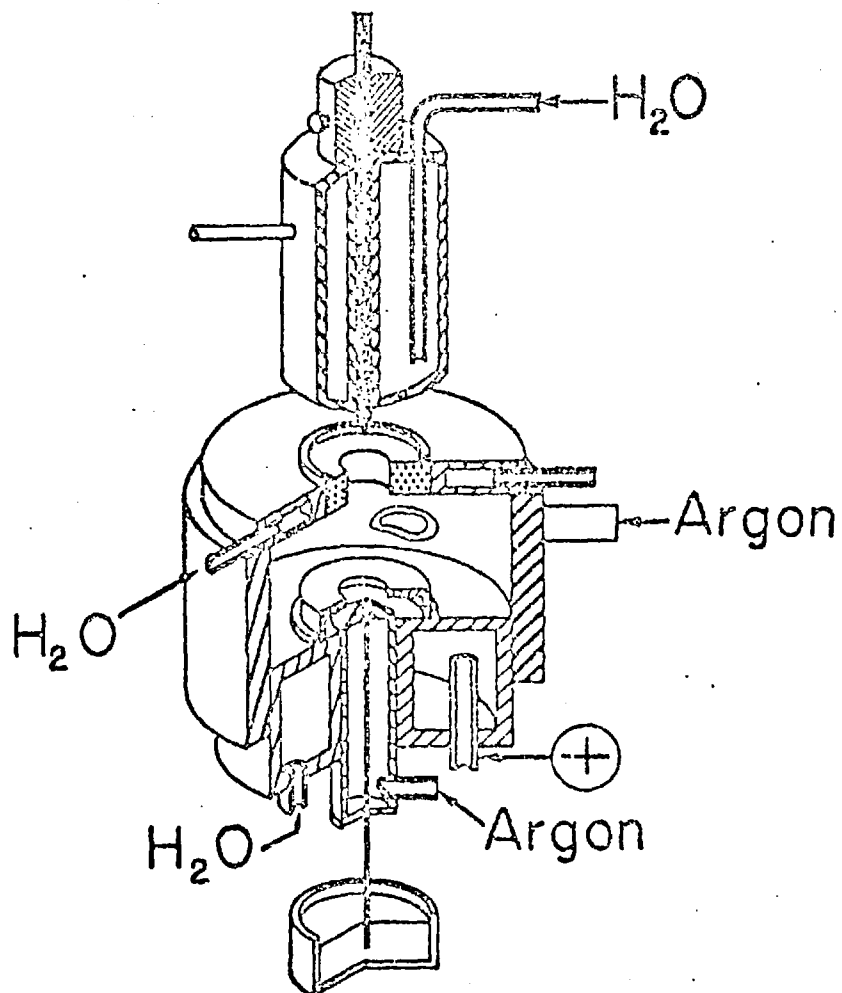


Figure 1.4. Gas-stabilised arc discharge.

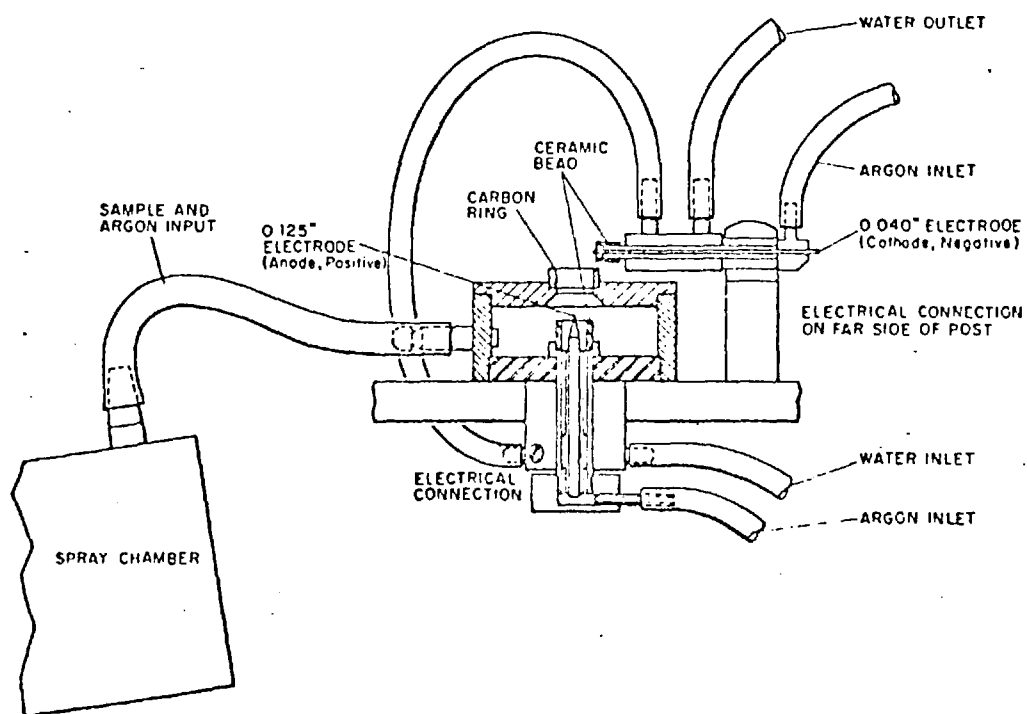


Figure 1.5. Elliott's 'Spectra Jet'.

plasma and the thermal compression of the arc column was provided by a coaxial flow of argon. The aerosol particles were generated by a pneumatic nebuliser, and were partially desolvated by passing them through a heated spray chamber and reservoir. The sample was then introduced tangentially into the 'jet-mixing' chamber. The solvent vapour was also allowed to pass into the 'jet-mixing' chamber, and no attempt was made to remove the solvent vapour. Elliott concluded that the sample particles were turbulently mixed with the plasma column at the base of the thermal pinch ring. This conclusion is difficult to envisage because the plasma possesses its highest temperature and current density within this region, and an aerodynamic barrier to the injection of the sample into the plasma itself should be present. However, the 'flame-like' plume that extended above the bent primary dc arc column should have been more receptive to the introduction of the sample particles. The Elliott plasma was the first to provide a physical separation of the main plasma and the dc primary column. Thus the intense argon recombination continuum which exists in the primary column was spatially resolved from the 'flame-like' plasma, where much greater line to background ratios were observed.

In an effort to increase the operational lifetime of the 'plasma-jet', Yamamoto<sup>(15)</sup> produced a new design (Figure 1.6). The primary arc discharge was formed between a copper anode and a bar-type thoriated tungsten cathode. Argon was used for sample nebulisation and as the tangential coolant gas. Yamamoto's plasma was free from electrode erosion, as shown by the absence of lines of the electrode materials from the spectrum. Electrode erosion was prevented by adjusting the sample and coolant gas flows so that the sample was carried from the discharge region before it impacted the anode or cathode. The plasma operated at

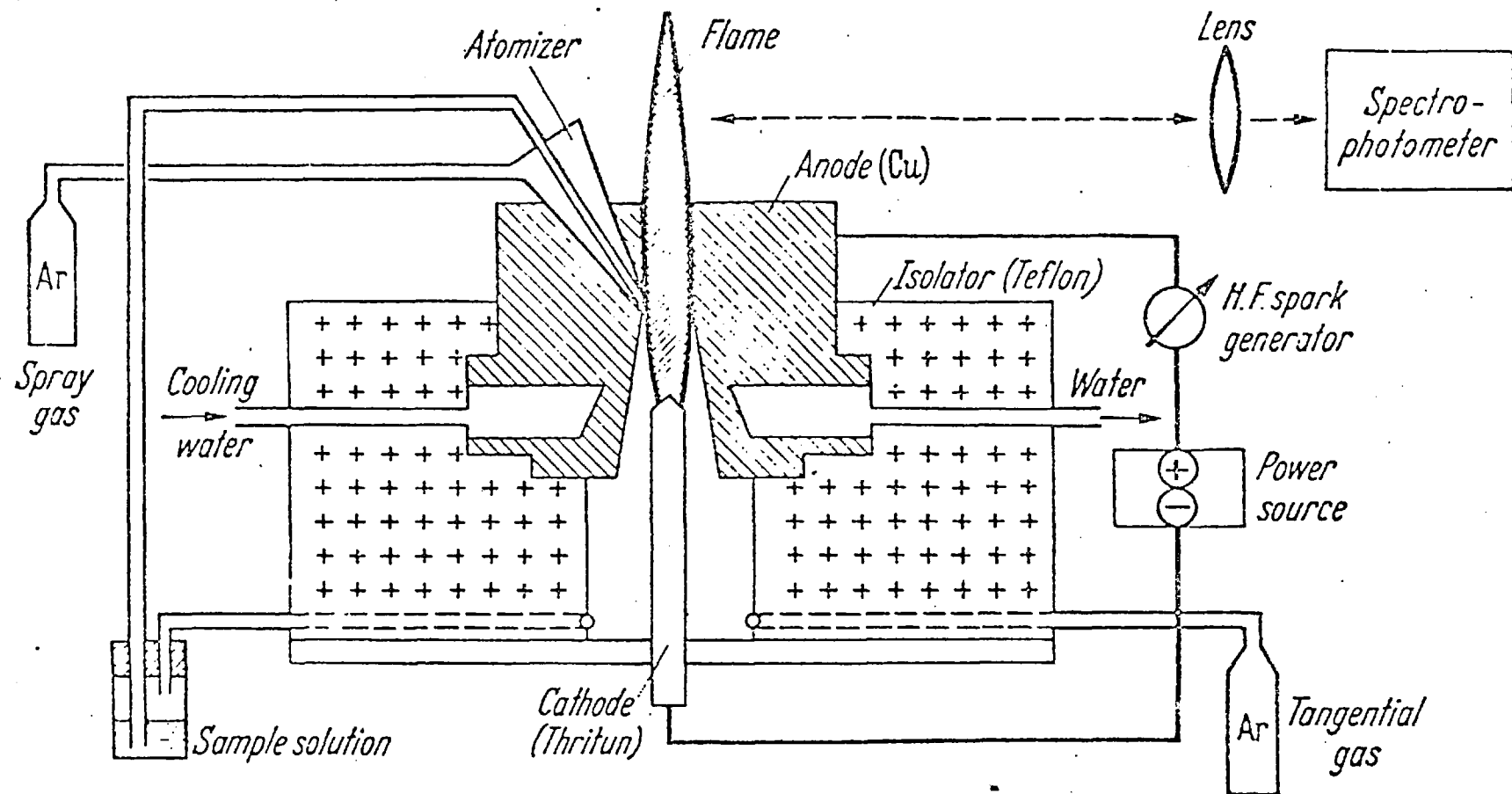


Figure 1.6. Yamamoto's 'Plasma-Jet'

very high currents in the range of 200-500 amps at a voltage drop of 23, and a generator output of 50 kw.

Kranz<sup>(16)</sup> in 1964, introduced another version of a transferred plasma which can be seen in Figure 1.7. The arc was ignited between the copper anode<sup>(2)</sup> and the cathode<sup>(1)</sup>, and the two copper discs<sup>(3)</sup> served as stabilisers. Tangential ports were provided in these discs for the introduction of nitrogen with an excess pressure of one torr. The arc plasma formed was transferred by the injected gas through the base of the inserts<sup>(5)</sup> into the atmosphere, perpendicular to the arc axis. Thus any material from the electrodes was ejected through the radial openings, leaving the plasma free of electrode impurities. The discharge was very stable for nitrogen flows between 5 to 12 l min<sup>-1</sup> and at arc currents of 20-60 amps. A nearly laminar plasma column approximately 15 cm long was formed, with a reported axial temperature of 6500 K at the exit. Kranz recommended the introduction of the sample with the tangentially injected nitrogen because he recognised the difficulties involved in injecting aerosol samples into the axial channels of plasmas. However, he did not discuss how effectively the aerosol particles penetrated the arc column.

Valente and Schrenk<sup>(17)</sup> obtained excellent detection limits in a very economical plasma that operated at a total argon flow rate of approximately 2.5 l min<sup>-1</sup>. The anode enclosure shown in Figure 1.8 consisted of a 1 cm internal diameter alumina tube enclosed at one end by a water cooled anode support, and a graphite electrically insulated water cooled orifice at the other end. The nebulised sample and most of the argon support gas entered the chamber tangentially at a point just below the central orifice, at a flow rate of approximately 1 l min<sup>-1</sup>. A small flow of argon (100 ml min<sup>-1</sup>) was injected at the anode support to prevent incoming samples from striking the hot alumina tube. The cathode enclosure

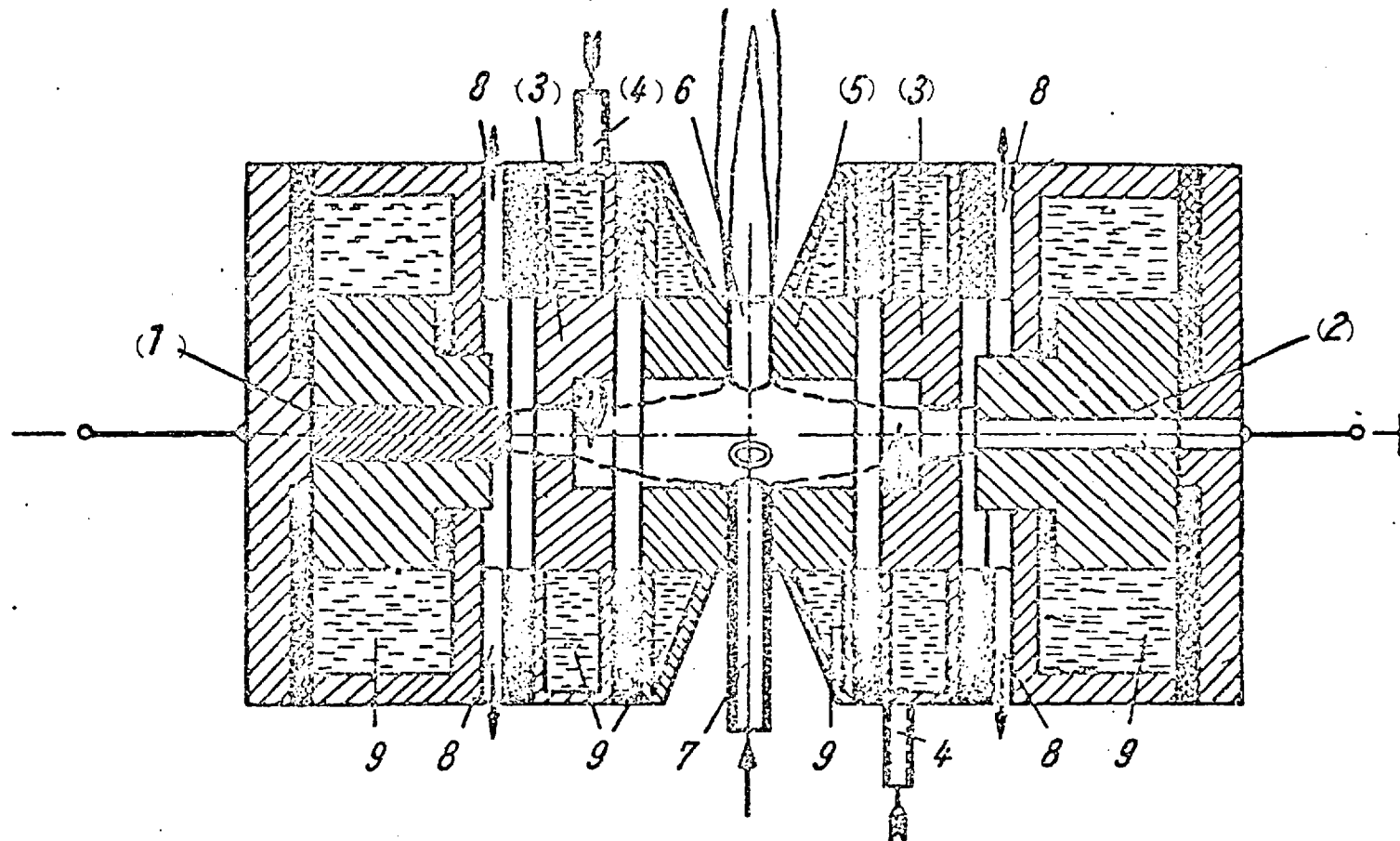


Figure 1.7. The Kranz transferred plasma.

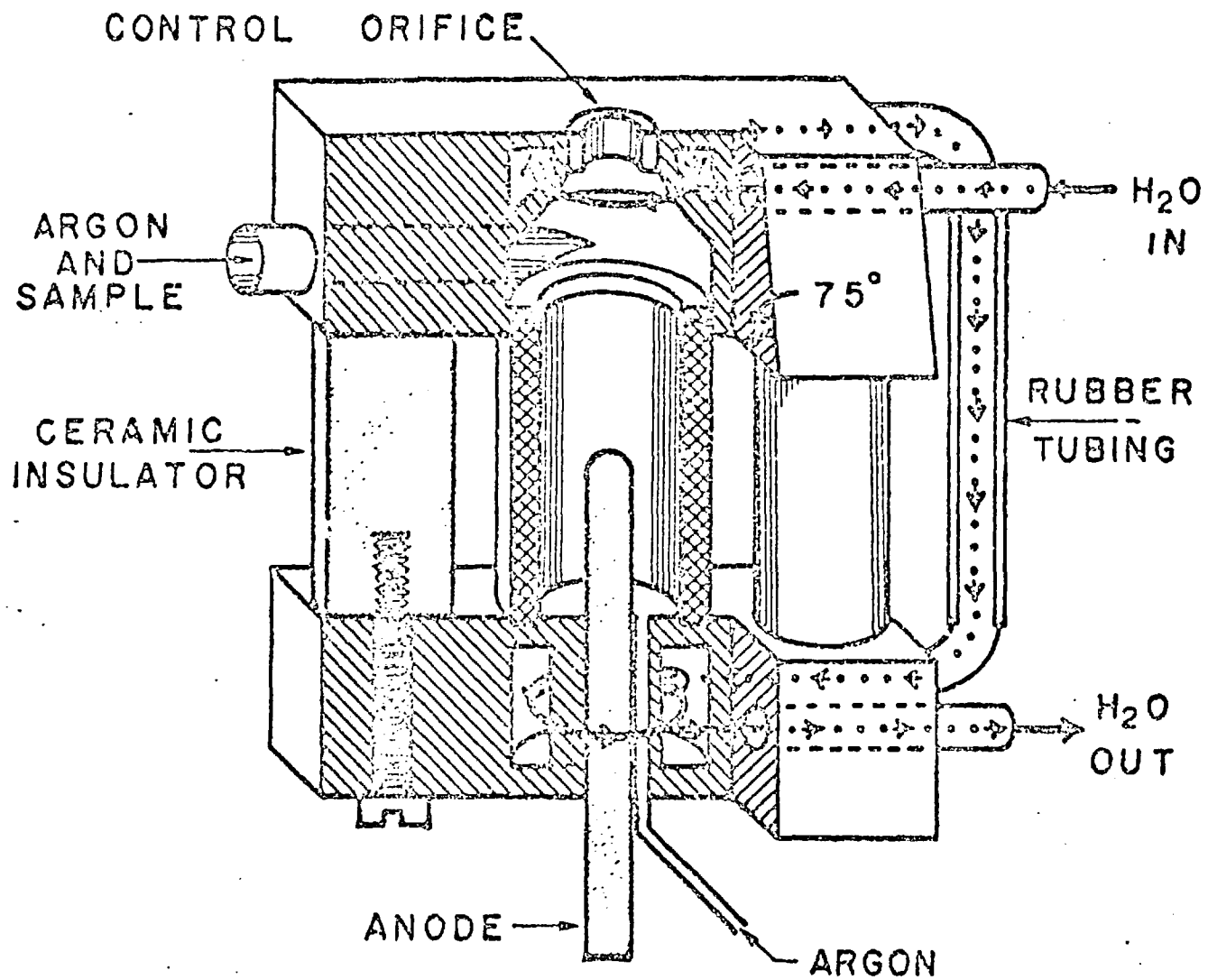
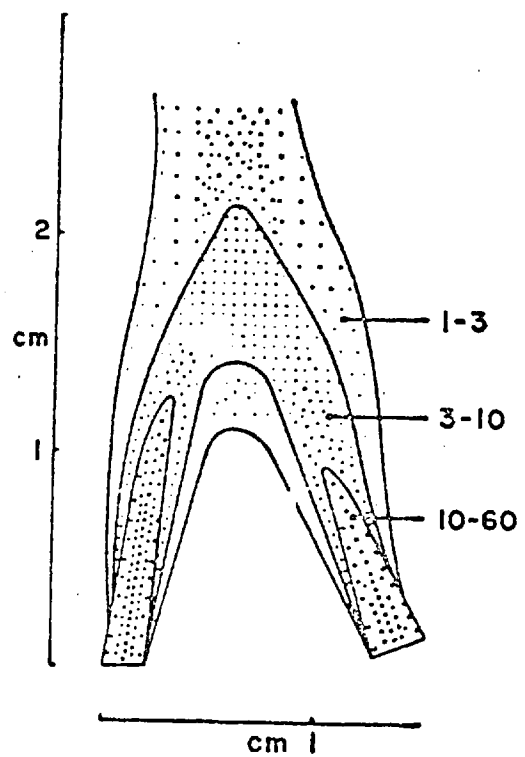
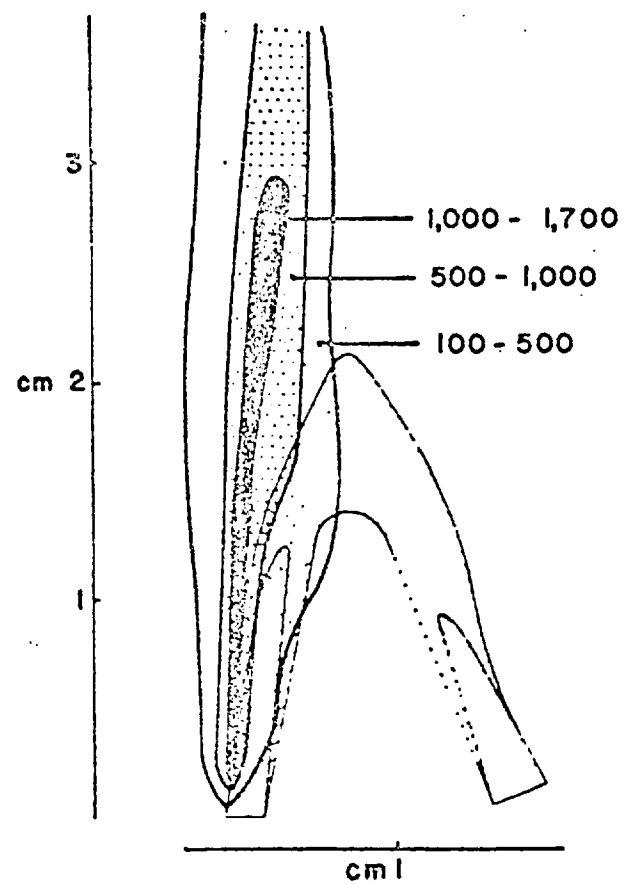


Figure 1.8.  
Anode chamber of the Valente-Schrenk plasma.

was identical to that of the anode. Ignition of the plasma was accomplished by aligning the anode and cathode chambers and then inserting one into the other for initiation of the discharge. The two assemblies were then drawn apart to produce a plasma 10-15 mm long. After the arc was ignited, one of the plasma units was rotated about the centre of the discharge to a position such that the angle between the axis of both jets was approximately  $30^{\circ}$ . This reduced turbulence by allowing the hot gases to expand in a common direction. Samples sprayed directly into the plasma immediately quenched the discharge, and the introduction of a wet aerosol from an indirect nebuliser resulted in poor sensitivity. A sample introduction system adapted from the one described by Veillon and Margoshes<sup>(18)</sup> was used to produce a dry aerosol, which was introduced into the anode chamber of the discharge by means of the tangential gas flow. This method of sample introduction resulted in an asymmetrical distribution of free atoms, as demonstrated in Figure 1.9, which also shows that there was quite a favourable spatial separation of background maxima and line emission maxima, resulting in unusually good detection limits. An analytical calibration graph for zinc was linear from 0.01 ppm to 20 ppm, a range of greater than three orders of magnitude. The detection limits obtained for several elements are shown in Table 1.3.



A



B

Figure 1.9. Plasma continuum background (A).  
Ca 4226.7 line emission intensity distribution (B).

TABLE 1.3 - Detection limits for the Valente/Schrenk plasma

| <u>Element</u> | <u>Wavelength nm</u> | <u>Det.lim. ppm</u> |
|----------------|----------------------|---------------------|
| B              | 249.77               | 0.4                 |
| Ca             | 393.37               | 0.002               |
| Cd             | 228.80               | 0.03                |
| Cr             | 425.43               | 0.003               |
| Fe             | 371.94               | 0.005               |
| La             | 399.58               | 0.07                |
| Li             | 670.78               | 0.001               |
| Ni             | 341.48               | 0.003               |
| Pb             | 283.31               | 0.03                |
| U              | 424.16               | 0.5                 |
| Y              | 371.03               | 0.008               |
| Zn             | 213.86               | 0.01                |

Merchant and Veillon<sup>(19)</sup> have recently investigated a dc transferred plasma for solution analysis. The plasma components are shown in Figure 1.10. The cathode and anode were constructed from graphite, the anode being insulated from the brass body of the unit by a bakelite insulator. Both the anode and cathode were water cooled. Very poor detection limits were obtained from emission and absorption measurements. This was attributed to the dry aerosol particles not penetrating the plasma boundary.

#### Recent applications of dc plasmas

Goto and Atsuya<sup>(20)</sup> have applied the 'plasma-jet', developed by Yamamoto, to the analysis of rare earth elements in a monozite sample. The detection limits obtained for several elements in solution, are given in Table 1.4.

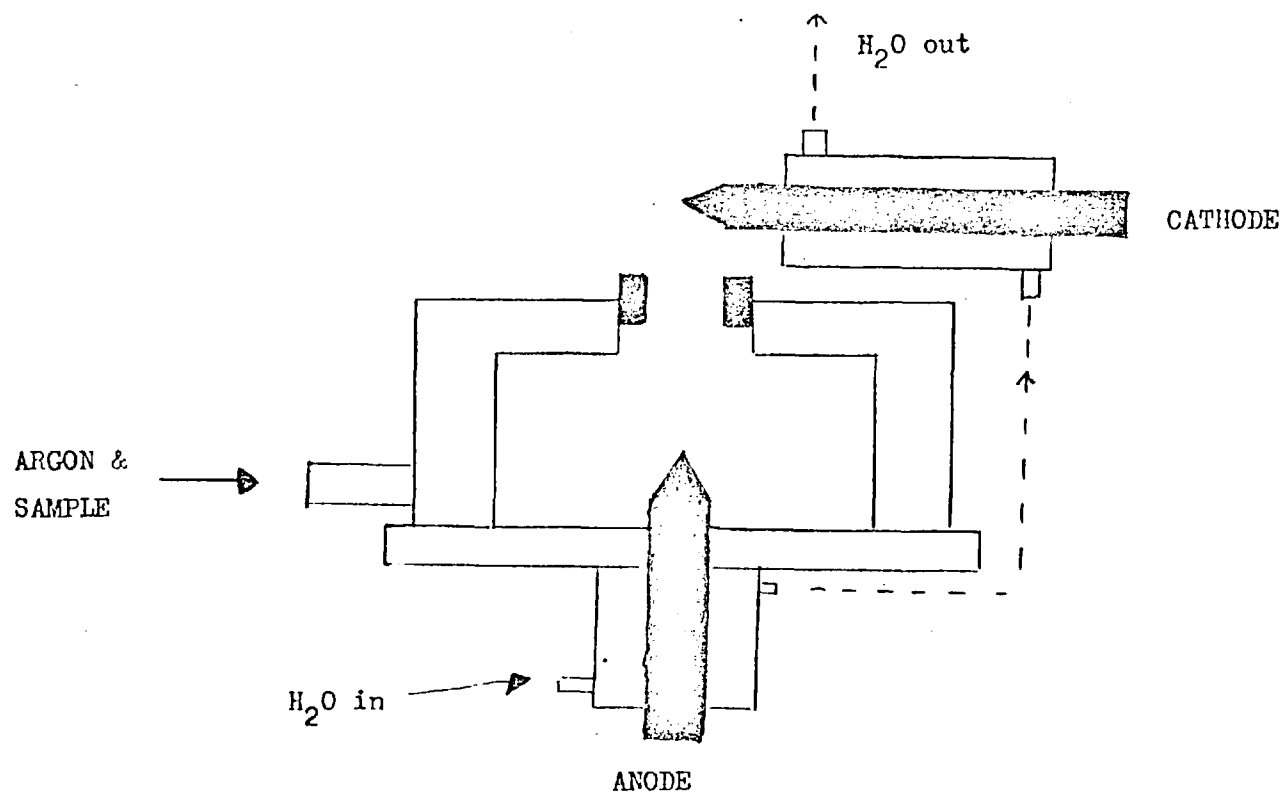


Figure 1.10.

Merchant-Veillon plasma.

TABLE 1.4 - Rare earth metal detection limits for a 'plasma-jet' (20)

| <u>Element</u> | <u>Wavelength nm</u> | <u>Det.lim. ppm</u> |
|----------------|----------------------|---------------------|
| Y II           | 360.1                | 0.1                 |
| La II          | 399.5                | 0.5                 |
| Pr II          | 440.8                | 2.7                 |
| Sm II          | 443.3                | 2.0                 |
| Ce II          | 218.0                | 3.7                 |

Marinkovic and Zmbova<sup>(21)</sup> have used their gas stabilised arc to determine trace impurities of Al, B, Be, Co, Cr, Fe, In, Mg, Mn, Ni, Pd, Rh, and Zn in high purity gold. When a solution containing 2% gold was sprayed into the plasma, detection limits for the above elements ranged from 0.01 to 1 ppm. However, when a solution containing 2% of gold and 0.25 M potassium chloride was nebulised, detection limits were decreased by about one order of magnitude.

A novel dc capillary arc plasma has been described by Jones and Dahlquist<sup>(22)</sup>. The plasma was used in conjunction with a remote sampling device which produced fine particles directly from the surface of a solid metal sample in which the sample acted as the cathode of a dc arc discharge. Rapid movement of the cathode spot produced uniform sampling over a well defined area. The solid particles were transported to the capillary arc discharge, in a stream of argon. For steel analysis it was found that matrix, interelement, and self-absorption effects in the aerosol generator/capillary arc plasma (AG/CAP) were very low when compared to the best values obtained with conventional sources. The system was very economical to operate, the total argon flow rate was about  $2.5 \text{ l.min}^{-1}$ , and electrode wear was negligible. The tantalum cathode however did require resharping every 6 hours, or every time the plasma was ignited.

## DC plasmas for atomic absorption analysis

Wendt and Fassel<sup>(23)</sup> and other workers have used high frequency plasmas as atom reservoirs for atomic absorption analysis. The dc arc discharge has received relatively little consideration as an atom reservoir. Marinkovic and Vickers<sup>(24)</sup> have described a long path-length plasma modified from the previous design<sup>(25)</sup>, for use as an atom reservoir for absorption measurements. Results indicated that the plasma sensitivity was not appreciably different from that obtained with chemical flames. The high background emission from plasma sources creates a problem when absorption measurements are made using hollow cathode lamps, because the lamps give comparatively weak emission signals. This problem could be solved by measuring absorption above the emission zone of the plasma, but in this region interference problems are increased due to condensation of the analyte and matrix atoms.

### Summary

The reported 'average' axial temperatures of transferred plasmas are in the region 7000 to 9000 K. How effectively the sample experiences this temperature has not been clearly delineated. Turbulence at the orifice through which the plasma is transferred is required for the aerosol sample to penetrate the thermally constricted arc column.

The emission spectra of plasmas supported by noble gases exhibit a rather intense recombination continuum. This background poses limitations on the ultimate powers of detection unless spatial resolution of the line and background emission is achieved. The best detection limits were obtained in the economical dc arc, described by Valente and Schrenk, in which this spatial resolution could be readily achieved.

Sirois<sup>(26)</sup> has explored a Margoshes and Scribner type 'plasma-jet' for interelement effects. He showed that manganese could be determined in solutions of high chromium stainless steel

alloys, zinc-base die castings, wrought aluminium, nickel steel, silicon bronze and cast iron by using a single direct calibration graph. Sirois concluded that the atoms of the vaporised sample acted as independent emitting species and hence were not subject to spurious interelement effects.

### High frequency plasmas

#### Mechanism of excitation

Under the influence of high frequency alternating fields, free electrons and ions are caused to oscillate at the applied frequency. In this way, electrons may acquire energies sufficient to excite and ionize atomic and molecular species. Biondi<sup>(27)</sup> has shown that for the fields generally applied, the energy acquired by electrons before the field is reversed is approximately  $4 \times 10^{-3}$  eV for a 3000 M Hz applied field. These energies are obviously too small to cause any excitation or ionization. However, the actual excitation mechanism in high frequency plasmas takes advantage of a subtle phenomenon that does not prevail in the dc discharges.

In dc discharges, the electron that is accelerated towards the anode gains energy as it falls through the applied potential. The electron loses some of its energy by elastic collisions with atoms and molecules, but continues to gain net energy from the applied potential until it has acquired enough to ionize an atom or molecule in an inelastic collision. In high frequency fields the electrons also lose energy through elastic collisions, with atoms or molecules, the loss being of the order  $M_e/M_{atom}$  of the electron's energy. However it can be shown theoretically that the kinetic energy of the electron increases on average between each collision. This gain results from an addition to the purely oscillatory velocity of the electrons brought about by a change in the time-phase relationships

at collision between the motion of the electron and the applied fields. An exact analysis in which collisions at all angles and the random motion of the electrons are taken into account, gives the result that, at a collision, the average electron increases its energy by twice the oscillatory energy<sup>(27)</sup>. After many thousands of such elastic collisions, the electrons can reach ionizing energies. Thus, to develop a high frequency excited 'flame-like' plasma it is in principle only necessary to transfer the fields efficiently from the HF generator to the flowing gas stream. This transfer has been achieved by means of coaxial cavities, waveguides, induction coils and capacitor loops. Depending on the physical circumstances electrodes may or may not be essential.

### 1.3.2 Single electrode plasmas

Plasma flames, generated by high frequency circuits at the end of appropriate conductors or electrodes, have been known since 1928<sup>(28-30)</sup>. Mavrodineanu and Boiteux<sup>(31)</sup> first suggested the use of this type of plasma as an excitation source for the analysis of solutions. Badarau et al in 1956<sup>(32)</sup> were the first to apply a single electrode plasma for the determination of trace elements. The physical properties were studied by other workers, notably Cristescu and Grigorovici<sup>(33)</sup>, Korolev and Zheenbaev<sup>(34)</sup>, Scholz<sup>(35)</sup>, and Roddy and Green<sup>(36)</sup>. In the period 1960 to 1965 several papers were published describing more advanced systems specifically designed for analytical purposes<sup>(37-40)</sup>.

In the system designed by Mavrodineanu and Hughes<sup>(41)</sup>, the plasma was established at the end of a conductor that formed part of the main inductor of a triode driven oscillator tank-circuit (see Figure 1.11). The frequency of operation was 30 MHz with a power output of 250 watts. It was surrounded by a quartz cylinder, the metal electrode on which the plasma was anchored participated

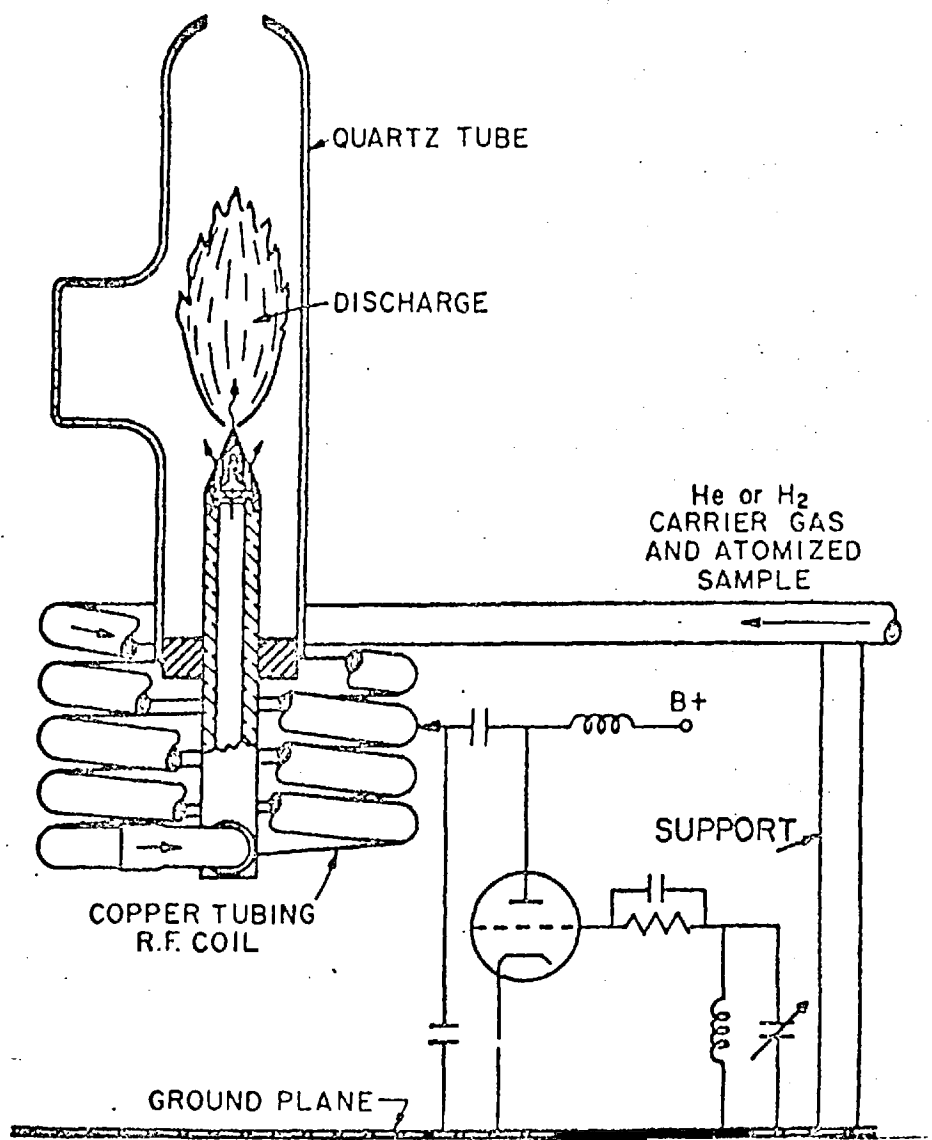


Figure 1.11. Mavrodineanu and Hughes 30 MHz single electrode plasma.

only slightly in the discharge, and direct sampling of the electrode tip was virtually insignificant at the power levels employed. Once the plasma was formed, stabilisation was achieved by tuning the radio frequency generator to match the impedance of the plasma.

Solutions were nebulised with helium and introduced into the grounded end of the  $\frac{3}{8}$ " tubular copper conductor of the tank-circuit inductor. The sample traversed the coil, then entered the plasma discharge through four small holes in the electrode tip. This particular method of sample introduction would not be expected to lead to efficient injection because systems that have employed similar schemes have shown that the emission of spectral lines from the sample predominates in the outer zone.

Solid samples were introduced into the plasma by substituting the metal electrode with various cratered tips machined from  $\frac{1}{4}$ " diameter graphite, into which the analyte was packed. During operation of the plasma, the sample slowly volatilised into the 'flame'. The system was used for the analysis of tin-lead solder, but no precision data or detection limits were given.

At the power levels normally used (200-500 watts), these plasmas exhibit vastly different gas and electronic temperatures. When molecular gases such as hydrogen or nitrogen are used, the energy received by the electrons from the high frequency field is transferred mainly through excitation of molecular vibration and through ionisation and dissociation processes. Therefore at atmospheric pressure, the electronic temperature should not be much higher than the translational gas temperature<sup>(42)</sup>. Hence, both thermal and electronic excitation should take place. When noble gas supports the plasma, the transfer of electron energy is rendered more difficult, thus the electron temperature may exceed gas temperatures

by an order of magnitude. Mavrodineanu and Hughes reported a gas temperature of approximately 2900 K for their helium plasma.

In 1964 West and Hume<sup>(43)</sup> described a 27 M Hz single electrode plasma torch, (see Figure 1.12). The plasma operated on nitrogen at power levels in the region of 500 watts. It appeared as a brilliant pink ribbon of light ca 3 mm in diameter and 8 cm high, surrounded by a much less brilliant area ca 2 cm in diameter and 12 cm in height. Conventional nebulisers were found to be unsatisfactory for sample introduction since, to obtain high stability in the plasma, a low gas flow rate of approximately  $2 \text{ l min}^{-1}$  was required. An ultrasonic nebuliser was used, which gave a sample introduction rate of approximately  $0.1 \text{ ml min}^{-1}$ . Preliminary results showed that 100 fold excesses of aluminium and phosphate had no effect on the emission intensities of calcium and strontium, indicating that the sample aerosol experienced a reasonably high temperature. Detection limits given for several elements can be seen in Table 1.5.

TABLE 1.5 - Detection limits obtained by West and Hume, with a 27 M Hz single electrode plasma torch

| <u>Element</u> | <u>Wavelength nm</u> | <u>Det.limit. ppm</u> |
|----------------|----------------------|-----------------------|
| Al             | 396.15               | 0.02                  |
| Au             | 267.6                | 0.02                  |
| Ca             | 422.7                | 0.005                 |
| Cd             | 228.8                | 0.1                   |
| Cu             | 324.8                | 0.001                 |
| Fe             | 372.0                | 0.015                 |
| Hg             | 253.6                | 0.2                   |
| V              | 437.9                | 0.015                 |

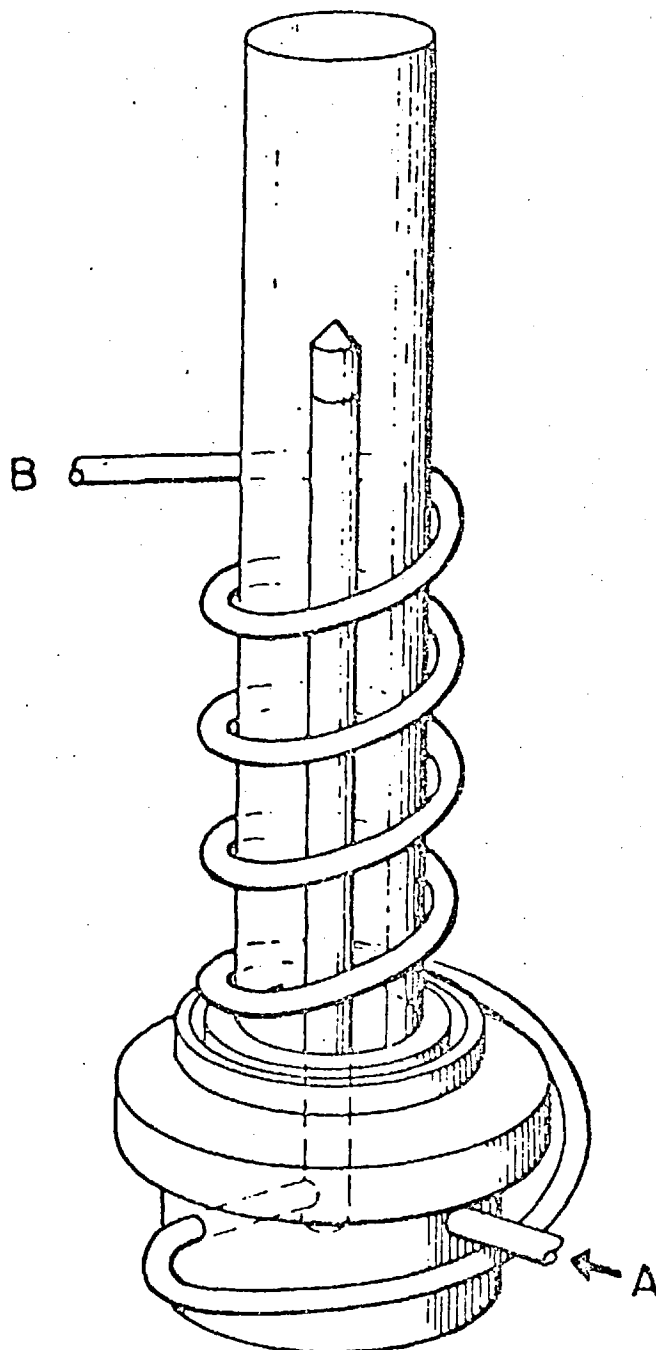


Figure 1.12. 27 MHz single electrode plasma.

Sample enters at A, cooling water circulates through the concentric copper tube B. The torch tip is constructed of molybdenum.

## Microwave excited single electrode plasmas

'Flame-like' single electrode plasma may also be generated at microwave frequencies. Early designs were published in 1951 by Cobine and Wilbur<sup>(44)</sup>. The generators employed were powered by commercial magnetrons operating at a frequency of 2450 M Hz. Mavrodineanu and Hughes<sup>(41)</sup>, Tappe and van Calker<sup>(39)</sup> and Jecht and Kessler<sup>(45)</sup>, independently described very similar systems based on the earlier designs of Cobine and Wilbur. Figure 1.13 shows a schematic diagram of the Mavrodineanu and Hughes version. The 2450 M Hz radiation from the magnetron was transmitted via a waveguide to the coaxial cavity. The gas stream flowed outward through the coaxial space, and the discharge was established at the conical tip of the central conductor. The cavity was tuned with an adjustable plunger.

Murayama<sup>(46)</sup> published a description of a microwave single electrode plasma, (see Figure 1.14) in which the discharge was generated at the tip of the coaxial line. Argon was used as the support gas and was introduced tangentially.

The electron temperature in these microwave plasmas exceeded the gas temperature as in the case of RF generated plasmas. According to Murayama, the excitation temperature along the axial channel of the plasma dropped from approximately 8000 K when the operating power was 50 W, to approximately 6500 K at 400 W. This suggests a trend towards 'thermalising' of the plasma at higher power levels. The gas temperature was independent of power and was measured by Murayama to be approximately 4600 K.

In a later paper, Murayama et al<sup>(47)</sup> used a microwave discharge plasma as an excitation source for spectrochemical analysis. Detection limits for twenty elements were given, most elements being in the range 1 to 0.01 ppm. Interelement effects were studied. Notably, the effect of the addition of 80 ppm of sodium was found to enhance signals from 100 ppm of zinc, barium,

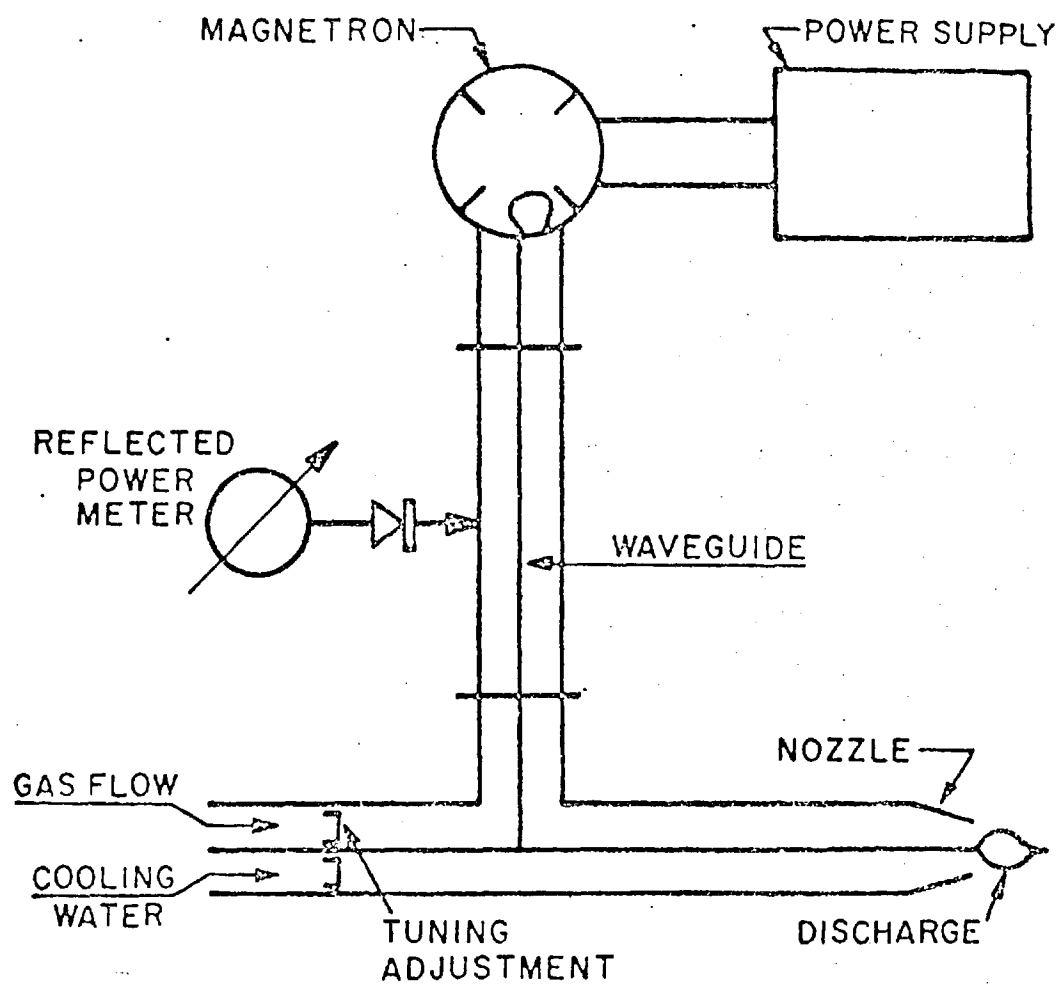


Figure 1.13. Schematic diagram of the Mavrodineanu and Hughes microwave plasma.

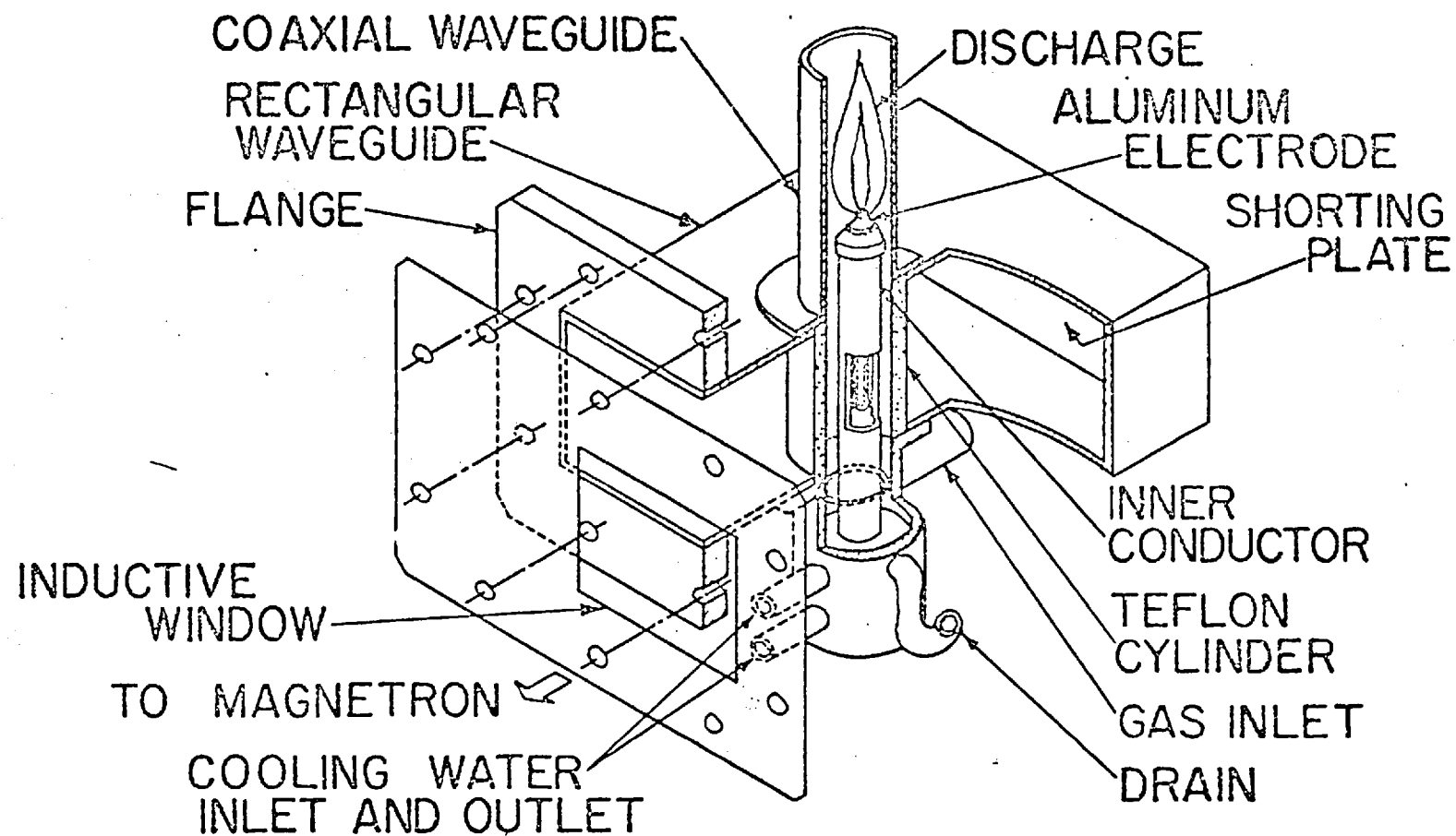


Figure 1.14. Murayama microwave plasma.

cadmium, mercury, aluminium, calcium and arsenic. Figure 1.15 shows the spatial enhancement of the As 228.8 nm line when sodium was present. The peak at the axial centre of the plasma showed that some of the sample apparently experienced higher electronic temperatures along the axial channel. This enhancement effect was not attributed to ionization suppression because similar results were obtained for other high ionization potential elements.

Figure 1.6 shows the effect of sodium, normally considered to be an ionization suppressant, which enhances the barium neutral atom lines approximately 5 fold. Surprisingly, the ion lines were also enhanced to an equal extent (Figure 1.17). Both the neutral atom and ion line emission of barium were highest near the outside of the plasma.

Murayama<sup>(48)</sup> published a paper in 1970 which showed that the addition of sodium to solutions of rare earth elements, enhances the emission intensities of the lightly charged ion-lines up to several orders of magnitude. Several interpretations of these effects were offered, in terms of measured and deduced physical properties of the plasmas.

### 1.3.3 Plasma-combustion flames

Mavrodineanu and Hughes<sup>(41)</sup> reported some preliminary observations on a single electrode plasma-combustion flame. This combination was achieved by burning a coal-gas flame on the plasma tip. Radio frequency energy was then coupled to the flame and a marked increase in light emission was achieved.

Rosenthal and Eyer<sup>(49)</sup> studied the effect of a 250 watt, 2450 M Hz microwave field on a sodium-seeded oxyhydrogen flame. The oxyhydrogen torch was confined laterally inside a quartz tube containing a small quantity of sodium chloride crystals. In this way the flame was constantly fed with sodium atoms. The power

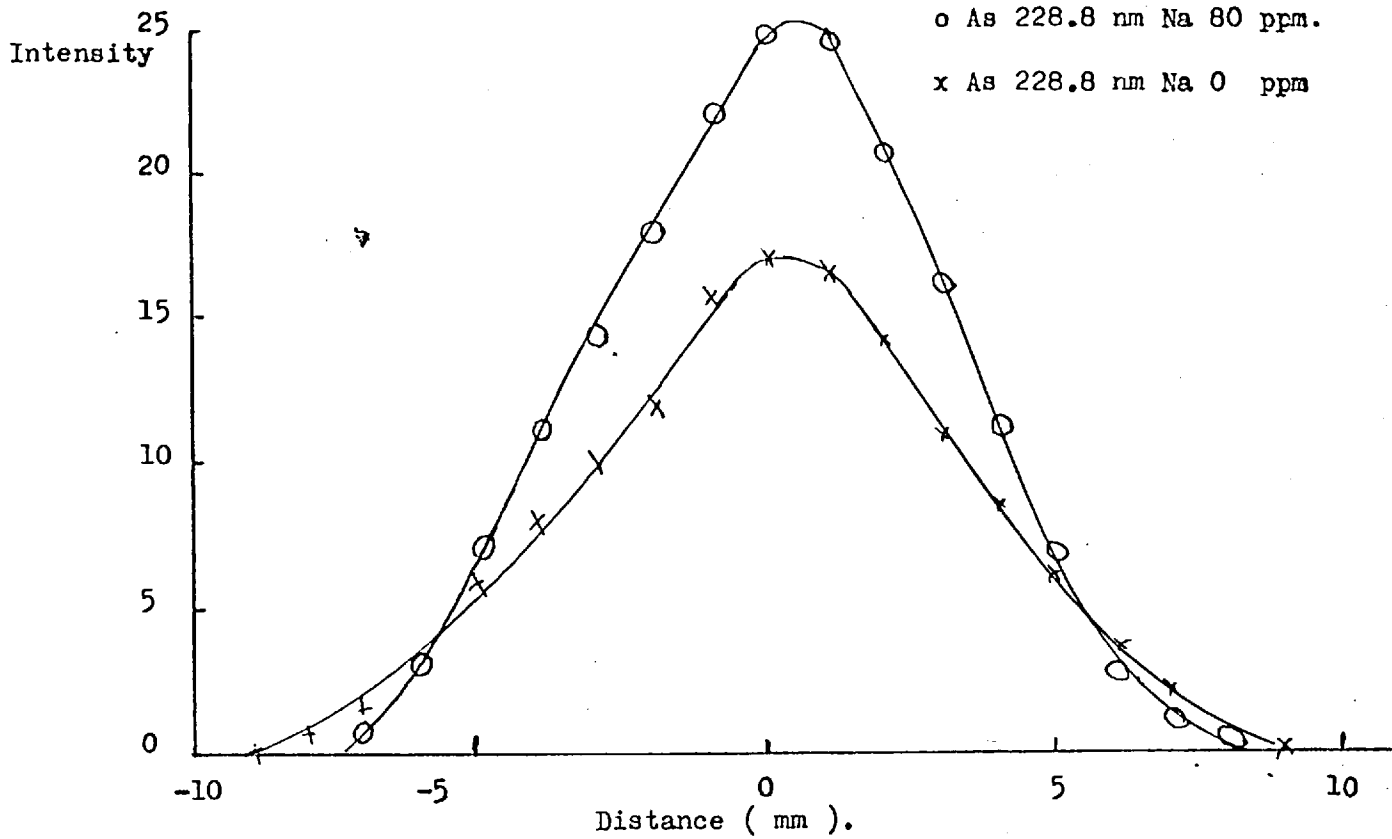


Figure 1.15. Enhancement of As signals in the presence of sodium.

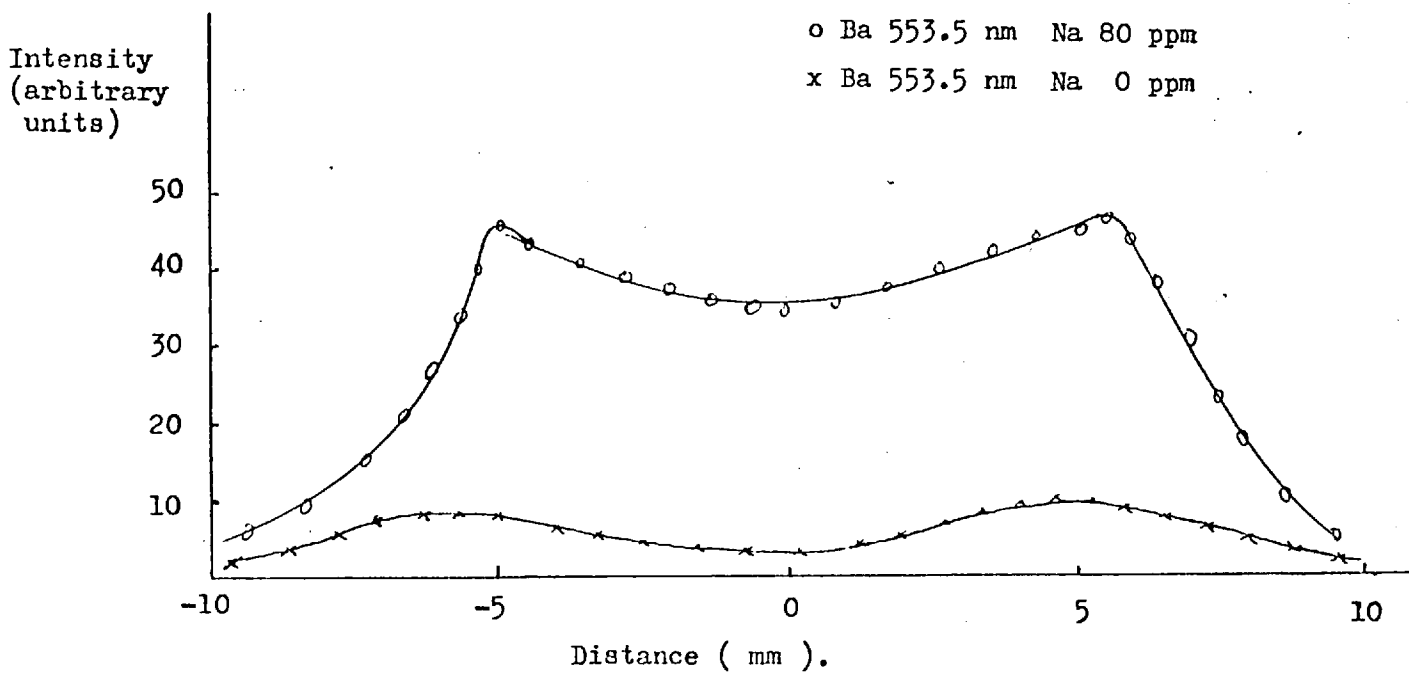


Figure 1.16. Effect of sodium on barium atom line emission profiles.

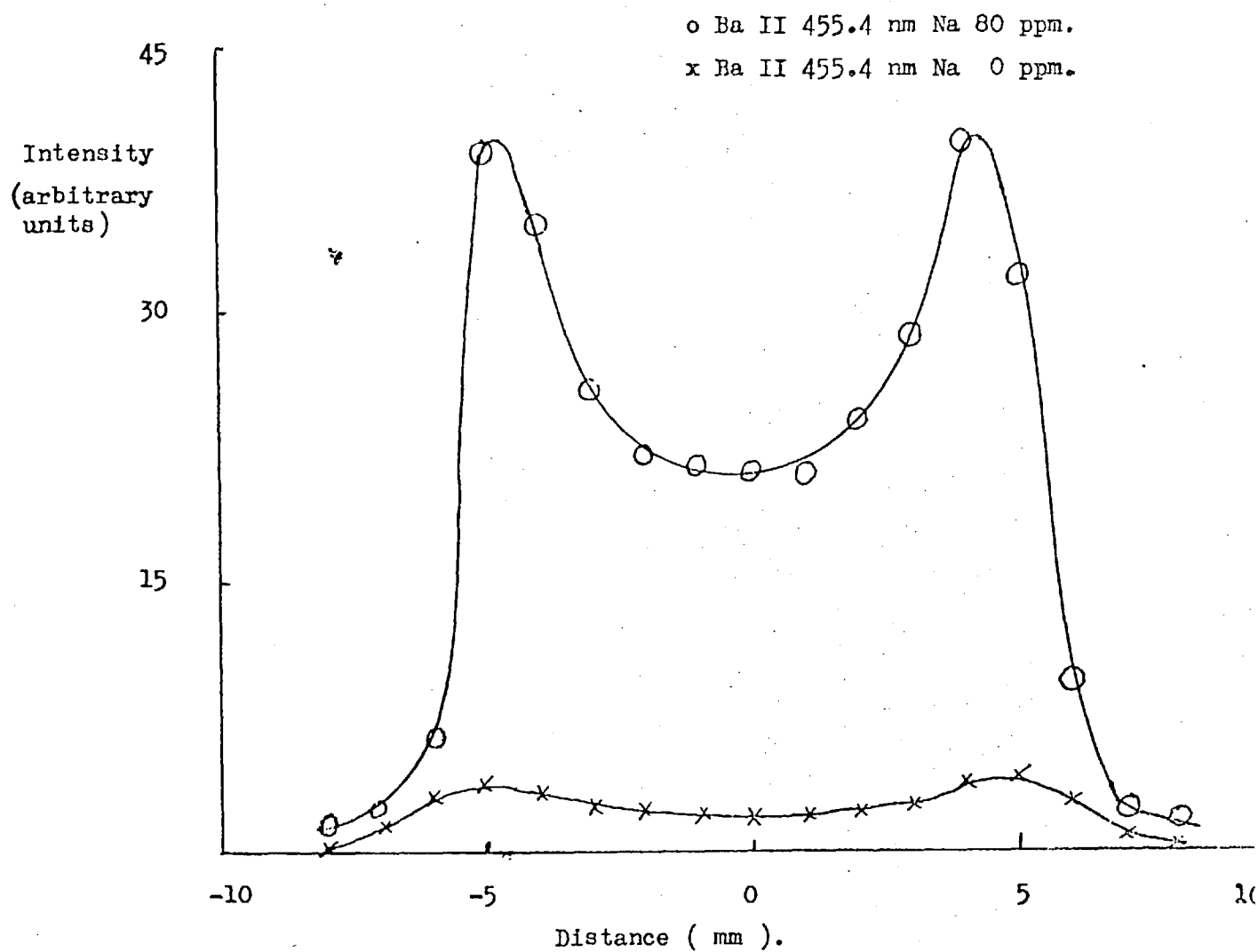


Figure 1.17. Effect of sodium on Ba ion line emission profile.

output from the magnetron was pulsed at 60 Hz, and when this was coupled to the flame, the brightness increased by a factor of 130. The enhancement was not limited to flames seeded with alkali metals, but appeared to be a much more widespread phenomenon.

#### 1.3.4 Inductively coupled (IC) plasmas

##### Formation

An IC plasma is formed inside a quartz tube which is placed inside an induction coil (see Figure 1.18). The coil is connected to a radio frequency generator, operating in the range 4-50 M Hz at power output levels of two to five kw. Ignition of the plasma may be accomplished by ionizing the support gas. This may be performed in two ways; (i) by use of a 'tesla' coil vacuum tester or (ii) by momentarily lowering a graphite rod down inside the quartz tube. The electrons and ions formed are then accelerated by the high frequency field. These high energy electrons cause further ionization, and as soon as the plasma is sufficiently ionized, eddy currents are induced which flow in azimuthal circular closed paths around the periphery of the plasma. Resistance to the current flow causes Joule heating which results in core temperatures of 9000 to 10,000 K. Such high temperature plasmas must be thermally isolated from the quartz tube walls. Reed<sup>(51)(52)</sup>, designed a vortex flow technique to cool and isolate the outer quartz tube (see Figure 1.19). Argon was introduced tangentially so that it spiralled up the quartz walls and the plasma was stabilised in the tube centre. The sample was injected up into the centre of the plasma via a small bore quartz tube.

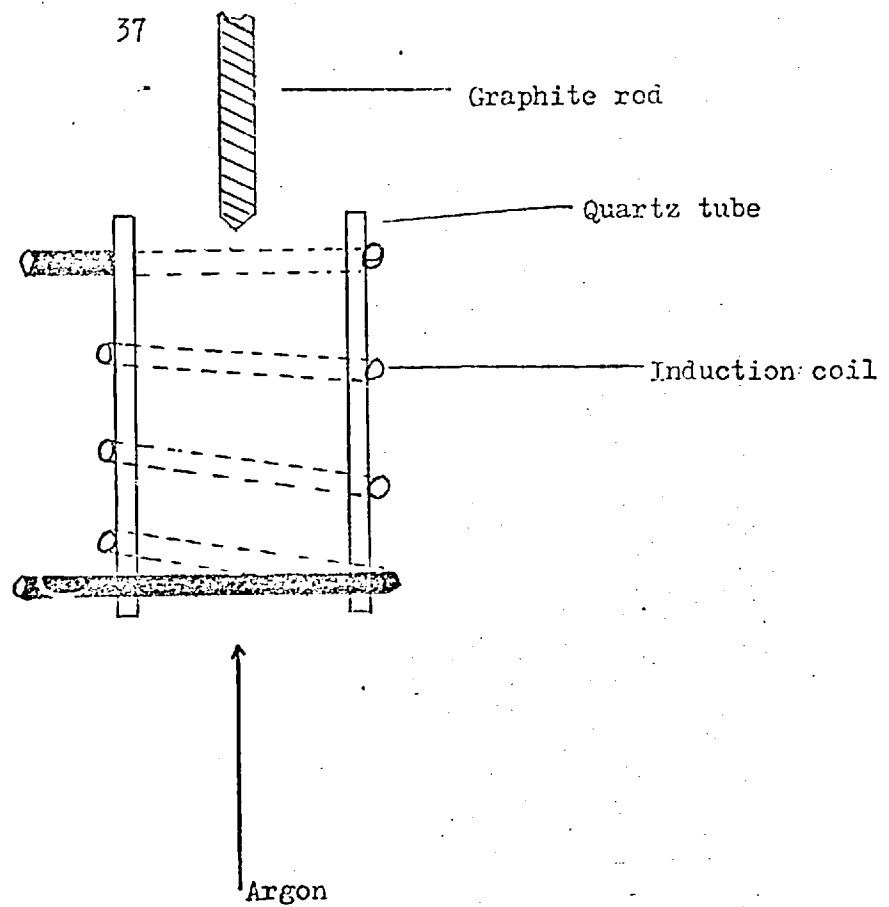


Figure 1.18. Inductively coupled radio frequency plasma.

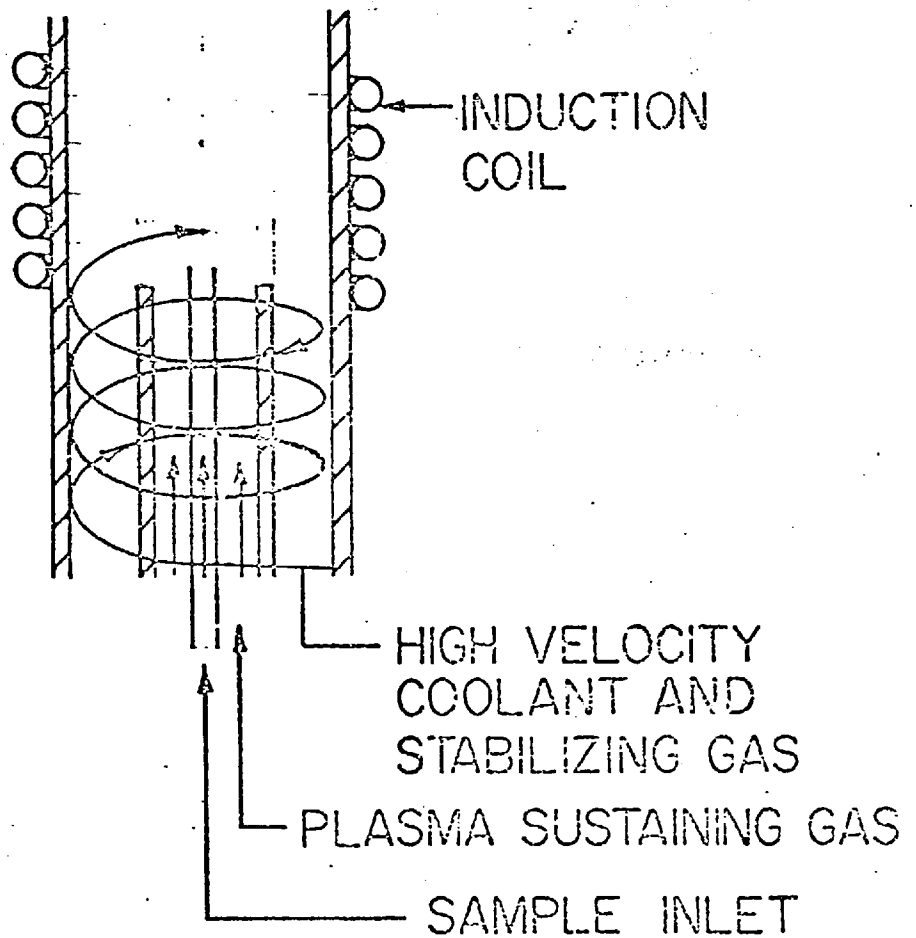


Figure 1.19. Vortex cooling system designed by Reed.

### Sample introduction

Plasmas generated at frequencies of 4-5 M Hz are tear-drop shaped (Figure 1.20 A) and sample material that encounters the steep thermal gradients tends to follow a path around the plasma. At higher frequencies (36 M Hz) the eddy currents flow more closely to the outer surface. This results from the well known skin depth effect, i.e. the depth at which the eddy current flows is inversely proportional to the square root of the RF frequency. In this way an annular 'doughnut' shaped plasma is formed (Figure 1.20 B). The doughnut hole, which is cooler than the doughnut, can be further developed by optimizing the flow velocity of the carrier gas which injects the sample. The cooler 'doughnut hole' presents a path of low resistance for sample injection into the axial channel of the plasma, even then, however, the sample does not experience the hottest part of the plasma.

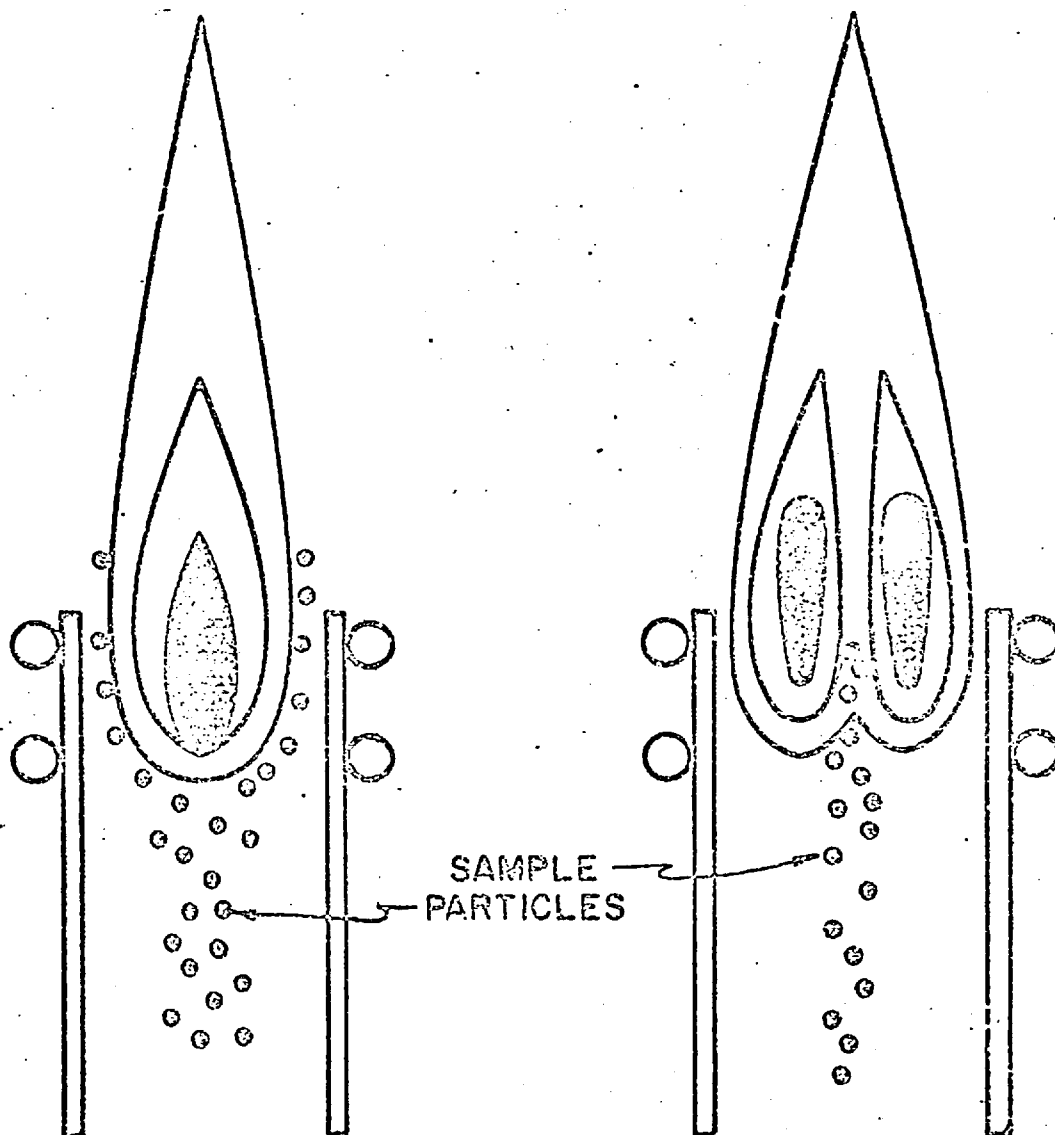
### Analytical development of inductively coupled radio frequency (IC RF) plasmas

Greenfield et al and Fassel et al <sup>(52-57)</sup> have pioneered the use of these plasmas as excitation sources for atomic emission and as absorption cells for atomic absorption spectrometry. They have shown numerous advantages afforded by IC plasma excitation.

The most important of these advantages are

- (i) The sample can be injected into a hot portion of the plasma
- (ii) The large plasma provides long residence times
- (iii) The plasmas have higher temperatures than combustion flames.
- (iv) They possess continuous temperature gradients from 9000 K

to room temperature, free atoms can be generated in the hottest zones and then observed in low temperature zones above the 'doughnut' where the background emission is lower.



LOW  
FREQUENCY

Figure 1.20 A.

RF Plasma 5 M Hz

HIGH  
FREQUENCY

Figure 1.20 B.

RF Plasma 36 M Hz

- (v) Large linear calibration ranges (4 orders of magnitude) are obtained.
- (vi) No electrode contamination is present.
- (vii) Self-reversal is practically eliminated.
- (viii) Excitation takes place in an inert environment.
- (ix) The technique is applicable to multi-element analysis.

There are also disadvantages which are:

- (i) Expense, large flow rates of argon are needed to act as coolant gas
- (ii) A limited tolerance for sample loading, partly due to the formation of large concentrations of molecular gases when aerosol droplets are decomposed. These gases cause an impedance mismatch, they absorb energy when excited and dissociated and this reduces the energy available for the ionization processes that sustain the plasma. The rate of aerosol introduction is therefore limited to  $0.1$  to  $0.2 \text{ ml min}^{-1}$ , which is below the level normally introduced into combustion flames.
- (iii) The condensation of aerosol droplets can take place at the sample injection orifice, this causes instability in the injection process. It has been overcome by employing a desolvator which removes the bulk of the water from the sample<sup>(18)</sup>, leaving dry solid particles for injection<sup>(55)</sup>.

Fassel et al<sup>(56)</sup> have used as ultrasonic nebuliser, combined with a desolvator, to introduce sample at a flow rate of  $0.6 \text{ ml min}^{-1}$ . Detection limits were improved by a factor of five. Figure 1.21 shows a diagram of the plasma tube configuration used by Fassel and co-workers.

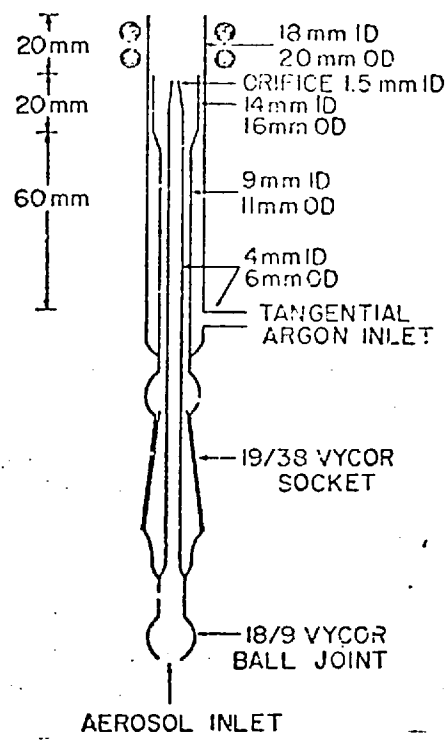


Figure 1.21. 'Fassel-type' plasma tube configuration.

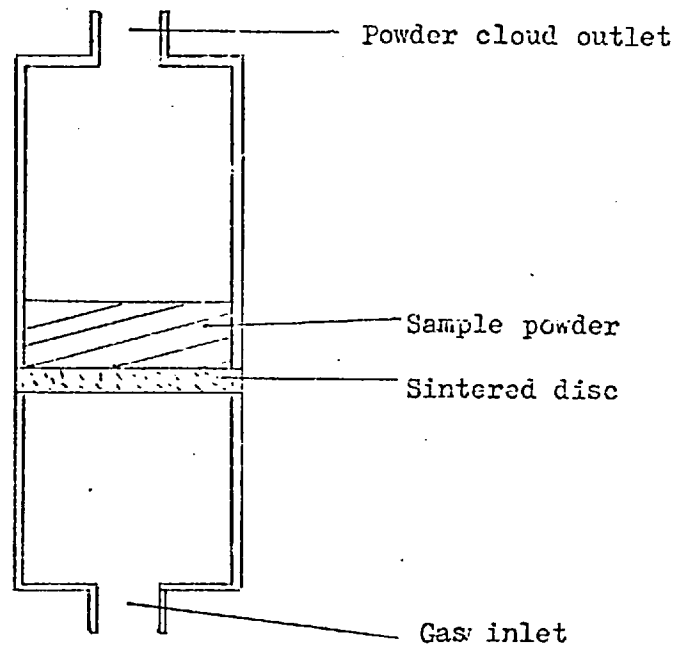


Figure 1.22. Fluidised bed chamber.

### Chemical interferences in IC RF plasmas

Phosphate and aluminium suppress the emission and absorption signals from calcium in combustion flames. Interference has been attributed to the formation of refractory pyrophosphates and aluminates leading to reduced efficiency of formation of alkaline earth atoms. Greenfield et al<sup>(52)</sup> and Wendt and Fassel<sup>(58)</sup> have shown that these chemical interferences were negligible in an RF plasma.

Later, Veillon and Margoshes<sup>(59)</sup>, who employed a modified sample introduction system, produced different results. They observed a rather surprising enhancement effect for phosphate on calcium emission and for aluminium on calcium. The disagreement may have been due to their sample injection tube that allowed the sample to drift up the tube into the 4.8 M Hz plasma, at which frequency the 'doughnut hole' was not developed.

### Analytical applications of IC RF plasmas

Morrison and Talmi<sup>(60)</sup> used a RF plasma furnace for the analysis of microsamples of solids and liquids. Microsamples of freeze-dried liver were analysed for Pb, Cd, K, Na, Al, Cs, Sr, P, Zn, Mn, Cu, Ag and Mg.

Mostyn and Hoare<sup>(61)</sup> have determined trace amounts of boron and zirconium in complex nickel alloys. The alloys were dissolved in hydrochloric acid and the solutions were introduced into the 36 M Hz plasma using ultrasonic nebulisation. No serious interference effects on the boron and zirconium signals were observed in the presence of 10,000 ppm Ni, Cr, Co and Fe.

Fassel et al<sup>(62)</sup> used a RF plasma for the determination of trace metals in microlitre volumes of biological fluids. 25  $\mu$ l samples of whole blood, serum and plasma were taken and analysed for several elements. The excellent detection limits obtained are shown in Table 1.6.

Ward et al<sup>(63)</sup> have used the RF plasma for the determination of phosphorus and sulphur; phosphorus was determined in acetic acid extracts of soil.

TABLE 1.6 - Detection limits obtained by Fassel et al<sup>(62)</sup> in blood and serum samples

| <u>Element</u> | <u>Wavelength<br/>(nm)</u> | <u>Detn. lim. ppm</u> |                    |
|----------------|----------------------------|-----------------------|--------------------|
|                |                            | <u>Serum</u>          | <u>Whole blood</u> |
| Al             | 396.1                      | 0.001                 | 0.005              |
| Co             | 345.3                      | 0.005                 | n.d.               |
| Cr             | 357.8                      | 0.001                 | n.d.               |
| Cu             | 324.7                      | 0.002                 | 0.008              |
| Mn             | 403.0                      | 0.002                 | 0.006              |
| Ni             | 351.5                      | 0.004                 | n.d.               |
| P              | 213.6                      | n.d.                  | 0.05               |
| Pb             | 405.7                      | n.d.                  | 0.002              |
| Zn             | 213.8                      | 0.008                 | 0.03               |

n.d. - no detection limit given.

### Powder analysis

Mostyn and Hoare<sup>(61)</sup> described a powder introduction device (a swirl-cup) which was used for the analysis of trace impurities in lithium salts and alumina. However, the preparation of standards presented some difficulty. The limit of detection for several elements was about 1 ppm.

Smith<sup>(64)</sup> used a fluidised-bed-chamber, with the powder sample supported on a sintered glass disc (see Figure 1.22). The fluidised-bed-chamber was vibrated continuously, using an electro-mechanical vibrator, which prevented gas channelling, and reduced surging. The system was capable of generating a stable surge-free powder cloud from most powders, providing they were sufficiently

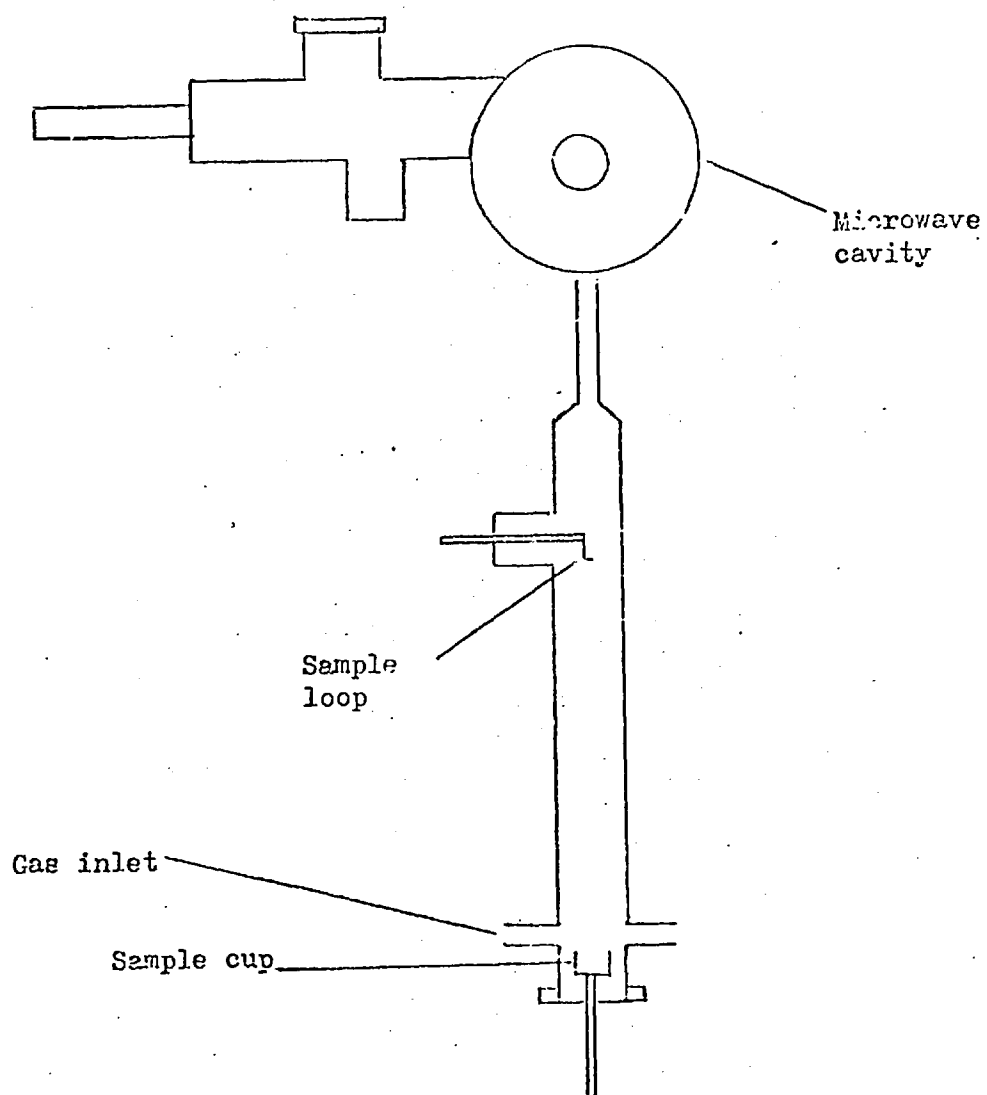


Figure 1.21

Microwave sample cell and plasma unit.

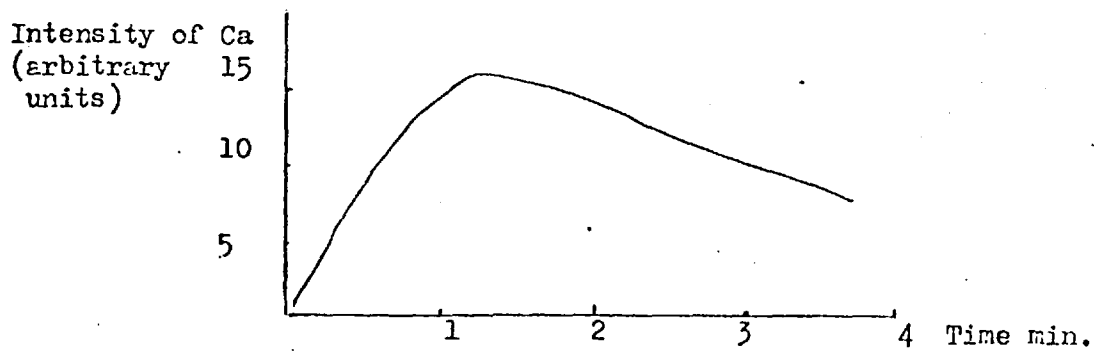


Figure 1.23 Graph of calcium emission vs. time of sample introduction.

finely ground (max. size 80 micron). With this system, powder segregation problems were encountered<sup>(65)</sup>. When clay samples were introduced, using the fluidised bed, the calcium emission signal (422.7 nm) increased to a maximum, then decreased gradually with time (Figure 1.23). To date, no suitable powder introduction device for quantitative analysis has been developed.

### Detection limits

For some elements, whose lowest excitation potentials are greater than 4 eV, flame atomic absorption and fluorescence give better detection limits. However, the excellent atomic fluorescence detection limits observed for Ag, Cd, and Zn (Table 1.7) were observed in low-background, relatively cool flames, such as those formed from hydrogen-argon-entrained air. These cool flames are subject to large matrix effects, and they are not normally used for analysis of real samples, unless extraction procedures are employed. The induction-coupled plasma detection limits for these elements show an improvement of one to three orders of magnitude over flame emission, and except for Cd and Zn are equivalent to, or better than, flame atomic absorption values.

The detection limits obtained for elements which tend to form exceptionally stable monoxide molecules (with dissociation energies greater than 7 eV) are generally 3 to 4 orders of magnitude superior to those obtained by flame emission and atomic absorption. The high temperature and inert chemical environment in the argon plasma prevents the formation of monoxide species.

### 1.3.5 Low wattage microwave plasmas

In 1965, Cooke et al<sup>(70)</sup> proposed the use of the low wattage microwave plasma, for the spectral identification of organic compounds eluted from a gas chromatograph. Nitrogen, chlorine, fluorine and sulphur were detected using both band and atomic emission spectra.

Bache and Lisk<sup>(71)</sup> employed this technique for the identification of halogen and phosphorus containing pesticides, separated from a mixture by gas chromatography. The method was capable of high sensitivity. Cooke suggested that it could be used as a general purpose chromatographic detector, if carbon atomic or band emission was monitored. The cyanogen bands were found to be particularly sensitive, and Cooke estimated the sensitivity to be sufficient to detect  $10^{-16}$  g of carbon.

Two years later, Runnels and Gibson<sup>(72)</sup> published the first paper concerning the characteristics of a low powered microwave plasma (sustained by argon) for metal excitation and analysis. The argon plasma was operated at 25 watts, was sustained in a quartz tube 1 mm internal diameter, 3 mm outer diameter, and the plasma obtained was 5-7 cm long. An Evenson type  $\frac{1}{4}$ -wave resonant cavity was used to couple the 2450 M Hz energy from the generator to the discharge, which was initiated by means of a tesla coil. The author showed that if the total amount of material entering such a discharge exceeded  $10^{-6}$  to  $10^{-5}$  g per second, it was extinguished. To overcome this problem, the sample was introduced from the solid phase, rather than from solution. This was accomplished by depositing 5 to 10  $\mu$ l of sample solution on a platinum filament, the solvent was then removed by evaporation. The filament was placed in the argon stream, which supported the plasma, and volatilisation was achieved by the passage of an electric current (6 amps) through the filament.

Metal acetylacetonates and trifluoro-acetylacetonates were used for samples because they were easily volatilised. Copper acetylacetonate was employed to optimise the operating parameters of the plasma. When the microwave power was increased from 25 to 100 watts the plasma increased in length. The emission intensity of copper (324.75 nm) however, decreased slightly and thus the

plasma was operated at 25 W, which was the minimum power that gave a stable discharge. For copper and all other metals studied, the maximum emission intensity occurred very near the lower end, or downstream of the discharge. No copper signal was obtained above 13 mm from the bottom of the plasma. The reason for this behaviour appeared to be that the copper plated the walls of the quartz tube. Table 1.8 shows the absolute detection limits obtained for five elements.

TABLE 1.7 - Comparative det.lim. for flame atomic emission (F.E.), atomic absorption (A.A.), atomic fluorescence (A.F.), and RF plasma emission

| <u>Element</u>                                       | <u>Wavelength<br/>(nm)</u> | <u>a<br/>Plasma<br/>emission</u> | <u>b<br/>F.E.</u> | <u>c<br/>A.A.</u> | <u>d<br/>A.F.</u> |
|------------------------------------------------------|----------------------------|----------------------------------|-------------------|-------------------|-------------------|
| <u>Elements with excitation potentials &gt;4 eV</u>  |                            |                                  |                   |                   |                   |
| As                                                   | 228.8                      | 0.1                              | 6                 | 0.25              | 0.1               |
| B                                                    | 249.6                      | 0.03                             | 0.3               | 2.0               | -                 |
| Cd                                                   | 228.8                      | 0.03                             | 2                 | 0.0006            | 0.000001          |
| Co                                                   | 345.4                      | 0.003                            | 0.05              | 0.007             | 0.01              |
| P                                                    | 213.6                      | 0.1                              | 3 (PO)            | -                 | -                 |
| Pb                                                   | 405.7                      | 0.008                            | 0.2               | 0.02              | -                 |
| Sb                                                   | 259.8                      | 0.2                              | 1.5               | 0.07              | 0.05              |
| Zn                                                   | 213.8                      | 0.009                            | 50                | 0.002             | 0.00004           |
| <u>Elements with excitation potentials &lt; 4 eV</u> |                            |                                  |                   |                   |                   |
| Al                                                   | 396.1                      | 0.002                            | 0.01              | 0.04              | 50                |
| Ba                                                   | 455.4                      | 0.0001                           | 0.001             | 0.01              | -                 |
| Cr                                                   | 357.8                      | 0.001                            | 0.005             | 0.005             | 0.05              |
| Fe                                                   | 371.9                      | 0.005                            | 0.05              | 0.005             | 0.008             |
| Ni                                                   | 352.4                      | 0.006                            | 0.03              | 0.008             | 0.003             |
| Sr                                                   | 407.7                      | 0.00002                          | 0.0001            | 0.004             | 0.03              |
| V                                                    | 437.9                      | 0.006                            | 0.01              | 0.11              | -                 |

| <u>Element</u>                                                     | <u>Wavelength<br/>(nm)</u> | <u>a</u><br><u>Plasma<br/>emission</u> | <u>b</u><br><u>F.E.</u> | <u>c</u><br><u>A.A.</u> | <u>d</u><br><u>A.F.</u> |
|--------------------------------------------------------------------|----------------------------|----------------------------------------|-------------------------|-------------------------|-------------------------|
| <u>Elements with stable oxides <math>D_o</math> (MO) &gt; 7 eV</u> |                            |                                        |                         |                         |                         |
| Ce                                                                 | 418.6                      | 0.007                                  | 10                      | -                       | -                       |
| Hf                                                                 | 339.9                      | 0.01                                   | 75                      | 2                       | -                       |
| La                                                                 | 408.6                      | 0.003                                  | 0.1                     | 3                       | -                       |
| Nb                                                                 | 405.8                      | 0.01                                   | 0.6                     | 2                       | -                       |
| Ta                                                                 | 301.2                      | 0.07                                   | 18                      | 2.1                     | -                       |
| Tb                                                                 | 401.9                      | 0.003                                  | 150                     | 0.5                     | -                       |
| Ti                                                                 | 334.9                      | 0.003                                  | 0.2                     | 0.1                     | -                       |
| U                                                                  | 409.6                      | 0.03                                   | 10                      | 39                      | -                       |
| W                                                                  | 400.8                      | 0.002                                  | 0.5                     | 1.2                     | -                       |
| Zr                                                                 | 343.8                      | 0.005                                  | 3                       | 1                       | -                       |

a - Fassel et al <sup>(56)</sup>

b - Fassel and Golightly <sup>(66)</sup>

b - Pickett and Koirttyohann <sup>(67,68)</sup>

c - Varian Techtron. A.A. detection limits

d - Winefordner, Svoboda and Cline <sup>(69)</sup>

TABLE 1.8 - Detection limits obtained by Runnels and Gibson <sup>(72)</sup>

| <u>Element</u> | <u>Absolute detection<br/>limit g.</u> |
|----------------|----------------------------------------|
| Ag             | $1 \times 10^{-11}$                    |
| Cu             | $5 \times 10^{-10}$                    |
| Fe             | $1 \times 10^{-11}$                    |
| Cr             | $1 \times 10^{-11}$                    |
| Co             | $1 \times 10^{-11}$                    |

Aldous, Dagnall, Sharp and West<sup>(73)</sup> described a microwave argon plasma supported at the mouth of a 2 mm quartz tube. Plating of the walls and devitrification problems encountered when the plasma was operated within the tube, were eliminated. A stable plasma was formed which was 20 mm in length and 1 mm in diameter with approximately 2 mm remaining inside the quartz tube.

The analyte was introduced into the plasma from a platinum or tungsten loop. The aqueous sample was placed in a sample cup (see Figure 1.24) and the platinum loop was dipped into the solution, the cup was then withdrawn leaving approximately 0.1 to 0.5  $\mu$ l of solution on the loop. The loop was dried by a passage of a small current. Once all the water had been removed, a large current was passed through the loop and the sample was volatilised into the argon stream and into the plasma. The transient signals produced were measured by means of an electronic amplifier/integrator designed specifically for such signals. Absolute detection limits were in the range 0.0005 to 0.1 ng.

Layman and Hieftje<sup>(74)</sup> developed a computer-controlled microarc sample introduction system for a microwave plasma. The sample was placed on a tungsten loop, then dried under an argon flow by passage of a small current through the loop. Following drying, the microarc was initiated between the sample loop (cathode) and a tungsten anode, the sample was efficiently vaporized into the plasma. Detection limits were quoted for Na, Ca, Li and B ranging between 0.01 and  $3 \times 10^{-12}$  g.

Fallgatter, Svoboda and Winefordner<sup>(75)</sup> have described a microwave plasma operating at 100 W. Samples were nebulised into the discharge using a desolvated sample introduction system, similar to that described by Veillon and Margoshes<sup>(18)</sup>. The microwave discharge was sustained inside a quartz tube 9 mm in diameter, the

discharge was 6 cm long and about 1 mm in diameter. The plasma column tended to wander about the quartz tube, so a copper wire was placed inside the cell to prevent this. The plasma formed, then tended to follow the contour of the quartz wall on one side of the cell. Detection limits obtained for several elements were no better than 0.02 ppm, these poor detection limits were obviously due to the large fraction of the sample not entering the microwave discharge. If calculations are performed on the volume occupied by the discharge, and the volume of the quartz cell, the fractional volume occupied by the plasma is only about 4%, i.e. 96% of the sample escapes without entering the plasma. The quartz cell also suffered from memory effects due to the sample plating the quartz tube walls.

Skogerboe and Lichte<sup>(76)</sup> have determined trace amounts of mercury in blood and plant leaves, using an atmospheric low powered microwave plasma. The solution samples were placed in a cell containing a reducing solution ( $\text{SnCl}_2/\text{HCl}$ ) and argon was bubbled through. The argon/ $\text{H}_2\text{O}$ /mercury vapour was passed through an anhydrous tube to remove water, and the dried argon was passed into a microwave discharge. The mercury 253.6 nm atomic emission line was monitored. The absolute detection limit was  $6 \times 10^{-11}$  g, and quantitative measurements on 10 ml samples containing 0.01 ppb Hg were made with a precision of 10-12%.

In 1973 Skogerboe and Lichte<sup>(77)</sup> described a microwave plasma for continuous sample introduction. The sample aerosol was produced using a system similar to that described by Veillon and Margoshes<sup>(18)</sup> with the nebuliser designed by Valente and Schrenk<sup>(17)</sup>. The Evenson  $\frac{1}{4}$ -wave cavity was modified as shown in Figure 1.25. The large tuning stub was removed and the 2 mm quartz tube carrying the sample and argon was inserted in its place, instead of using the more conventional transverse configuration. This change alone

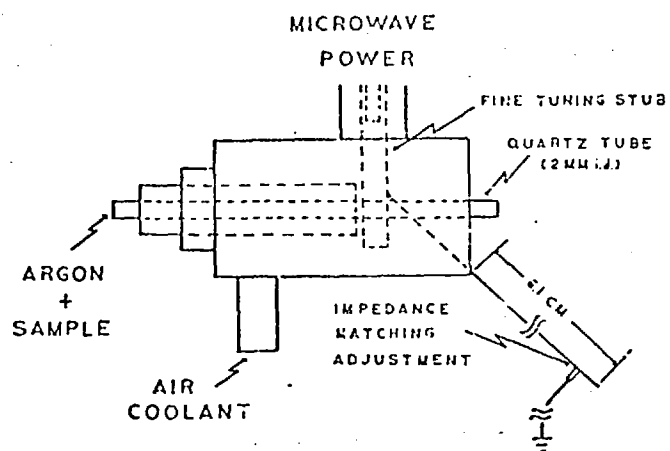


Figure 1.25. Diagram of cavity and tuning system.

permitted the ignition and maintenance of the plasma even when the argon support gas was saturated with water vapour. In the transverse coupling arrangement small amounts of water quenched the discharge. To increase the tuning efficiency of the cavity a second modification was performed. A 20-gauge copper wire was attached to the fine tuning stub and was extended at  $45^\circ$  to the cavity axis, the best length of wire was found to be 6.1 cm. The wire was then grounded.

An argon flow of approximately  $1 \text{ l min}^{-1}$  was used to nebulise the sample (at an uptake rate of  $1.5 \text{ ml min}^{-1}$ ) into the plasma, which was operated at 100 W. The plasma was viewed end-on, thus the problems of quartz devitrification and plating effects were negligible. Memory effects were not serious and were observed to have a maximum duration of one minute, except for boron and selenium. Unusually good detection limits were obtained for several metals, these being at least one order of magnitude better than any reported for atomic absorption, emission or fluorescence (Table 1.9) This was thought to be due partially to the elimination of the background by means of a vibrating refractor plate system, described by Snelleman et al<sup>(78)</sup>.

TABLE 1.9 - Comparative detection limits for microwave plasma  
emission, radio frequency inductively-coupled plasma  
emission and flame atomic absorption spectrometry

| <u>Element</u> | a<br><u>Wavelength<br/>(nm)</u> | <u>Detection limit ppm</u> |             |             |
|----------------|---------------------------------|----------------------------|-------------|-------------|
|                |                                 | <u>A.A.</u>                | <u>R.F.</u> | <u>M.P.</u> |
| As             | 193.7                           | 0.25                       | 0.1         | 0.03        |
| B              | 249.8                           | 2.0                        | 0.03        | 0.01        |
| Cd             | 228.8                           | 0.0006                     | 0.03        | 0.0004      |
| Co             | 240.7                           | 0.007                      | 0.003       | 0.06        |
| Hg             | 253.6                           | 0.2                        | -           | 0.003       |
| Pb             | 405.8                           | 0.02                       | 0.008       | 0.005       |
| Se             | 196.0                           | 1.1                        | -           | 0.04        |
| V              | 437.9                           | 0.11                       | 0.006       | 0.08        |
| Zn             | 213.9                           | 0.002                      | 0.009       | 0.0006      |

A.A. - Atomic absorption detection limits (Varian Techtron Australia)

R.F. - Radio frequency inductively-coupled plasma<sup>(56)</sup>

M.P. - Microwave plasma described by Skogerboe<sup>(77)</sup>

a - Wavelengths used by Skogerboe.

## THEORY OF ATOMIC EMISSION

### CHAPTER 2

## 2.1 ORIGIN OF SPECTRAL LINES

According to quantum mechanics, spectral lines originate from transitions between energy levels of atoms or ions. When a transition from a higher energy state  $q$  to a lower state  $p$  occurs, the frequency  $\nu$  of the quantum of light emitted is related to the energy difference between the two states by the Bohr frequency equation:

$$h\nu = E_q - E_p \quad (1)$$

where  $h$  is Planck's constant.

In 1917 Einstein introduced the probability treatment of transitions between quantum states. He considered the spontaneous radiative transition  $q \rightarrow p$  and showed that the number of atoms leaving the state  $q$  per second by spontaneous emission was proportional to the number  $N_q$  present in that state. This is represented in equation (2).

$$\frac{-dN_q}{dt} = A_{qp} \cdot N_q \quad (2)$$

The constant  $A_{qp}$  is called the transition probability or the Einstein coefficient of spontaneous emission.

If the upper level  $q$  is involved in other transitions such as  $q \rightarrow p_1$ ,  $q \rightarrow p_2$ ,  $q \rightarrow p_3$  etc. then equation (2) reads:

$$\frac{-dN_q}{dt} = N_q \sum_p A_{qp} \quad (3)$$

where  $\sum_p A_{qp}$  represents the sum of the probabilities for all the possible transitions that can occur. The quantity  $\sum_p A_{qp}$  is known as the damping constant, its reciprocal is the mean lifetime  $\tau_q$  of the relevant state. A clear distinction must be made between the transition probability of a spectral line, and the damping constant of an energy level, the former is of greater interest as it is directly related to the observed line intensities.

## 2.2 SPECTRAL LINE INTENSITIES AND SPECTRAL FLUX

The spectral lines emitted by plasmas and flames consist of small ranges of frequencies. This is a result of natural, Doppler and collisional broadening and the Stark effect. The spectral flux  $\Phi_\lambda$  denotes the radiation emitted at a specified wavelength ( $\lambda$ ) per unit frequency interval (measured in watts). The total flux  $\Phi(\lambda)$  or intensity (also known as the radiant flux) is measured by integrating over the line profile, thus:

$$\Phi(\lambda) = \int_{\text{profile}} \Phi_\lambda d\lambda \quad (4)$$

NB. The radiant flux ( $\Phi$ ) of a source is defined as the amount of radiant energy emitted into space in unit time.

The spectrometers used in analytical spectrometry possess relatively large spectral bandpasses in comparison with atomic line half-widths. Therefore, the measured intensity of an atomic line represents the integrated intensity over the whole line profile.

## 2.3 Geometrical aspects of an emission source

### Emission from a point source

The flux from a point source S to a surface of area  $dA$  at a mean distance  $D$  from S is proportional to the solid angle ( $dw$ ) subtended by  $dA$ . The solid angle is given by:

$$dw = \frac{dA \cos Q}{D^2} \quad (5)$$

$\cos Q$  is the angle between the normal on the surface and the mean ray in the pencil of radiation being considered (see Fig. 2.1). The flux at  $dA$  is therefore:

$$d\Phi = I_r dw = \frac{I_r dA \cos Q}{D^2} \quad (6)$$

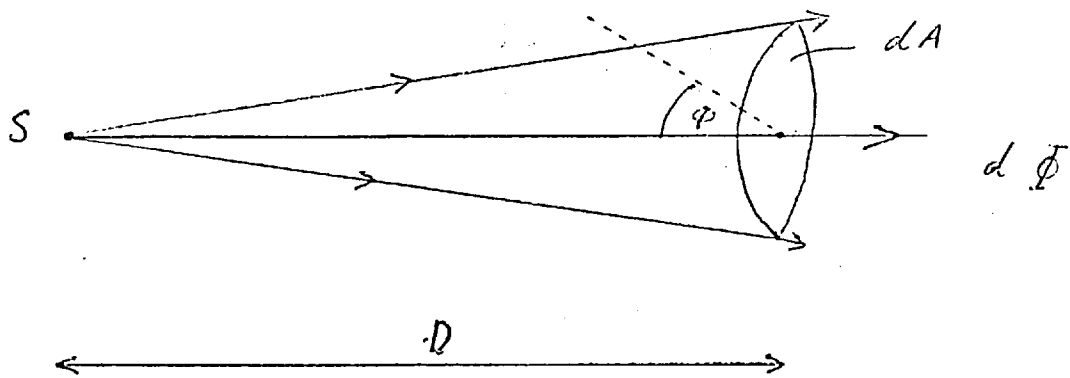


Figure 2.1. Emission from a point source.

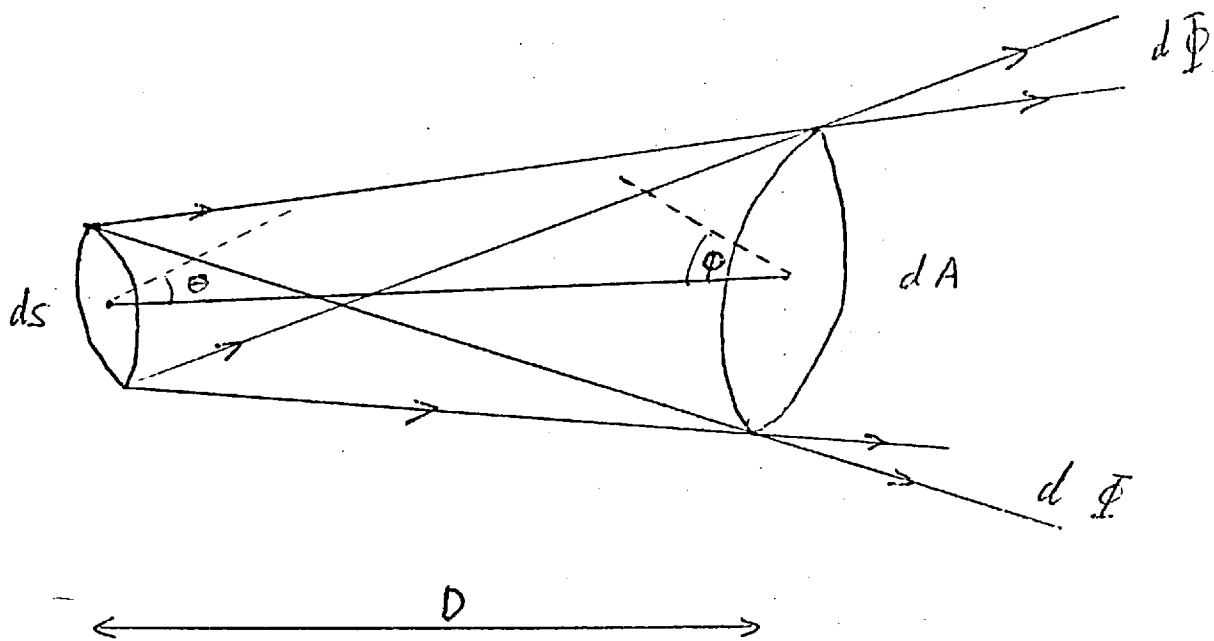


Figure 2.2 Emission from a disc source.

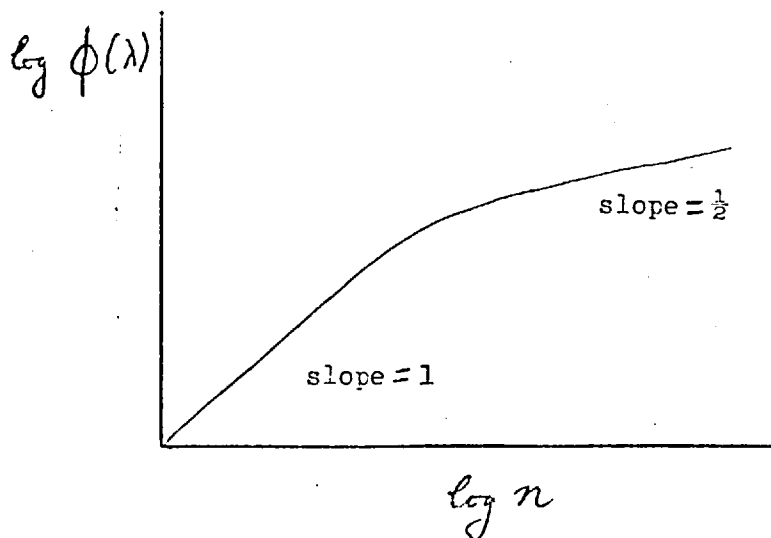


Figure 2.3. An ideal analytical growth curve.

$I_r$  is called the radiant intensity and has the dimension of flux per unit solid angle. From a practical point of view this model is not satisfactory as emission sources are always three-dimensional. A more suitable way to represent the flux at the area  $dA$  is to consider the source as a small disc of area  $dS$  radiating to the surface  $dA$  (see Figure 2.2). In this treatment it is assumed that the distance  $D$  between the areas is large compared with the size of the areas  $dA$  and  $dS$ , thus the solid angle at which  $dA$  is seen from any point on  $dS$  is approximately constant. The total flux at  $dA$  then becomes:

$$d\phi = \frac{B dS \cos \theta dA \cos \theta}{D^2} \quad (7)$$

The constant  $B$  is known as the brightness, or luminance of the source, and it is the rate at which radiation energy is emitted from unit area per unit solid angle, its dimensions are  $J \cdot \text{sec}^{-1} \cdot \text{sr}^{-1} \cdot \text{m}^{-2}$ . The brightness of a source is often loosely equated to intensity  $I$ , however, it must be realised from the above considerations that  $B$  cannot be increased by focusing of the source, this only increases the flux per unit area at a given surface i.e.  $I$ .

#### Emission from a volume source

The emissive power per unit solid angle, ( $J$ ) is defined as the total flux flowing from the unit volume divided by  $4\pi$ .  $J$  is expressed in  $J \cdot \text{sec}^{-1} \cdot \text{sr}^{-1} \cdot \text{m}^{-3}$ . If we consider a homogeneously radiating gaseous layer with a thickness  $\ell$ , the intensity  $I$  and emissive power  $J$  are related by:

$$I = J \cdot \ell \quad (8)$$

Generally equation (8) can be expressed as:

$$I = \int_0^{\ell} J(y) dy \quad (9)$$

where the integration is performed over the depth of the source along the direction of viewing ( $y$ ). Obviously equations (8) and (9) only apply if self-absorption is negligible since the quantity  $J$  is directly related to the number of radiative transitions per second per unit volume. If the number of transitions per sec per  $m^3$  leading to the emission of a photon of energy  $h\nu$  is equal to  $N$ , the emissive power ( $J$ ) is given in equation (10);

$$J = \frac{N h \nu}{4\pi} \quad (10)$$

Thus the intensity  $I$  is,

$$I = \frac{\ell N h \nu}{4\pi} \quad (11)$$

The absolute intensity of an atomic line is given by:

$$I_{qp} = \frac{\ell}{4\pi} A_{qp} N_{aq} h \nu_{aq} \quad (12)$$

where  $N_{aq}$  is the number of atoms in state  $q$ .

Equations (10) and (11) relate to uniform emission along the line of observation. However, when a typical emission source is considered, the geometrical relationships between  $I$  and  $J$  are more complex. A more complete account is given in Boumans<sup>(42)</sup>.

All the relationships already discussed have been concerned with absolute quantities of radiation energy. Normally in spectrochemical analysis absolute line intensities are not used. Instead relative intensities are measured for the element of interest, and the variation of the intensity of a spectral line with the content of the relevant element is plotted graphically. This curve represents the analytical working curve. If the working curve is to be relied upon for subsequent analyses, all the instrumental factors should remain constant.

## 2.4 Thermal Equilibrium in Emission Sources

If an emission source such as a plasma or a flame exists in partial thermo-dynamic equilibrium, the processes that occur in the source can be treated as if the gas mixture was contained inside a furnace at the same temperature as the source. The atomic and molecular excitation can then be described by the Boltzmann distribution law, and ionisation by Saha's equation. According to Lochte-Holtgreven<sup>(79)</sup> the concept of thermodynamic equilibrium is characterised by four different types of temperature, viz.

1. The electron temperature, which is determined by the kinetic energy of the electrons ( $\frac{1}{2} m_e v^2$ ).
2. The gas temperature, the kinetic energy of the neutral gas atoms.
3. The excitation temperature which describes the population of the various energy states.
4. The ionisation temperature, which governs the ionisation equilibria.

A gaseous system in complete equilibrium can be characterised by the following conditions:

1. The velocity distribution of all free particles in all energy levels satisfies Maxwell's equation.
2. For each kind of particle the relative population of energy levels conforms to the Boltzman distribution law.
3. Ionisation of atoms, molecules and radicals is described by Saha's equation and the dissociation of molecules with the general equation for chemical equilibria.
4. The density of radiation is consistent with Planck's law.

In a plasma which is not enclosed by walls with the same temperature as the gas, the radiation density does not satisfy Planck's law due to radiation loss. However, energy lost by radiation may only be a few percent of the total energy. For this reason a state of partial thermal equilibrium in each volume element in a non-homogeneous source is known as local thermal equilibrium (LTE).

## 2.5 Electron Temperature and Gas Temperature in an Air DC Plasma

According to Finkelnburg and Maecker<sup>(80)</sup> a uniform electron temperature is established after only a few collisions which take place in  $10^{-17}$  to  $10^{-12}$  sec. However, the time necessary for reaching equilibrium between electron temperature and gas temperature is much longer due to the small mass of the electron. When an electron collides elastically with a heavy particle, it only loses a very small fraction ( $2 m_e / m_h$ ,  $m_e$  = mass of electron,  $m_h$  = mass of heavy atom) of its <sup>excess</sup> energy.

Calculations performed by Boumans<sup>(81)</sup> for a dc arc burning in nitrogen at 6000 K and 1 atm., show the collisional period of electrons with heavy particles to be about  $2 \cdot 10^{-11}$  sec. Since the required number of collisions needed for equilibrium is  $\frac{1}{2} m_h / m_e = 2.5 \times 10^4$ , complete exchange of energy takes approximately  $5 \times 10^{-7}$  sec. However, during this period the electrons continuously acquire more energy from the electric field, and thus the system reaches an equilibrium state where the electron temperature is far greater than the gas temperature.

Furevich and Podmoshenski<sup>(82)</sup> have measured the electron and gas temperature of an arc burning in air and they concluded that the electron temperature did not exceed the gas temperature by more than 0.5%. The discrepancy between the calculations based on elastic collisions and the experimental measurements is due to electrons giving up their excess energy by inelastic collisions, leading to excitation of vibrational levels of molecules and radicals.

For inert gases, which do not have any vibrational degrees of freedom, thermal equilibrium is more difficult to establish. However, according to Gurevich and Podmoshenski only a small amount of molecular gas impurity, such as  $N_2$  or  $CO_2$  in argon, is sufficient for LTE to be reached.

### Excitation temperature

The population of energy levels for each kind of particle in a LTE source follows a Boltzmann distribution viz.

$$N_q/n_o = g_q/g_o \exp (-\epsilon_q/kT) \quad (13)$$

where  $n_o$  is the density of atoms in the ground state,  $\epsilon_q$  is the excitation energy of the state  $q$ , and  $T$  is the absolute temperature. Equation (13) can be rewritten in the form:

$$N_q = n g_q/Z \exp (-\epsilon_q/kT) \quad (14)$$

where  $Z$  is the partition function (derived from statistical mechanics) of the particular atom, and  $n$  is the total density of atoms. The partition function  $Z$  varies slightly with temperature, so for a fixed concentration of  $n$ , the increase in the population of state  $q$  with temperature, departs from the exponential form. The degree of departure depends on the relative rate at which  $Z$  rises with temperature.

The absolute intensity of a spectral line can now be represented by substituting equation (14) into equation (12) to give:

$$I_{qp} = \frac{\ell}{4\pi} A_{qp} h\nu_{qp} n \frac{g_q \exp (-\epsilon_q/kT)}{Z} \quad (15)$$

The absolute intensity  $I_{qp}$  can be calculated if the transition probability  $A_{qp}$  is known.

## 2.6 Calculation of Transition Probabilities

In order to calculate the transition probability  $A_{qp}$ , it is necessary to consider a steady state system where (i) radiation is emitted by the source, (ii) radiation is absorbed (self-absorption) and (iii) stimulated emission occurs. The probability for emission at the frequency  $\nu$  is represented by  $A_{qp}$ , the probability for absorption is  $B_{pq}$ . The number of normal emission transitions is:

$$dN_{qp} = A_{qp} N_q dt \quad (16)$$

The number of absorption transitions is:

$$dN_{pq}^* = B_{pq} p(\nu) N_p dt \quad (17)$$

where  $p(\nu)$  is the spectral volume density of radiation. The stimulated or induced emission is given by:

$$dN_{qp} = B_{qp} p(\nu) N_q dt \quad (18)$$

At equilibrium  $dN_{qp} + dN_{qp}^*$  must be equal to  $dN_{pq}$ . Thus,

$$(A_{qp} + B_{qp} p(\nu)) N_q = B_{pq} p(\nu) N_p \quad (19)$$

From equation (13):

$$N_p/N_q = g_p/g_q \exp - (h\nu/kT) \quad (20)$$

The density function, obtained from statistical mechanics,  $p(\nu)$  is expressed by Planck's radiation law, i.e.

$$p(\nu) = \frac{8\pi L \nu^3}{c^3} \frac{1}{\exp (h\nu/kT) - 1} \quad (21)$$

Thus the Einstein coefficients  $B_{qp}$  and  $A_{qp}$  can be deduced from equations (19) to (21).

$$B_{qp} = (g_p/g_q) B_{pq} \quad (22)$$

$$A_{qp} = \frac{8\pi h \nu^3}{c^3} B_{qp} \quad (23)$$

The  $A_{qp}$  coefficients may be determined by quantum mechanical calculations.

### Oscillator Strength

The classical theory of light emission/absorption by atoms involved the concept of oscillator strength, which is still in use. It is the number of classical oscillators that produce the same absorption effect for the transition  $p \rightarrow q$  as one atom in the state  $p$ . The oscillator strength ( $f_{pq}$ ) is related to  $A_{pq}$  by the equation:

$$A_{pq} = \frac{8\pi^2 e^2}{\lambda^2 M_e c} f_{pq} \quad (24)$$

Equation (24) provides a route for the determination of oscillator strengths and Einstein coefficients from spectral line intensity measurements.

### 2.7 Atomic Line Profiles

The physical shape of an atomic line is governed by several broadening factors.

1. Natural Broadening - is due to the finite lifetime of an atom in the excited state (i.e. Heisenberg's uncertainty principle).  
The natural width is independent of the atom environment, and it is of the order of  $10^{-5}$  nm.
2. Resonance Broadening - (Holtsmark) is due to the perturbation of the emitting atoms by atoms of the same type. In analytical emission sources the partial pressure of the analyte element rarely exceeds  $10^{-3}$  torr, thus this type of broadening is negligible.
3. Stark Broadening - is caused by non-uniform electrical fields perturbing the energy levels of emitting atoms. In an emission source containing a considerable number of ions and electrons

(e.g. dc arc, high voltage spark), the excited atoms in the immediate vicinity of the charged particles are subject to large local electric fields. The emitted spectral lines are split due to their quantized orientation in the fields. However, these localised fields are continually changing and inhomogeneous, giving rise to diffuse lines. Atoms with low mass numbers are broadened more than those with high mass number.

4. Zeeman Broadening - The atomic line is split into several components by very high magnetic fields. This broadening effect is negligible.
5. Hyperfine Structure - This is not an actual broadening process, it can be attributed to a non-zero value of the nuclear spin and/or the presence of several isotopes. Each line consists of a number of separate hyperfine components each acting as an independent line. For elements with an even atomic number and just one isotope, there is no hyperfine structure to the spectrum. The hyperfine structures of atomic lines are very difficult to measure, and they can only be resolved using an interferometer.
6. Doppler Broadening - is caused by the emitting atoms having different component velocities along the line of observation. The broadening is symmetrical about the mean wavelength of the line. The Doppler half-width is proportional to  $(T/M)^{1/2}$  and is given by:

$$\Delta\lambda_D = \frac{\lambda_o}{C} \sqrt{\frac{8(\ln 2)RT}{M}} \quad (25)$$

$\Delta\lambda_D$  = Doppler half-width (Å)

$\lambda_o$  = wavelength of the centre line

C = velocity of light ( $\text{cm.s}^{-1}$ )

R = gas constant ( $\text{ergs. K}^{-1}.\text{mole}^{-1}$ )

M = atomic weight of the emitting atoms

$T$  = the temperature of the atoms.

7. Lorentz Broadening - or pressure broadening of atomic lines is caused by collision of the emitting atoms with other atoms or with foreign gas molecules. As the pressure of the foreign gas is increased the emission line is broadened, the maximum of the line is shifted and the line becomes asymmetrical. If it is assumed that the broadening is symmetrical the Lorentz half-width is given <sup>(83)</sup> by:

$$\Delta\lambda_L = \frac{2\lambda_o^2 \sigma_c^2 P_f}{\pi c k T} \left[ 2\pi R T \left( \frac{1}{M_a} + \frac{1}{M_f} \right) \right]^{\frac{1}{2}} \quad (26)$$

$C$  = speed of light cm. sec.<sup>-1</sup>

$P_f$  = pressure of foreign gases mm Hg

$M_a$  = atomic weight of absorbing or emitting species

$M_f$  = effective (average) molecular weight of the foreign gas molecules, in atomic mass units

$\sigma_c$  = effective cross section for collisional broadening

$\Delta\lambda_L$  = Lorentz half-width

### Total line widths

The total half-intensity width  $\Delta\lambda_T$  is expressed as:

$$\Delta\lambda_T = \left[ (\Delta\lambda_D)^2 + (\Delta\lambda_L + \Delta\lambda_R + \Delta\lambda_N)^2 \right]^{\frac{1}{2}} \quad (26)$$

$\Delta\lambda_N$  = the natural half-width

$\Delta\lambda_R$  = the resonance half-width

Since the resonance and natural broadening are small in comparison to the Doppler and Lorentz, equation (26) may be simplified to give:

$$\Delta\lambda_T = \left[ (\Delta\lambda_D)^2 + (\Delta\lambda_L)^2 \right]^{\frac{1}{2}} \quad (27)$$

Calculations performed by Winefordner et al<sup>(83)</sup> show that the most important factor influencing the total half-intensity width of a line is the wavelength of the transition. A good example is the beryllium 457.267 nm line which has a maximum half-intensity width of 0.0083 nm in a  $H_2/O_2$  flame with a temperature of 2650K, whereas the 234.861 line has a maximum half-width of 0.0033 nm. The combination of Lorentz and Doppler profiles is called the Voigt function.

## 2.8 Self-absorption of spectral lines

Radiation emitted from a source is subject to absorption on its passage to the outside. The absorption is due to atoms of the same kind as those causing the emission. An atom is capable of absorbing the relevant radiation if it populates the lower level of the transition and during the absorption process it is excited to the corresponding upper level. Only a few of these atoms in the upper state are de-excited by spontaneous emission, because in a thermal source the excitation energy is predominantly converted by collisions of the second kind into kinetic energy. Therefore, an absorbed quantum of light has only a small chance of being re-radiated, and thus self-absorption weakens the intensity of spectral lines.

Absorption is strongest at the peak of the line, hence self-absorption tends to flatten the profile, this obviously results in an increase in the half-intensity width. In the extreme case of self-absorption in a non-homogeneous thermal source, the centre of the line may be reversed, this phenomenon is termed 'self-reversal'. In a homogeneous thermal source, self-reversal does not occur; however, with increasing concentration of the emitting and absorbing particles the intensity at the centre of the line asymptotically

approaches the intensity of the blackbody radiation at that temperature. (Planck's upper limit.) The peak spectral flux is then independent of the atomic concentration, although the integrated flux continues to increase as its square root. An ideal growth curve is represented in Figure 2.3, the slope of the log/log graph is 1 at low concentrations and  $\frac{1}{2}$  at high concentrations.

## THE CAPILLARY ARC PLASMA - ONE SHOT

### SAMPLE INTRODUCTION

#### CHAPTER 3

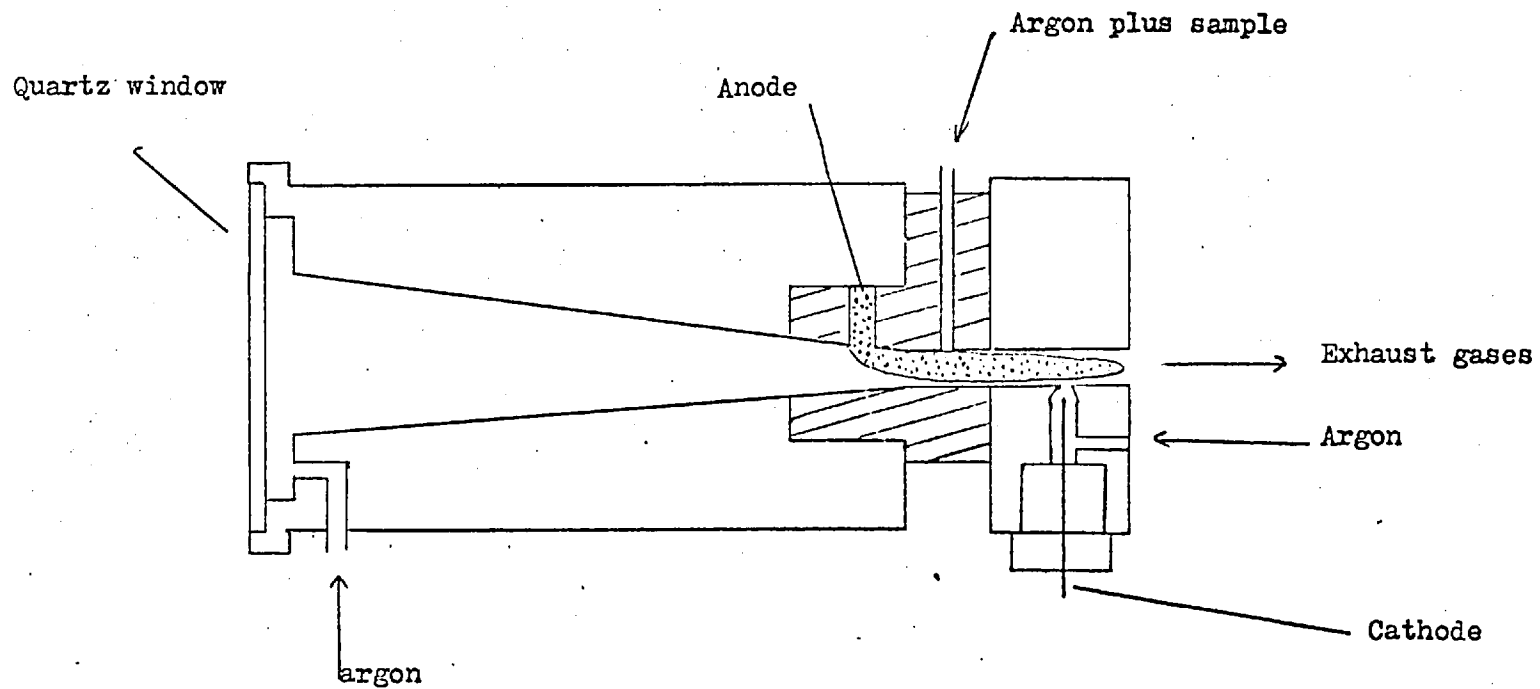
### 3.1.1 INTRODUCTION

A DC Capillary Arc Plasma (CAP) (Applied Research Laboratories Ltd, Luton, Beds.) was investigated for its potential for solution spectrochemical analysis. An identical plasma has been used by Jones, Dahlquist and Hoyt<sup>(22)</sup> for the analysis of copper, molybdenum, chromium, manganese and other elements in steel between 1 and 0.003%. The CAP, operating on argon at atmospheric pressure, was combined with an aerosol generator which produced fine particles directly from the surface of the solid metal sample. The aerosol was carried in a stream of argon and introduced radially into the CAP discharge. The light from the plasma was observed axially through a quartz window, using a direct reading spectrograph.

### 3.2.1 THE DC CAPILLARY ARC PLASMA

The plasma unit consisted of four main parts: (i) a cathode block; (ii) a tantalum electrode and boron nitride insulator; (iii) a boron nitride plasma channel, and (iv) an anode block. Both the anode and cathode blocks were made of copper and were both water-cooled ( $1 \text{ l.min}^{-1}$ ). A special brass cut-away cathode block, also water-cooled, was used in later studies to view the plasma tail-flame. The whole plasma unit is illustrated in Figure 3.1 and the various parts of it are shown in Figures 3.2, 3.3 and 3.4 (see also Plate 3.1).

The cathode was a piece of tantalum wire 2.5 mm in diameter which was sharpened to a point with an angle of ca  $30^\circ$  and held in place in the cathode block inside a screw-in boron nitride holder. The electrode, positioned at right angles to the main plasma column, was flushed with argon to prevent excessive wear. The anode contact was made with the copper body of the anode block through a 2 mm hole in the boron nitride plasma channel.



Capillary Arc Plasma

Figure 3.1.

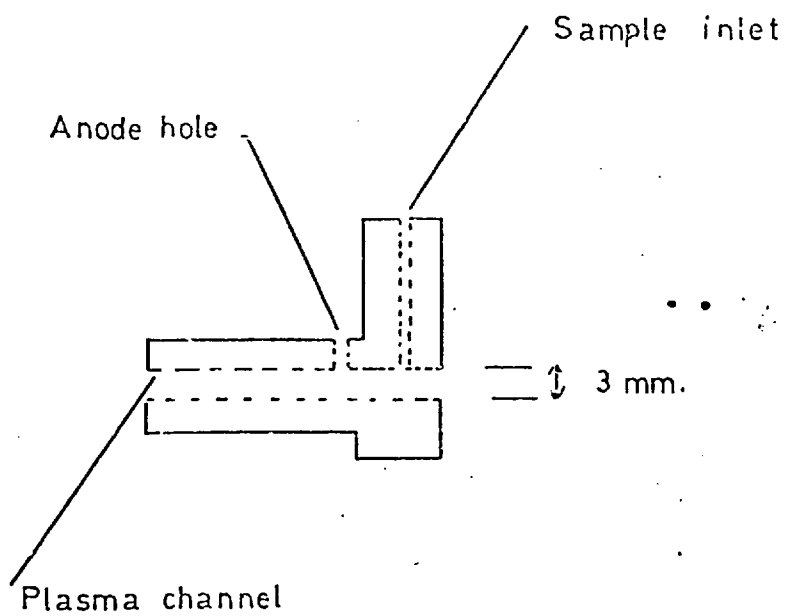


Fig. 3.2 Boron nitride plasma channel

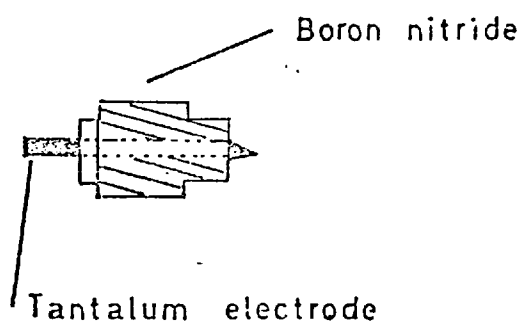


Fig. 3.3 Electrode and holder

Fig. 3.4 a Cathode Block

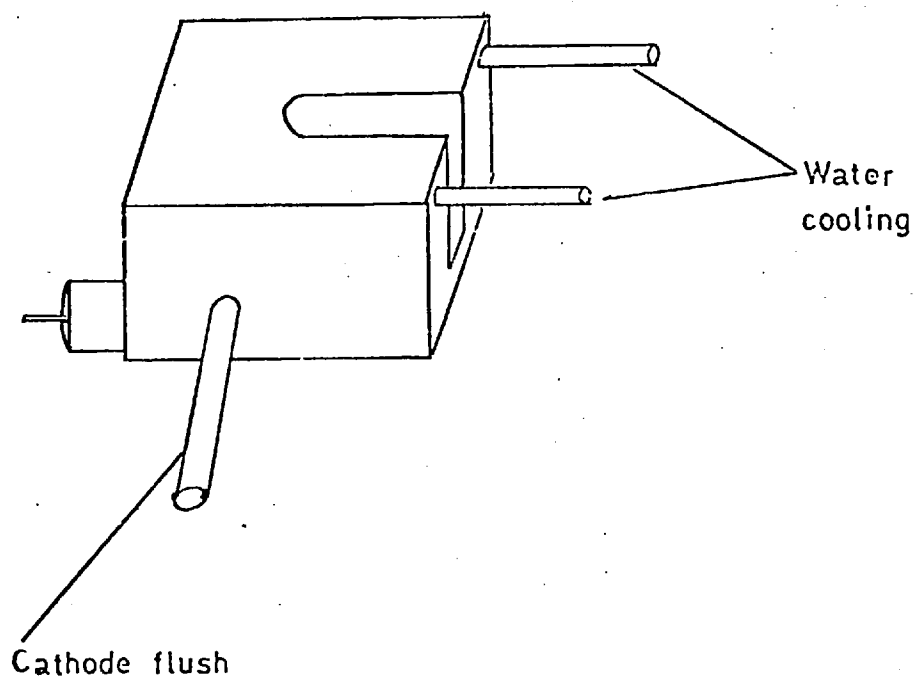
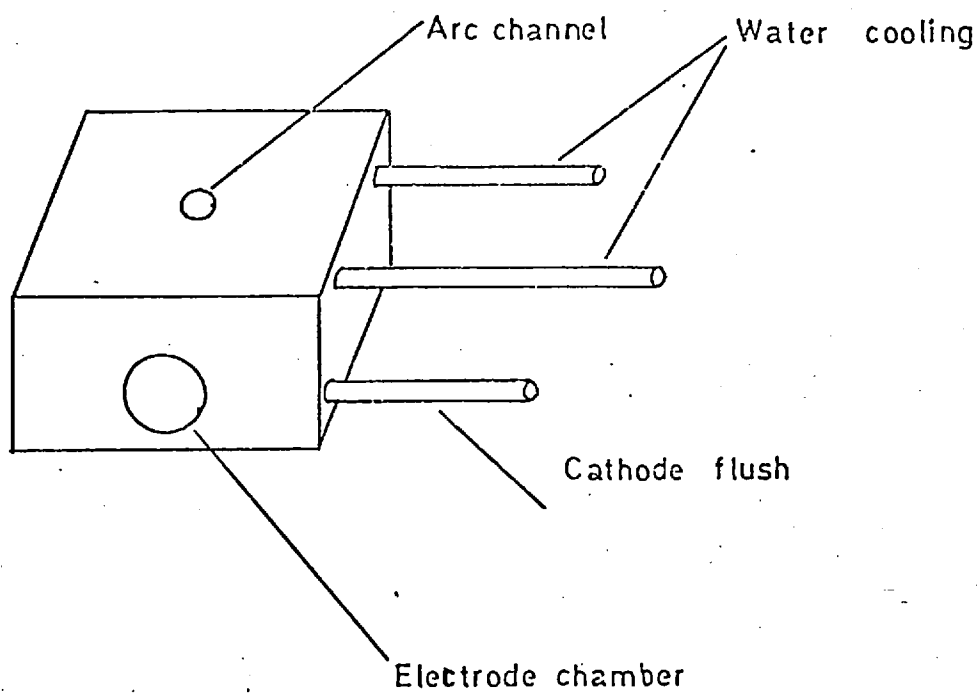


Fig. 3.4b

Cut-away Cathode Block

1. Cathode block
2. Anode block
3. Quartz window

4. BN plasma channel
5. Cut-away cathode block
6. Cathode plus BN holder

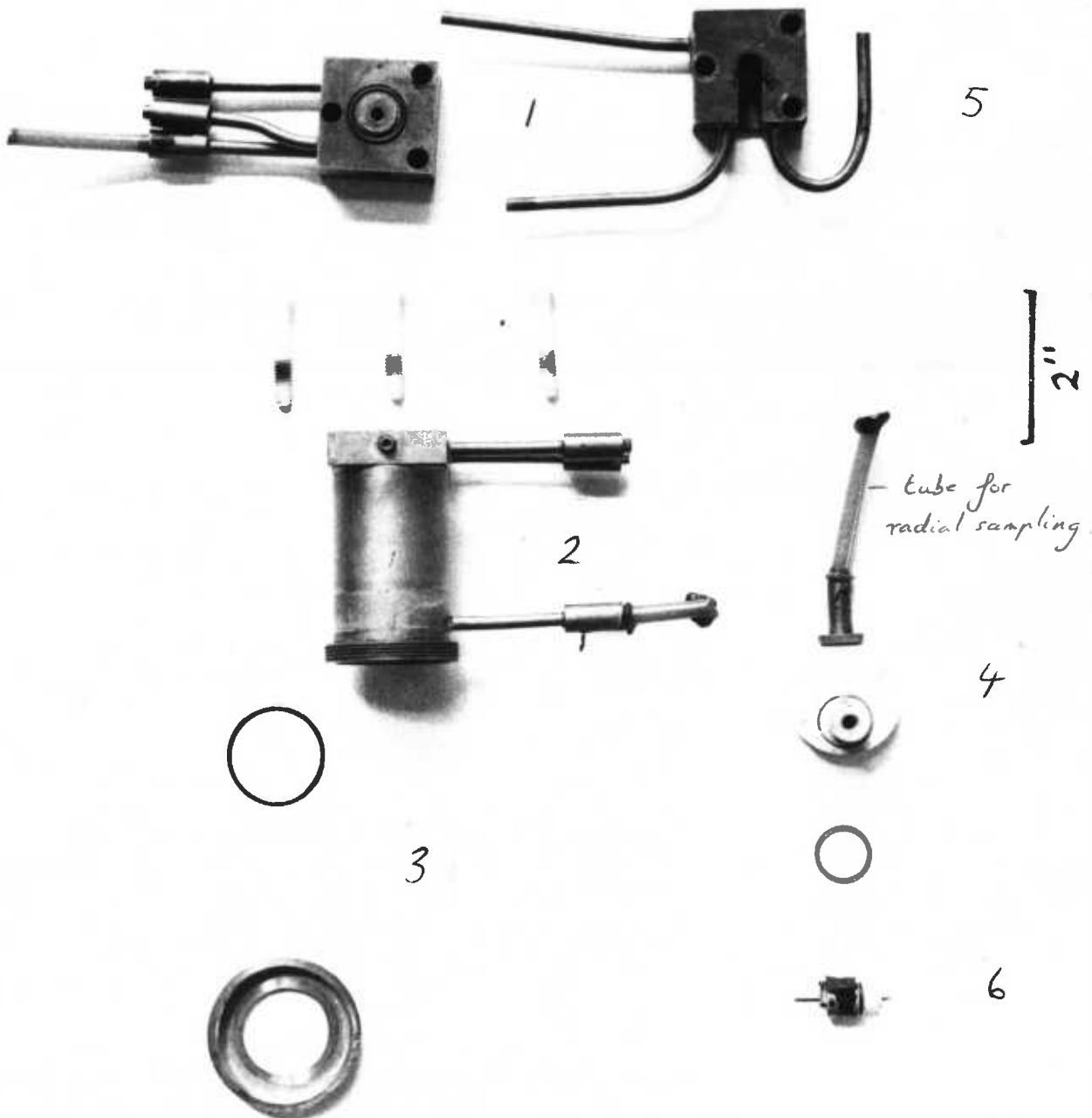


Plate 3.1

The whole assembly was clamped together with three insulating polythene screws and 'O' ring seals were incorporated to prevent gas leakages. The seals were provided between the quartz window and the anode block, between the anode block and the boron nitride plasma channel and between the cathode block and the boron nitride plasma channel. The last two 'O' ring seals were important because they prevented gas leakage out of the CAP.

The CAP was originally designed for use with three argon flow streams. The main plasma flow entered over the quartz window and then passed into the plasma channel. The sample flow entered the plasma radially through a 1 mm orifice in the boron nitride channel. Argon was continuously flushed through the cathode chamber then passed through a 1 mm orifice and entered the plasma 2.5 mm <sup>to the right of</sup>  $\wedge$  the boron nitride plasma channel.

Three flow meters (capacity  $0-3 \text{ l.min}^{-1}$ ) (Meterate Ltd, Hemel Hempstead, Herts) were used to monitor all gas-flow rates. The meters were calibrated for argon at atmospheric pressure before use. The flow system used is shown in Figure 3.5. Argon was initially supplied at a pressure of  $4 \text{ lb.in}^{-2}$ , but instability in the gas flow was noticed. To overcome this problem, the cylinder head pressure was set at  $15 \text{ lb.in}^{-2}$  and the coarse valves were closed down to limit the gas flow. The cathode flush which operated at much lower flow rates than those of the sample or main plasma, was controlled with a fine needle valve (Whitley type 22RS 4). The CAP was initially used at the gas flows as recommended by ARL which were: cathode flush  $0.13 \text{ l.min}^{-1}$ ; sample flow  $1.36 \text{ l.min}^{-1}$ ; plasma flow  $1.03 \text{ l.min}^{-1}$ . These flows were modified in the light of later experience.

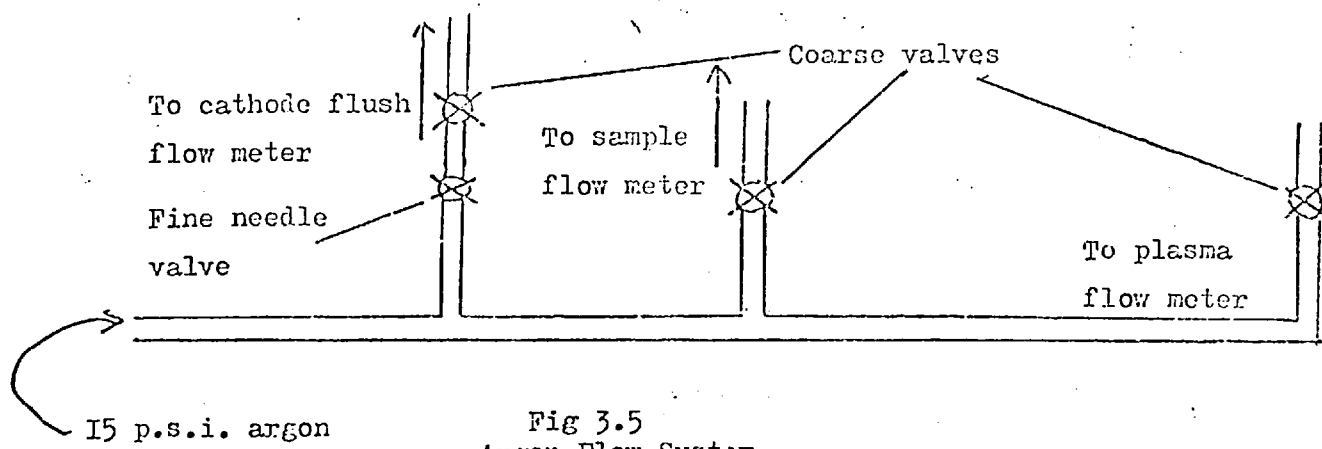


Fig 3.5  
Argon Flow System.

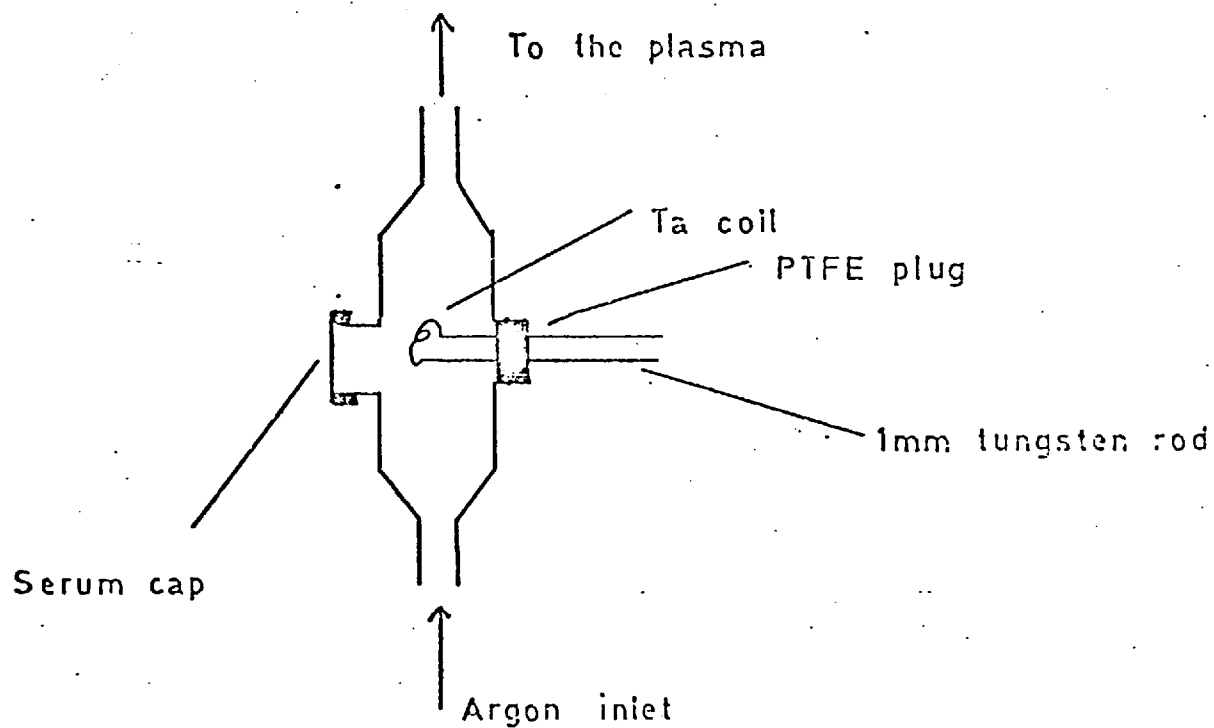
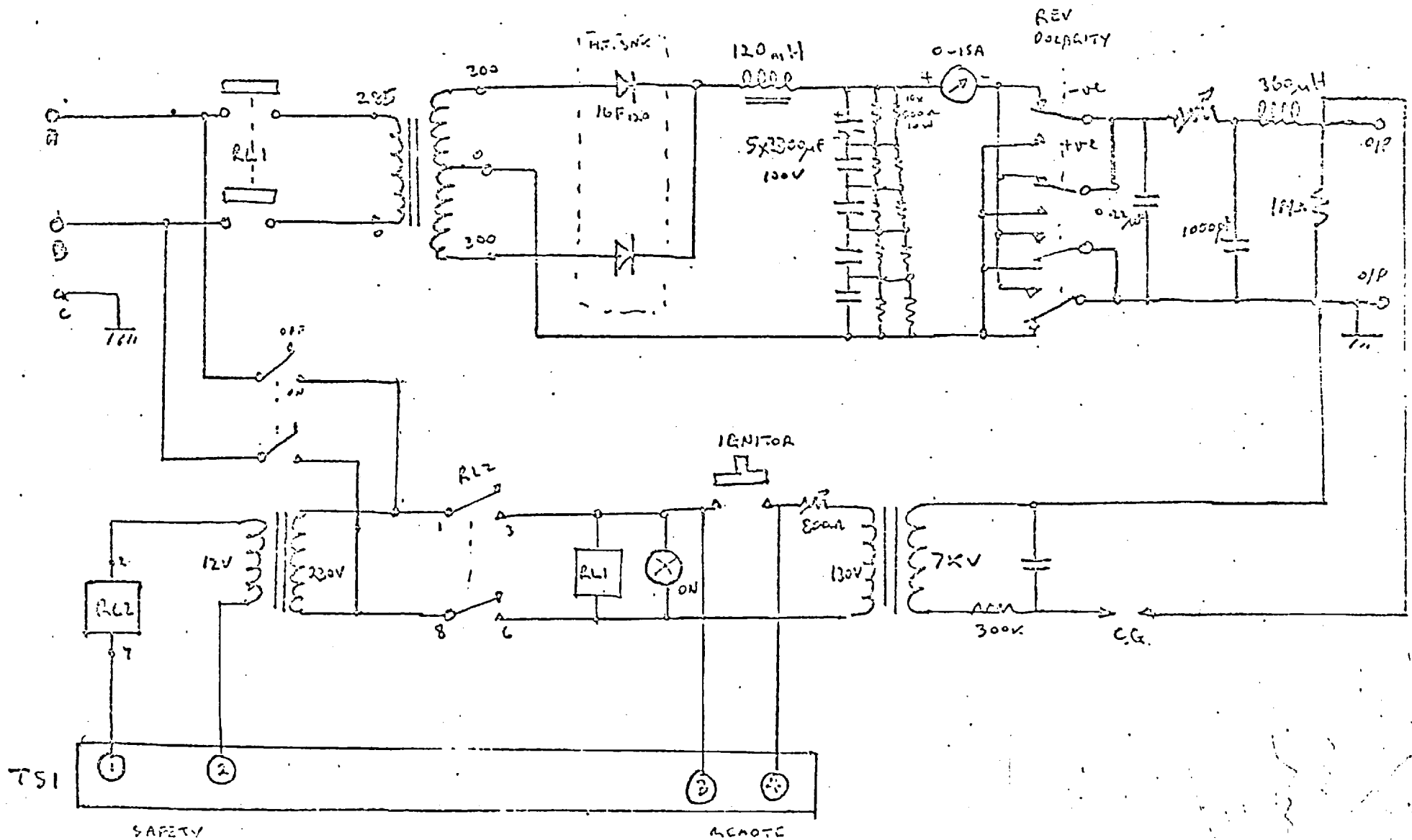


Fig. 3.6. Sample cell

CIRCUIT DIAGRAM FOR 10A D.C. ARC

10/11/72

76A



### 3.2.2 Procedure for the ignition of the plasma

After several weeks operation the following procedure was adopted for plasma initiation:

1. Cooling water was switched on at a rate of about  $1 \text{ l.min}^{-1}$ .
2. The cathode chamber was cleaned with a blast of compressed air, which removed all the cathode deposits left from the last ignition, and also ensured that the cathode flush orifice was not blocked. If this operation was not carried out, the plasma could become unstable leading to melting of the cathode. The melted part was then difficult to remove.
3. A correctly sharpened electrode was inserted into the electrode holder and screwed into the cathode chamber.
4. The CAP was flushed with argon for two minutes, using the above flow rates, to remove all the air from the system.
5. The igniter button was pressed (25 kV tesla-coil) until the arc was initiated; then a few minutes was allowed for stabilisation. If stabilisation was not achieved, which was shown by a long green tail-flame and a spluttering noise, the igniter button was pressed again. If this procedure did not stabilise the discharge, the cathode flush flow was momentarily increased to about  $1 \text{ l.min}^{-1}$  and usually the plasma was stabilised on the tantalum electrode. If, after a period of 15 minutes, the arc still failed to stabilise, the power was switched off, the CAP was allowed to cool and the above procedure was repeated using a sharp electrode.
6. As a last resort, the anode was cleaned with fine emery cloth.

### 3.2.3 Electrode wear

Electrode wear was found to be about 2 mm after 7 hours continuous operation. The arc was started and stabilised within one minute with a correctly prepared conical electrode, which was

sharpened on a grindstone to give a point approximately 5 mm long with an angle of about  $30^{\circ}$ . When the ignition and stabilisation of the plasma was difficult the electrode seemed to wear badly, but when the arc was ignited and stabilised quickly the wear was only slight.

### 3.2.4 Signal measurement

The plasma was viewed by focussing an image of the tail-flame or the arc core on the slit of a modified Unicam SP900 prism spectrophotometer, as described by Sharp et al<sup>(84)</sup>. The monochromator had been fitted with an EMI 9601 B photomultiplier (which consists of eleven dynodes of the box and grid type, with a typical gain of  $4.10^6$ ) and it was connected to a -1000 V (Brandenburg Type 475R) EHT supply. The photomultiplier output was connected across a Servoscribe potentiometric chart recorder, fitted with a  $10k\Omega$  load resistor. Transient signals were measured on a storage oscilloscope (Telequipment Type DM53A) damped with a  $0.047\mu F$  capacitor. Photon counting measurements were made on a six digit Venner frequency meter (Venner Electronics, Kingston-on-Thames, Surrey. Type TSA 6636/3) as described elsewhere<sup>(84)</sup>. Integration of the transient signals was performed with a stable dc analogue integrator.

### 3.2.5 Investigation of plasma operating parameters

Initially the plasma was operated at a current of 10 amps, and the argon flow rates were as stated previously.

#### Plasma stability

To assess the stability of the plasma, its core was viewed directly by placing the quartz window adjacent to the monochromator entrance slit. The wavelength of viewing was chosen at the mercury 253.6 nm line, using a spectrometer slit width of 0.05 mm; (i.e. ca 0.22 nm). Ten-second photon counts were measured over a period of several hours. The results of 79 photon counts showed that the maximum drift over 30 minutes was only 2.3%.

From one count to the next the maximum drift was 1.5%. The percentage relative standard deviation of the 79 counts was 0.79%. From one photon count to the next the average 'noise' on the signal was 0.55%. Longer operating times of up to five hours showed that the plasma emission did not drift more than about 2%.

#### Effect of argon flow rates on plasma stability

The cathode flush flow rate was not critical for arc stability so long as it was within the region  $0.1\text{--}0.2\text{ l.min}^{-1}$ . However, it was observed that high sample introduction flow rates did cause plasma instability. To study the effect of variation in sample flow rate, the main plasma flow was fixed at  $1.06\text{ l.min}^{-1}$  and the cathode flush at  $0.13\text{ l.min}^{-1}$ . The arc was viewed through the quartz window and sixteen ten-second photon counts were taken for several different sample flow rates. The percentage standard deviations for each set of photon counts are shown in Table 3.1. From the table, it can be seen that the arc was more stable when the sample was kept below  $1.7\text{ l.min}^{-1}$ . Above  $2\text{ l.min}$  the plasma could be heard to become more unstable, and was pushed over to one side of the boron nitride insulator.

TABLE 3.1 - Effect of argon flow rate on the precision of background measurement

| <u>Sample flow rate <math>\text{l.min}^{-1}</math></u> | <u>Rel. std. deviation %</u> |
|--------------------------------------------------------|------------------------------|
| 1.42                                                   | 0.32                         |
| 1.65                                                   | 0.23                         |
| 1.85                                                   | 0.51                         |
| 2.1                                                    | 0.54                         |
| 2.4                                                    | 1.4                          |
| 2.7                                                    | 1.3                          |
| 2.8                                                    | 1.0                          |

Increasing the sample flow rate from 1 l.min<sup>-1</sup> to 2.5 l.min<sup>-1</sup> caused a 5% reduction in the background intensity of the plasma.

### Arc current

The arc was found to operate quite well between 8 and 13A, however, it could be operated at currents as low as 6A but instability was often encountered. Increasing the arc current from 8 to 11A caused the background intensity to double.

### 3.2.6 Spectrum scan

The arc core was viewed using a spectrometer slit width of 0.04 nm and a spectrum scan was performed over the region 200 to 600 nm, using the SP900 scanning motor. The scan showed that the background emission was remarkably high above 300 nm. This was due to an actual increase in the background intensity of the arc and a large increase in the bandpass of the prism instrument. The intensity of the arc reached a maximum in the neighbourhood of 350 nm, which seems to be the argon recombination continuum<sup>(85)</sup> whose intensity is related to the effective temperature of the arc. Temperature measurements were made by Skogerboe<sup>(85)</sup>, based on the relative intensities of the argon lines. At an arc current of 6A, the temperature was 2500K, at 9A 3000K and from 12 to 20A remained essentially constant at about 5700K.

In the shorter wavelength region, below 300 nm, the monochromator was accurate enough to enable identification of atomic lines. The only strong line present was at 247.8 nm and this was assigned to carbon from impurities in the argon. A weak line in the region of 249 nm was thought to be boron, volatilised from the boron nitride plasma channel.

### 3.2.7 Sample introduction

The Unicam SP900 pneumatic nebuliser was found to be unsuitable for sample introduction because it only operated

efficiently at relatively high flow rates of about  $4 \text{ l.min}^{-1}$  at  $30 \text{ lb.in}^{-2}$ . At sample flow rates suitable for the arc (i.e. less than  $2 \text{ l.min}^{-1}$ ) the nebuliser produced large droplets which caused the arc to be unstable and droplets condensed at the sample introduction orifice. In order to overcome these problems the nebuliser was removed from the conical spray chamber and incorporated into a desolvator system, consisting of a heated glass tube, a condenser and a liquid trap. The output from the desolvator was passed into the plasma, but instability was again observed.

To investigate the analytical potential of the plasma, it was decided to use a one-shot method for sample introduction. This method has been used previously within this department for a low wattage microwave induced plasma<sup>(73)</sup>. The borosilicate glass cell employed for the one-shot technique can be seen in Fig. 3.6. A serum cap was used to seal the sample introduction port and the heating/atomiser coil was made from tantalum ( $1\frac{1}{2}$  turns of  $0.25 \text{ mm}$  diameter Ta wire). The tantalum was spot-welded on two small pieces ( $1.5 \times 1.5 \text{ mm}$ ) of nickel foil, which were spot-welded on two  $1 \text{ mm}$  diameter tungsten electrodes, held in a PTFE plug.

Platinum and tungsten were also tried for heating/atomiser coils, but platinum could only be heated to about  $1500^\circ\text{C}$  before it became deformed (it melts at  $1769^\circ\text{C}$ ). Tungsten has a high melting point but it is easily oxidised and becomes brittle. Tantalum was chosen because of its high melting point ( $2996^\circ\text{C}$ ) and its resistance to oxidation. The tantalum coil employed in these studies lasted for thousands of samples.

The sample cell was connected to the radial sample introduction port with a short piece of nylon tubing. To operate this system the serum cap was removed from the sample cell and a  $5 \mu\text{l}$  aqueous sample was placed on the tantalum coil from an Eppendorf pipette. A small current from the variac/transformer power supply

was passed through the tantalum coil to remove the water, followed by a larger current to atomise the sample into the argon stream of the plasma.

### OPTIMAL OPERATING CONDITIONS

#### 3.3.1 INTRODUCTION

Cadmium was chosen to optimise the plasma operating conditions, because it was easily volatilised off the tantalum coil, and also it had a strong resonance line in the low background region of the plasma (resonance line at 228.8 nm). Initially the arc was viewed by focussing a 1:1 image on the spectrometer slit using an f 1.5, 50 mm quartz lens.

Before cadmium emission was measured the monochromator was profiled on the 228.8 nm line. This was accomplished by the observation of a cadmium electrodeless discharge tube coupled to a Microtron 200 generator with a  $\frac{1}{4}$ -wave Evenson type cavity.

5  $\mu$ l samples of 1 ppm cadmium sulphate were volatilised into the plasma, and the signals were initially recorded on a Servoscribe potentiometric recorder. However, the recorder response time was too slow to follow the rapid transient signals, so the signals were displayed on the storage oscilloscope. The best signal/noise ratios were obtained using spectrometer slit widths between 0.075 and 0.15 mm.

#### 3.3.2 Optimal gas flow rates

The effect of sample flow-rate on the transient signal from 1 ppm cadmium sulphate (5  $\mu$ l) was investigated by varying the argon flow-rate from 1.38 l.min<sup>-1</sup> to 0.4 l.min<sup>-1</sup>. Arc current was set at 10 amps and all other operating parameters were held constant. The peak height of the signal on the oscilloscope was not greatly affected except at low flow rates below 0.6 l.min<sup>-1</sup> where multiple emission peaks were obtained: these can be seen in Figure 3.7.

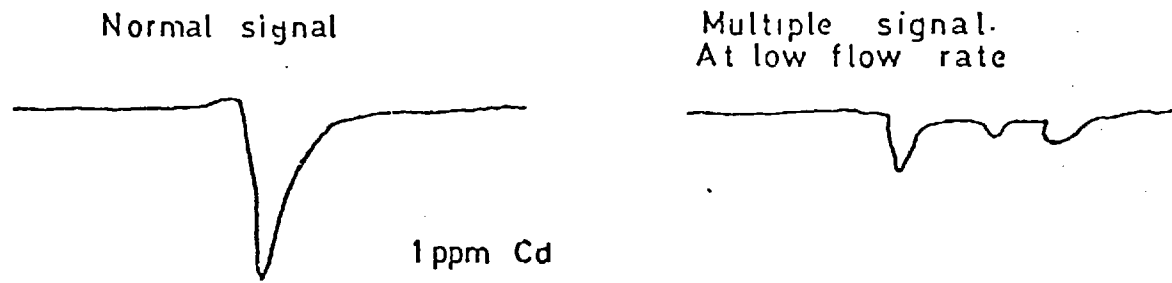


Fig. 3.7 . Transient signals from cadmium

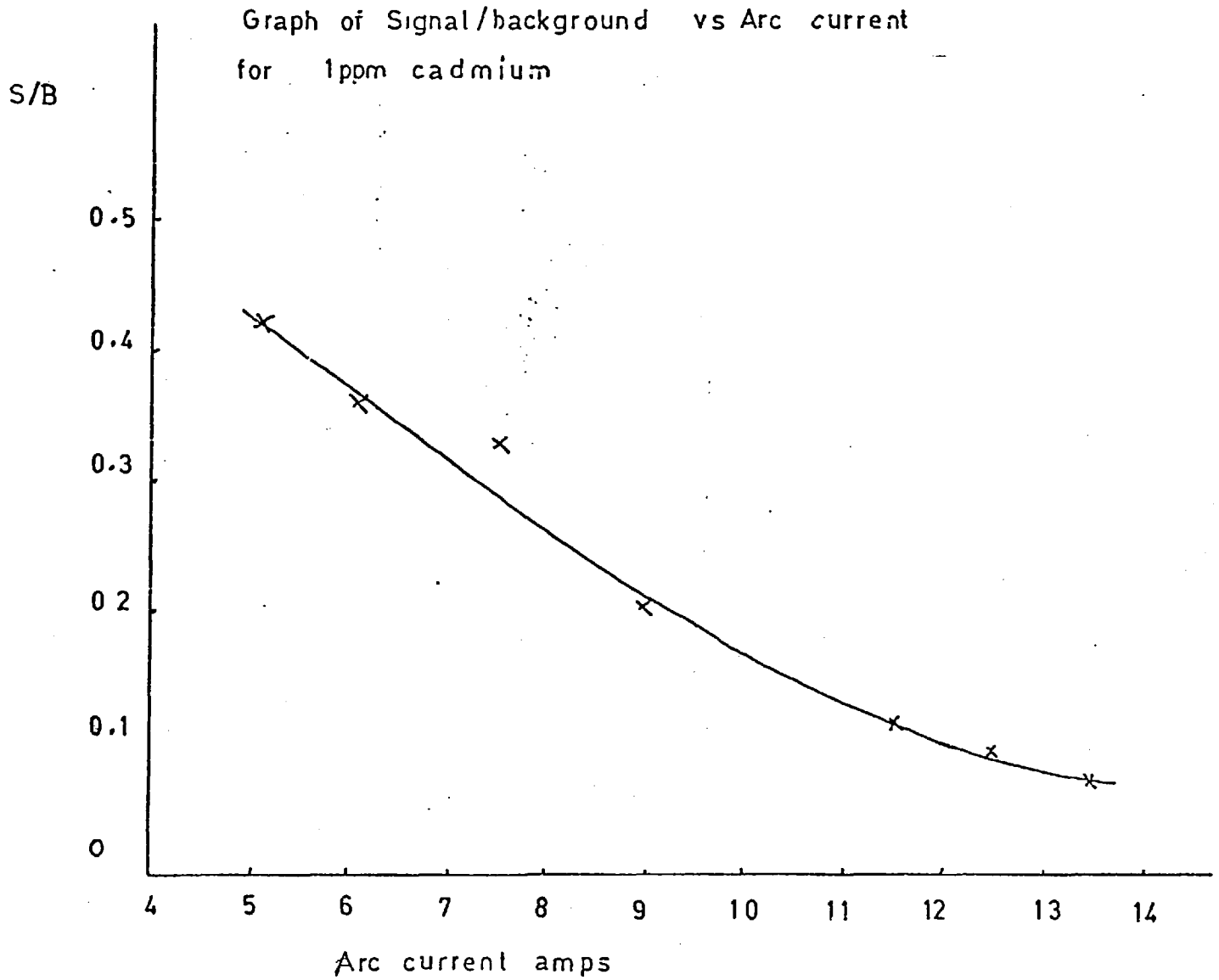


Fig. 3.8

Variation of the main plasma flow between 0.4 and 1.5 l.min<sup>-1</sup> did not significantly alter the signals from 1 ppm cadmium.

### 3.3.3 Arc current

The arc current was optimised by using the gas flow-rates previously determined; 5 µl samples of 1 ppm cadmium were introduced at various arc currents between 5 and 12 amps. The signal to arc-background ratio for the 228.8 nm line was measured and plotted against arc current (Figure 3.8). This graph suggested that better signals were obtained at lower arc currents, but the noise and instability of the arc became a problem below 8A. The best signal-to-noise ratios were obtained at arc currents of 10 amps and above. The signal from the cadmium did not vary much over the whole range of currents used; it was the change in the background emission that was responsible for the slope of the graph.

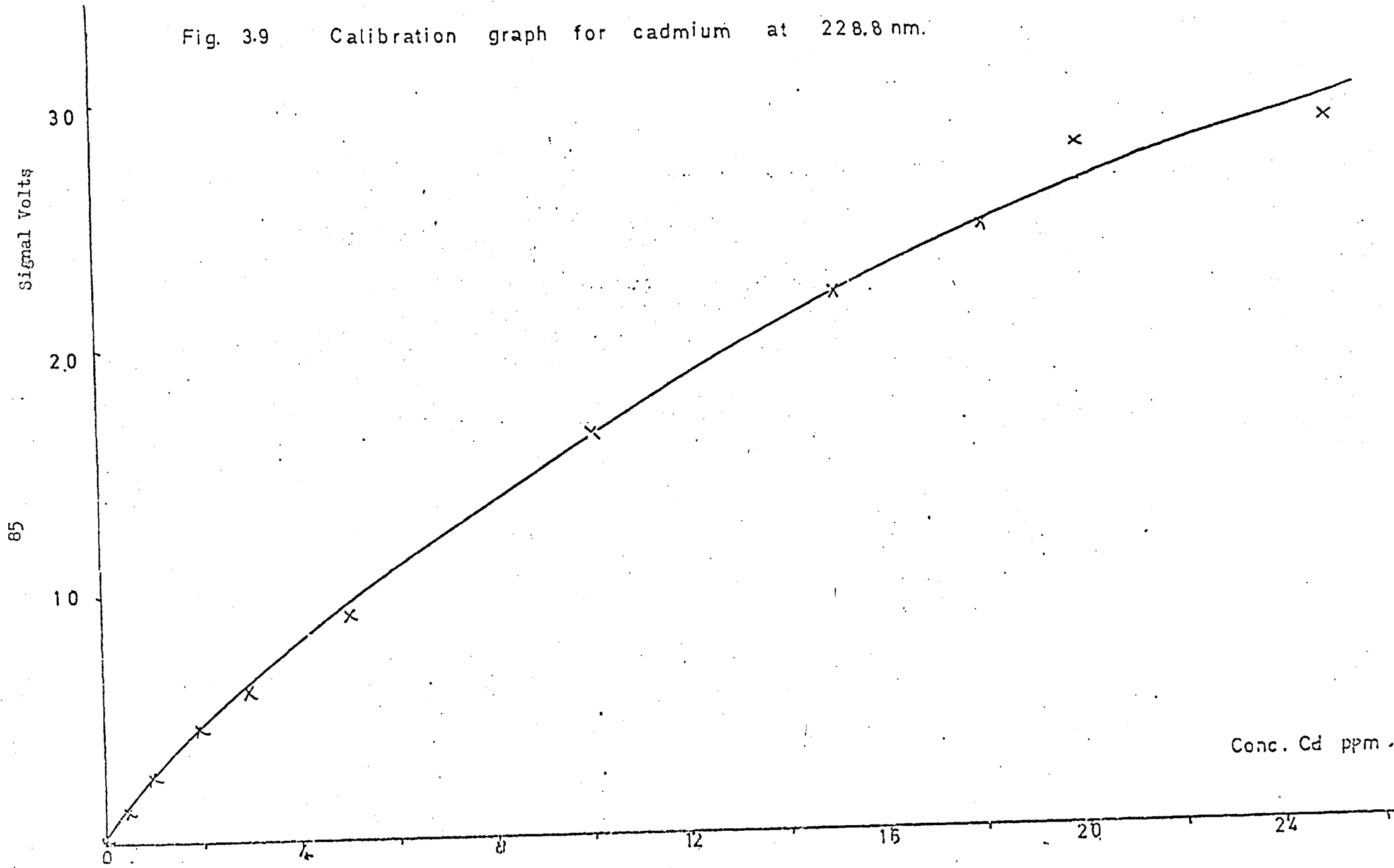
### 3.3.4 Heating rate of the tantalum sampling coil

The height of the transient signal from cadmium was found to increase when faster heating rates were used. The time for full scale response of the damped oscilloscope was about 0.1 sec. A heating rate to give the maximum of the peak signal after about 0.3 sec. was therefore chosen. For a 1 ppm cadmium sample, the total duration was about 1 second.

### 3.3.5 Calibration graph

A calibration graph for cadmium (228.8 nm) was plotted between 0 and 25 ppm by measuring the peak heights of the signals on the oscilloscope, the graph can be seen in Figure 3.9. The curvature in the region of 20 ppm was probably due to the combined effects of self-absorption and the increase in the duration of the signal. Signals from 20 ppm Cd were found to have a total duration of 2 sec., whereas signals from 2 ppm cadmium had a duration of 1 sec.

Fig. 3.9 Calibration graph for cadmium at 228.8 nm.



The detection limit for Cd at 228.8 nm was found to be 0.01 ppm for a 5  $\mu$ l sample ( $5 \times 10^{-11}$  g absolute). The detection limit calculated from signal-to-noise measurements was 0.008 ppm (S/N = 2). Precision measurements were made on 1 ppm and 0.1 ppm solutions. The percentage standard deviations on 40 samples were 6.5% and 11.1% respectively.

### Observation at other wavelengths

The 361.0 nm and 326.1 nm lines were viewed, but no signals could be seen for 1000 ppm cadmium. The signal was lost in the high background of the plasma. It was concluded that the arc core was not suitable for measurement of atomic lines above 300 nm.

#### 3.3.6 Observation of the arc core through the tail-flame

The arc was aligned with the tail-flame of the plasma facing the monochromator. An image approximately 0.5 cm was focussed on the spectrometer shutter and the position of the image on the slit was adjusted to give maximum background emission signal. Samples of cadmium were introduced as before and similar results were obtained, it was therefore concluded that the source was optically thin.

#### 3.4.1 OBSERVATION OF THE TAIL-FLAME

To observe the tail-flame at  $90^\circ$  to the plasma flow, the brass cut-away cathode block was used. An inverted 1:1 image of the tail-flame was focussed on the spectrometer shutter, using the lens arrangement as shown in Figure 3.10. The visible part of the tail flame was about 0.5 cm long and 0.35 cm in diameter at its base. When the plasma was operated with the cut-away block, it was more difficult to ignite and stabilise. The whole of the plasma column was noisy in comparison with normal operation.

Cadmium samples were introduced into the arc and the centre of the tail-flame was viewed. No emission at 228.8 nm was

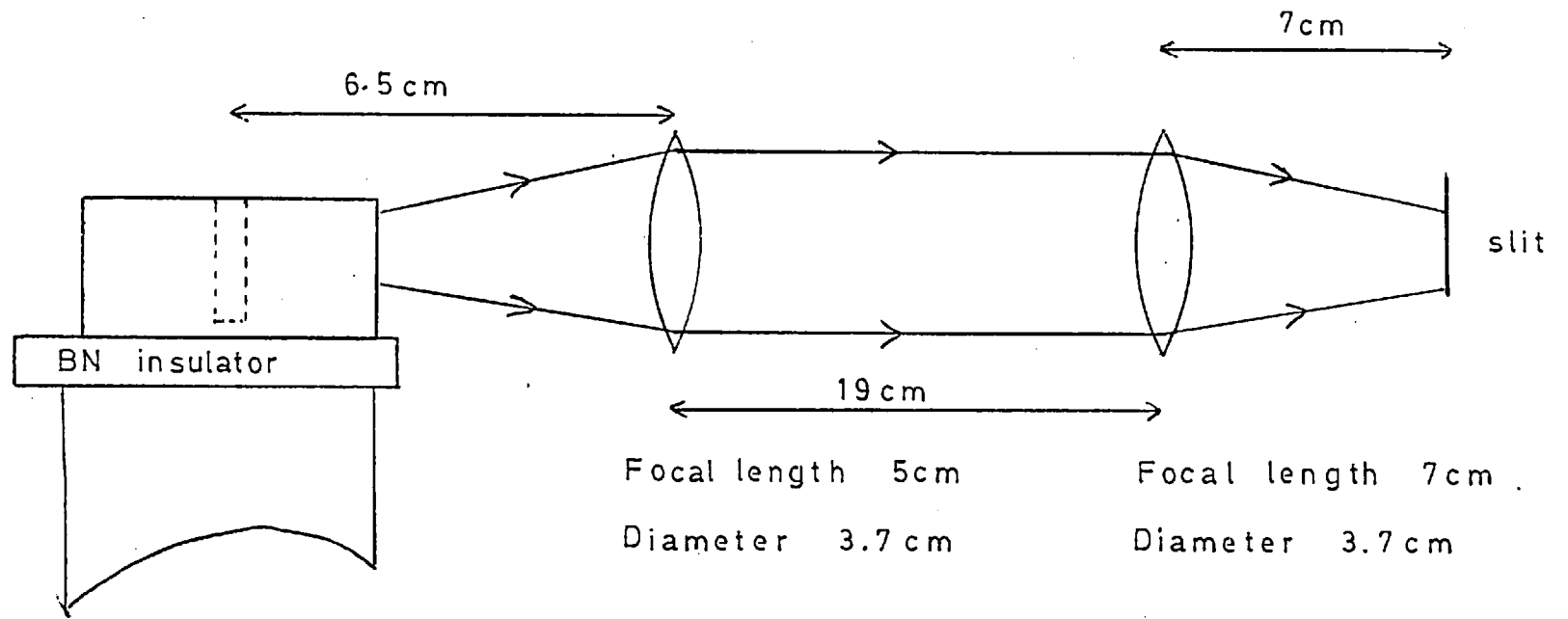


Fig. 3.10. Optics for tail flame viewing.

Graph of signal / background for Cd vs. position  
of viewing

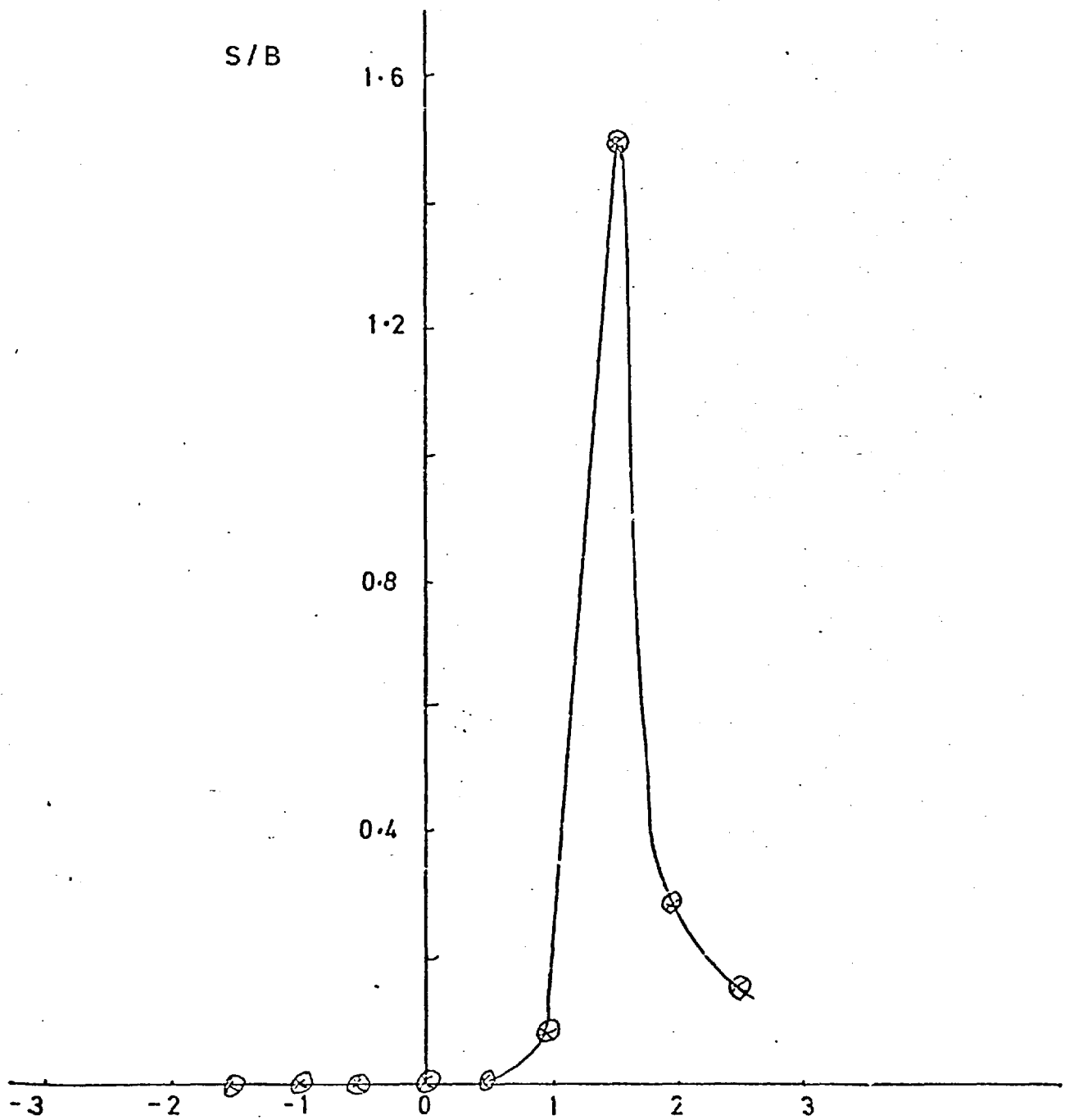


Fig. 3.11.

mm from the centre  
of the plasma.

Fig. 3.12.

Graph of signal/background v.s. height of  
observation in the plasma for 10 ppm Cd.

89

S/B

7

6

5

4

3

2

1

0

2

4

6

8

10

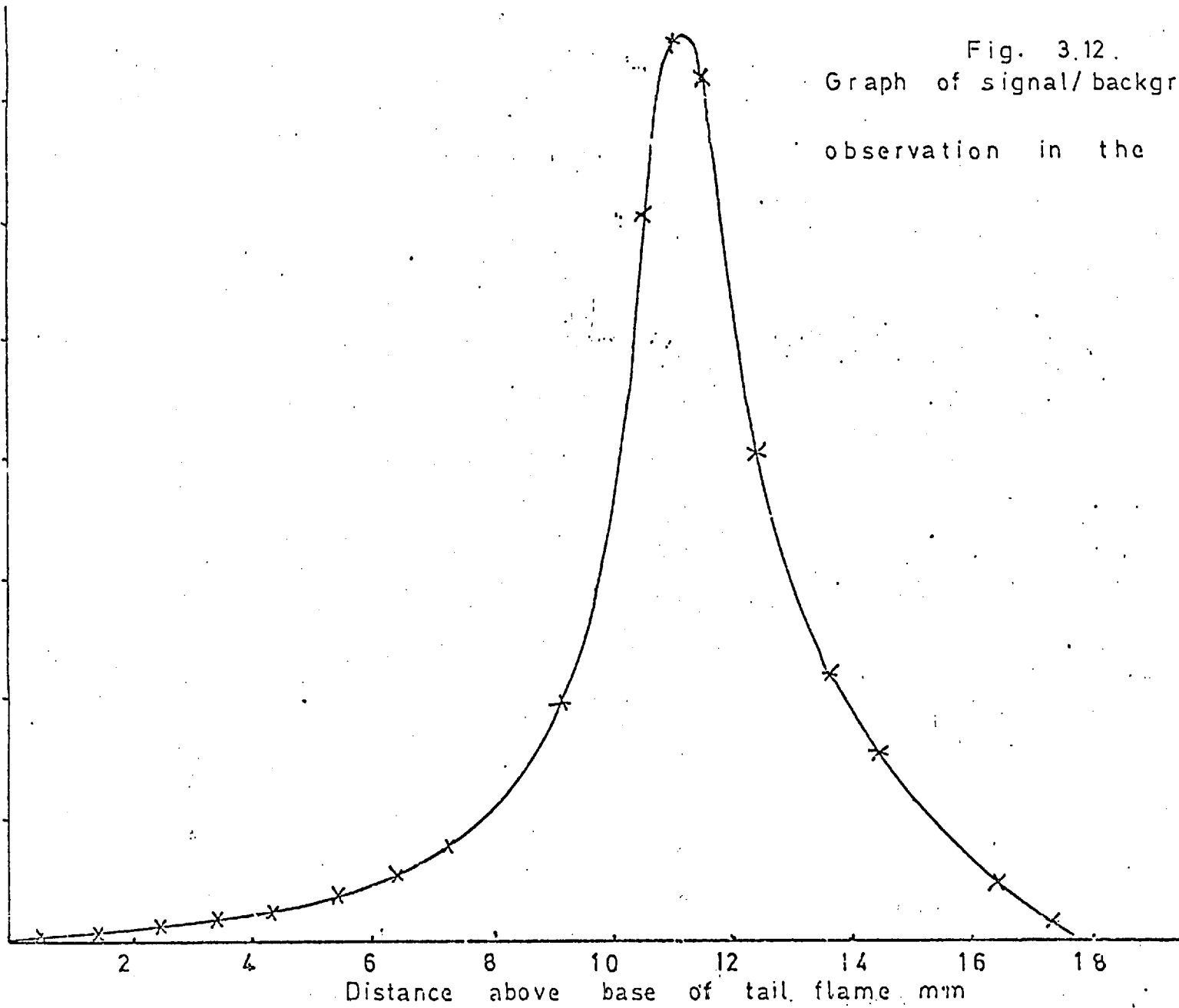
12

14

16

18

Distance above base of tail flame mm



seen. It was soon realised that signals could only be observed near the edge or higher up in the tail-flame. The signal was also very dependent upon the sample flow rate. Figure 3.11 shows the changing signal/background ratio from 10 ppm cadmium obtained by scanning across the plasma with a narrow vertical slit. It can be seen that the sample only entered one side of the tail-flame.

Figure 3.12 shows a plot of the signal/background ratios against height of observation. From this graph it can be seen that large signal/background ratios were observed at heights 11 mm above the base of the tail-flame. However, at this height in the tail-flame the flicker noise became quite large. The signal/noise ratio from 10 ppm cadmium, high in the tail-flame, was less than the signal/noise ratio when viewing the edge.

#### 3.4.2 Flow rate optimisation

Figures 3.13 and 3.14 show the variation in the signal/background ratio for 10 ppm cadmium when the flow rates were varied. The tail-flame was viewed 1.5 mm from its centre with a spectrometer slit of 0.15 mm. At low and high sample flow rates no signal could be observed.

It was mentioned previously that at high sample flow rates the plasma was pushed over to one side of the channel. To show that the loss in signal at high flows was not due to this effect, the tail-flame was viewed at several positions across the plasma, but still no signals were observed.

The best viewing position for cadmium emission at 228.8 nm, using a 0.1 mm spectrometer slit, was 1.5 mm from the centre of the plasma and 4 mm above the base of the tail-flame. Here, the best signal/noise ratios were observed and a detection limit of 0.01 ppm was obtained.

Signal/background (10 ppm Cd) v.s. sample flow rate

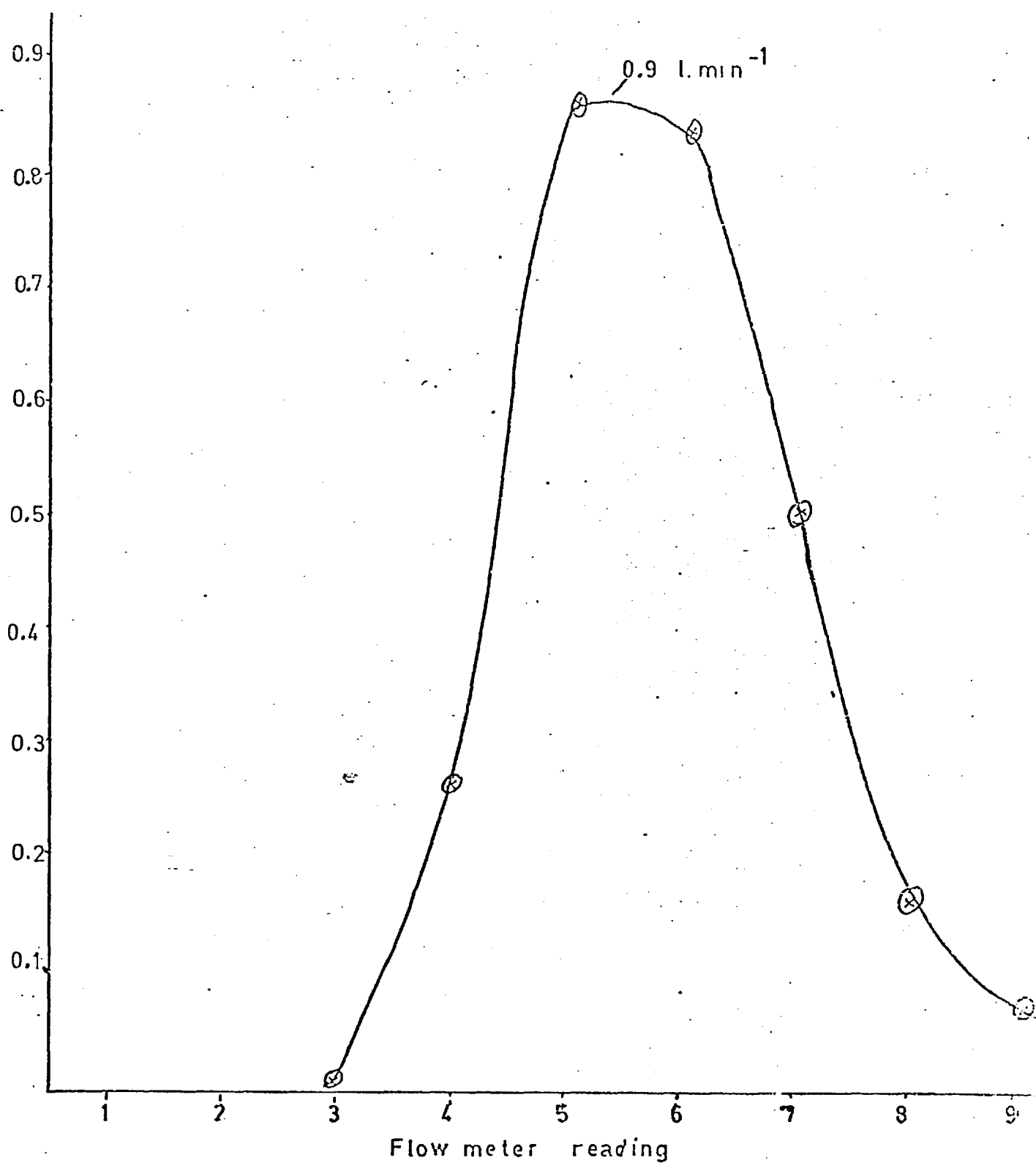


Fig. 3.13

Signal/background (10 ppm Cd) vs plasma flow.

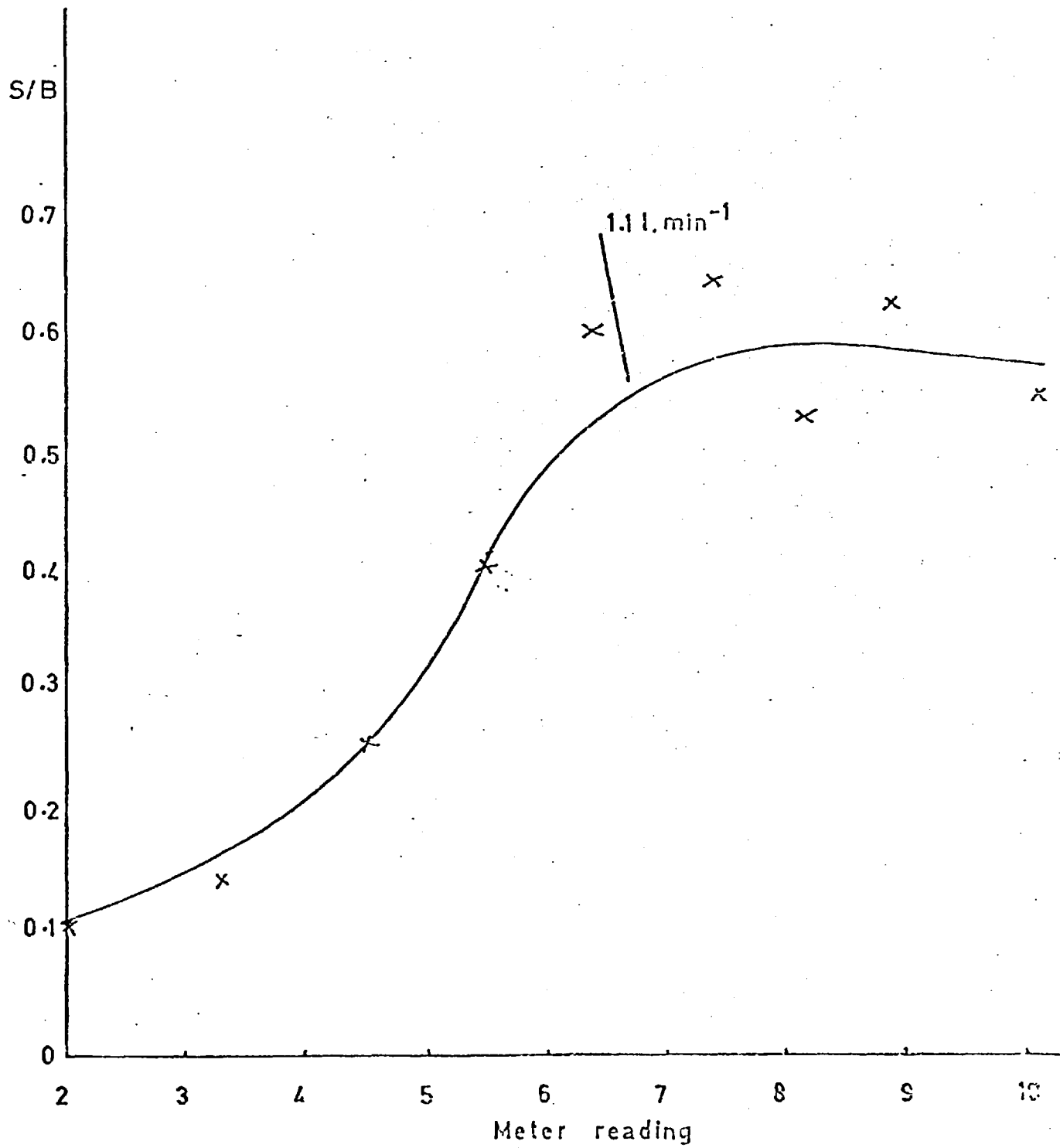


Fig 3.14

Graph of signal/background vs. arc current  
for 10 ppm Cd

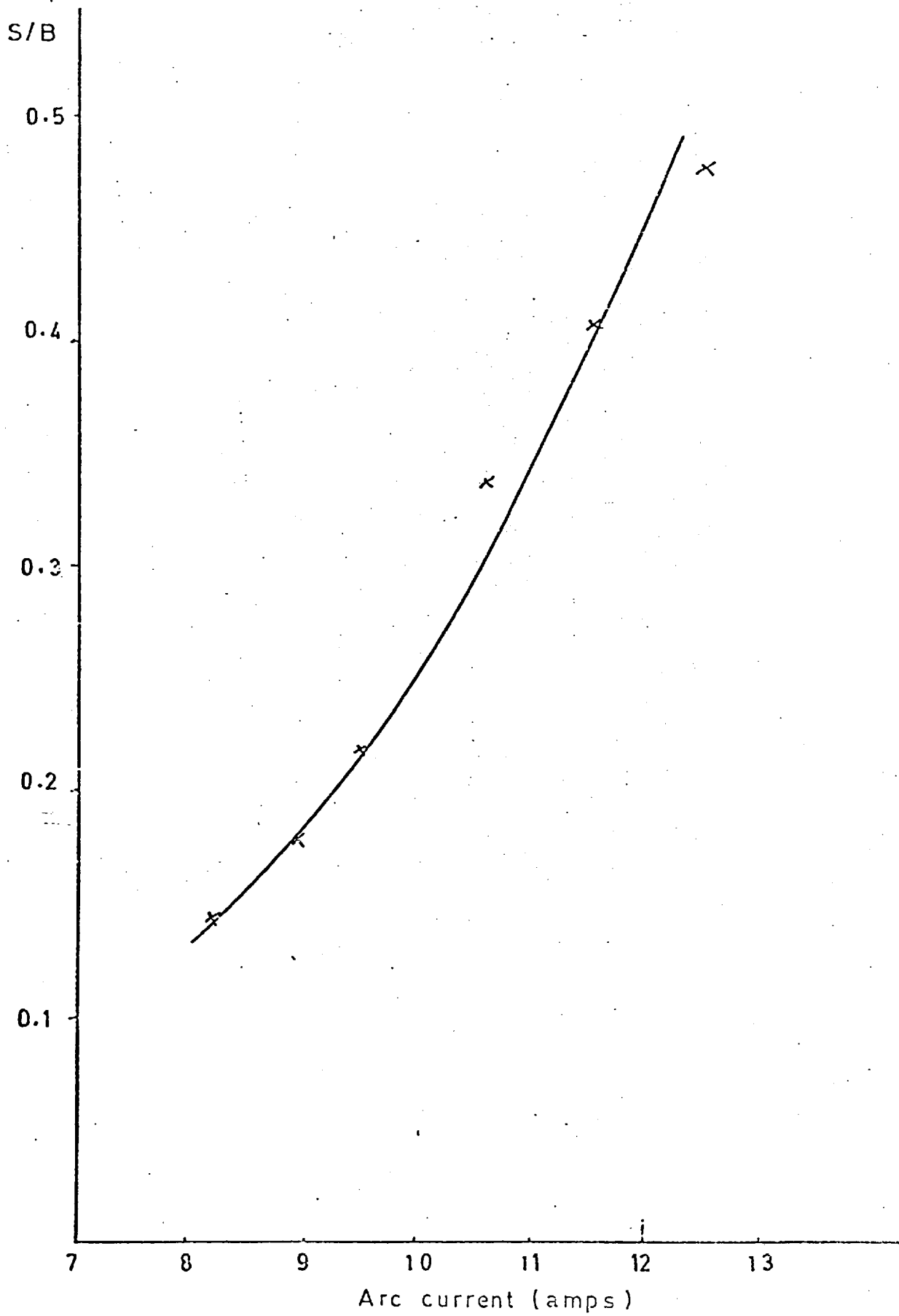


Fig . 3.15

### 3.4.3 Arc current

The full length of the tail-flame was viewed approximately 1.5 mm from the centre with a spectrometer slit width of 0.1 mm. No attempt was made to optimise the position for the best emission intensity from the cadmium, because good signals were obtained from 10 ppm. Signal measurements were made for several arc currents between 8 and 12.5 amps. A plot of signal/background against arc current (Figure 3.15) shows that at higher currents better signals were observed and also the signal/noise ratio was improved.

### 3.4.4 Operation of the arc on the sample flow

Figure 3.11 indicates that the sample is rejected by the hot expanding plasma gas. In order to try to overcome this problem, the plasma was operated on the sample and cathode flush flows. 10 ppm samples of cadmium were introduced into the plasma, but the sensitivity was low. The arc was also operated on the main plasma flow and cathode flush. The sample cell was connected into the main plasma flow, and samples were again introduced, but only small signals were recorded.

### 3.4.5 Analysis at 326.1 and 361.0 nm

The signal from 1 ppm cadmium could easily be seen at 326.1 and 361.0 nm. The detection limits for 5  $\mu$ l samples were 0.1 and 0.05 ppm respectively. Observation of the analytical signal in the tail-flame was considered preferable to observation through the arc core, because of the considerably lower continuum emission in the spectral region at wavelengths greater than 300 nm. The relative intensities of the 326.1, 361.0 and 228.8 nm lines were difficult to compare because the spectral bandpass of the monochromator varied with wavelength.

Signal

Calibration curve for Cd in the tail flame.

mV

140

120

100

80

60

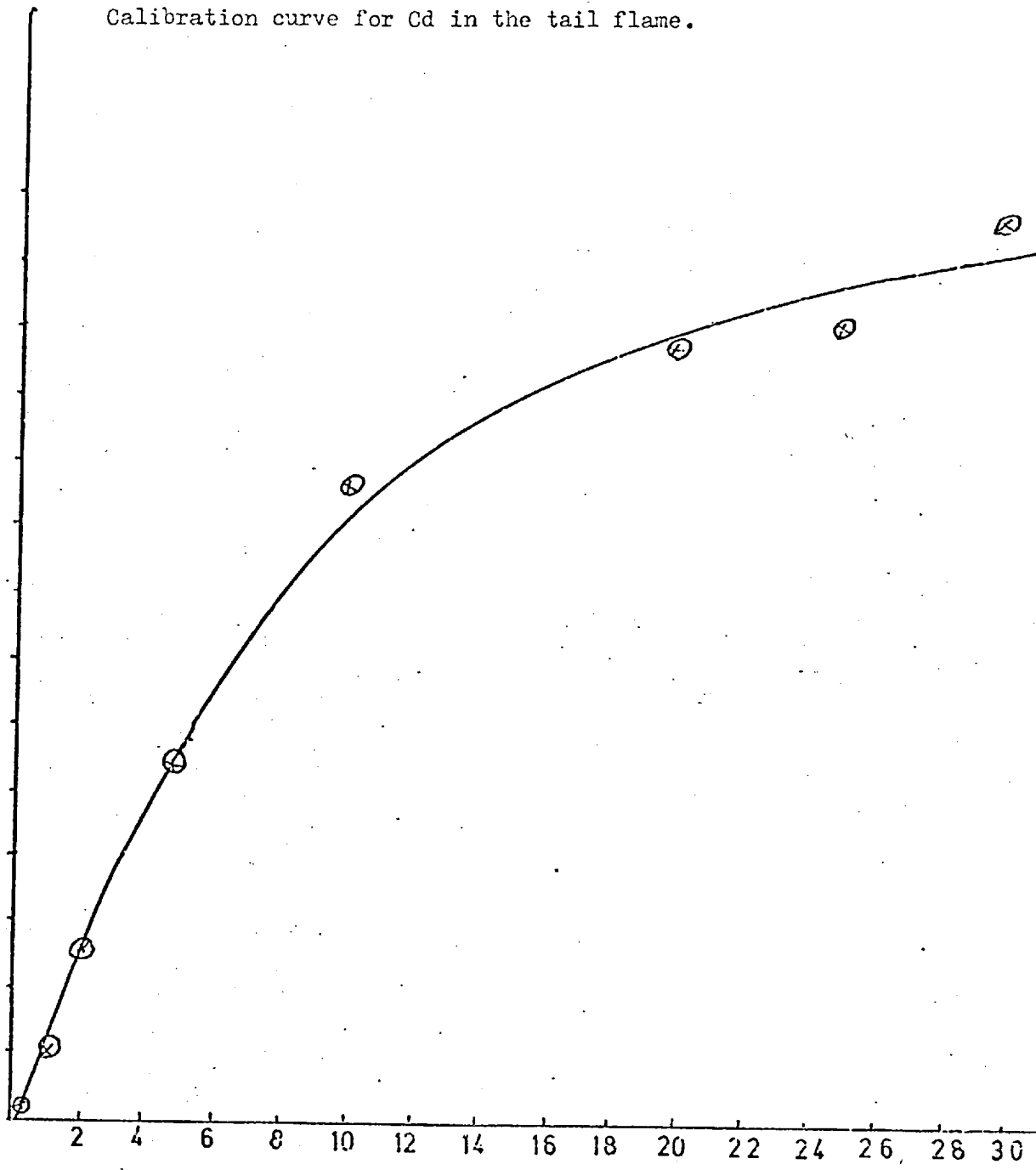
40

20

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30

Conc. ppm.

Fig . 3.16



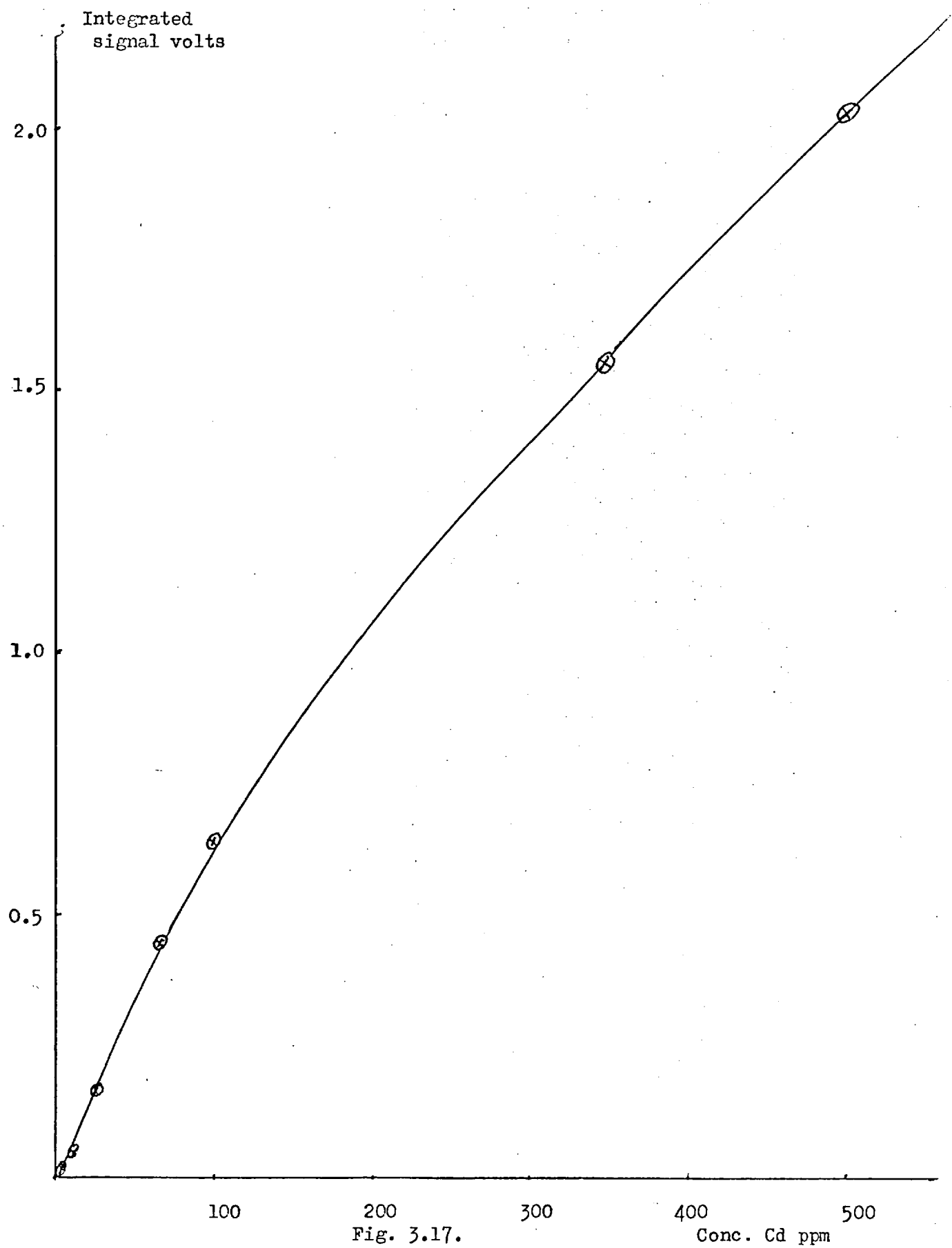
### 3.4.6 Calibration graph

A calibration graph for cadmium at 228.8 nm was plotted from 0.1 to 30 ppm. The graph (Figure 3.16) was similar in shape to that produced from the arc core. Another calibration graph was constructed using the transient signal integrator, which was capable of integrating the signal without effect from the plasma's background emission. The output from the integrator was fed into a Servoscribe potentiometric recorder. An analytical growth curve from 0 to 500 ppm cadmium is shown in Figure 3.17. Use of this integrator increased the linear range of the graph, and the small amount of curvature was probably due to self-absorption. The precision of this method of signal measurement was established using a 1 ppm solution of cadmium, and the percent standard deviation for 20 samples was 5.3%.

### 3.4.7 Interferences

- (i) Signals from 1 ppm cadmium in the presence of 100 fold excesses of various interferences were measured, using the peak height recorded on the oscilloscope. Table 3.2 shows the interference effects along with any comments on peak-signal shape. The positive interferences from arsenic and antimony were due to changes in the rate of volatilisation from the tantalum coil. This was indicated by broader signals. The positive interferences from the iron could not be explained in terms of spectral interference, but latter work showed that the monochromator leaked light of other wavelengths.
- (ii) Integration - It was thought that any interferences due to differing rates of volatilisation from the tantalum coil would be eliminated by use of the integrator. In the case of the interferences due to aluminium, sulphate and chloride, this was found to be the case (see Table 3.2).

Graph of integrated signal vs. conc. Cd



### 3.4.8 Analysis of other elements

The other elements investigated were arsenic, zinc, lead, mercury and iodine. The position of viewing the tail-flame for each of these elements was optimised, and detection limits were measured. Theoretical detection limits were calculated from signal/noise ratios. Table 3.3 shows the detection limits, position of viewing the tail-flame and calculated detection limits.

### 3.4.9 Other methods of sample injection

To try to overcome the sample rejection problem a high velocity sample input was created by inserting a 20 gauge stainless steel tube with an internal diameter of 0.6 mm into the tangential sample introduction port. The stainless steel tube was connected to the sample cell and samples were introduced in the normal way. However, it was found that the sample did not enter the central regions of the plasma.

An alternative method for high velocity sample introduction involved injecting the sample along the axis of the plasma. This was performed by removing the quartz window and inserting a 'Tufnol' plastic plate fitted with a copper sleeve (Figure 3.18) to allow introduction of a 20 gauge stainless steel tube (0.6 mm internal diameter). The tube was then raised to within 3 mm of the plasma anode. Unfortunately, the tube melted at the tip. The melting problem was overcome by using alumina tubing cemented to the end of a piece of 17 gauge stainless steel tubing. It was possible to move this alumina tubing to within 1 mm of the plasma anode, without any damage being done to the injection orifice. Various tube sizes from 0.2 mm to 0.86 mm internal diameter were tried and the 0.38 mm tube was found to be the best for sample injection, at a flow rate of  $0.4 \text{ l.min}^{-1}$ . The detection limit for cadmium was about 0.005 ppm. The results, however, tended to be erratic from day to day. This was thought to be due to movement of the injection

TABLE 3.2 - Interference of 100 ppm concentration of various ions on the signal for cadmium (1 ppm) at 228.8 nm

| <u>INTERFERENT</u>                               |     | <u>INTERFERENCE %</u> | <u>COMMENT</u>  |
|--------------------------------------------------|-----|-----------------------|-----------------|
| Fe as $\text{FeCl}_3$                            | (a) | 600                   | -               |
| $\text{NO}_3^-$ as $\text{HNO}_3$                | '   | 0                     | -               |
| $\text{BO}_3^{3-}$ as $\text{H}_3\text{BO}_3$    | '   | 0                     | -               |
| As as $\text{Na}_3\text{AsO}_4$                  | '   | 2000                  | -               |
| Sb as $\text{SbCl}_3$                            | '   | 400                   | -               |
| $\text{SiO}_4^{4-}$ as $\text{Na}_4\text{SiO}_4$ | '   | -30                   | Broader peaks   |
| $\text{PO}_4^{3-}$ as $\text{H}_3\text{PO}_4$    | '   | 0                     | -               |
| V as $\text{NH}_4\text{VO}_3$                    | '   | 0                     | Narrow peaks    |
| $\text{Cl}^-$ as $\text{HCl}$                    | '   | -25                   | -               |
| $\text{SO}_4^{2-}$ as $\text{H}_2\text{SO}_4$    | '   | -25                   | -               |
| Na as $\text{NaCl}$                              | '   | 0                     | Broader peaks   |
| Al as $\text{Al}_2(\text{SO}_4)_3$               | '   | -30                   | Broader peaks   |
| $\text{NO}_3^-$ as $\text{HNO}_3$                | (b) | 0                     | -               |
| Na as $\text{NaCl}$                              | '   | 60                    | -               |
| $\text{SO}_4^{2-}$ as $\text{H}_2\text{SO}_4$    | '   | 0                     | -               |
| Al as $\text{Al}_2(\text{SO}_4)_3$               | '   | 0                     | -               |
| $\text{PO}_4^{3-}$ as $\text{H}_3\text{PO}_4$    | '   | 0                     | -               |
| $\text{SiO}_4^{4-}$ as $\text{Na}_4\text{SiO}_4$ | '   | -20                   | Variable signal |
| Fe as $\text{FeCl}_3$                            | '   | 300                   | -               |
| $\text{BO}_3^{3-}$ as $\text{H}_3\text{BO}_3$    | '   | 0                     | -               |
| $\text{Cl}^-$ as $\text{HCl}$                    | '   | 0                     | -               |
| Sb as $\text{SbCl}_3$                            | '   | 200                   | -               |
| As as $\text{Na}_3\text{AsO}_4$                  | '   | 1400                  | -               |
| V as $\text{NH}_4\text{VO}_3$                    | '   | -40                   | Variable signal |

(a) Interferences using oscilloscope measurement

(b) Interferences using integration measurement

TABLE 3.3 - Analytical data for various elements in the plasma

| <u>ELEMENT</u> | <u>WAVELENGTH<br/>(nm)</u> | <u>DET. LIMIT<br/>(ppm)<br/>(5 <math>\mu</math>l sample)</u> | <u>CALCULATED<br/>DET. (ppm)<br/>LIMIT</u> | <u>POSITION OF VIEWING</u> |
|----------------|----------------------------|--------------------------------------------------------------|--------------------------------------------|----------------------------|
| As             | 228.8                      | 0.25                                                         | 0.25                                       | 1.5 mm and above           |
| Zn             | 213.8                      | 0.25                                                         | 0.2                                        | 1.5 mm and above           |
| Pb             | 261.4                      | 1.5                                                          | 0.7                                        | 4 mm and above             |
| Hg             | 253.6                      | 1                                                            | 0.7                                        | 1.5 mm and above           |
| I              | 206.1                      | 50                                                           | 14                                         | 1 mm and above             |

## High velocity sample introduction.

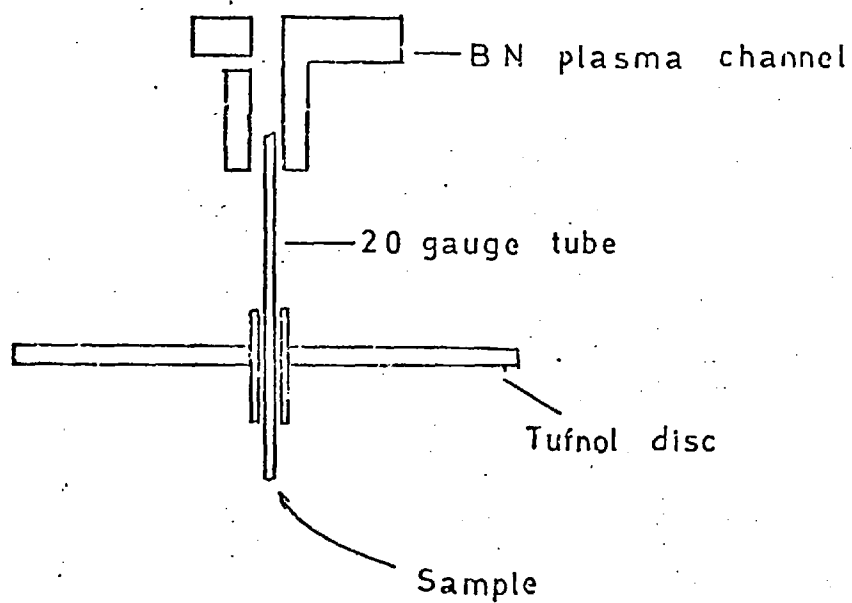


Fig. 3.18.

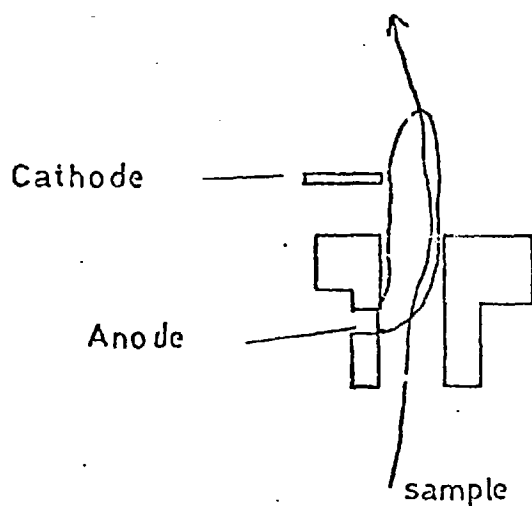
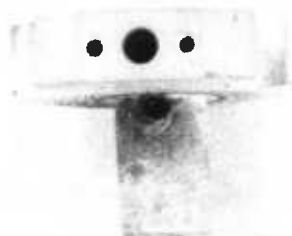


Fig. 3.19. Sample passage through the plasma.



BN plasma channel



High velocity injector



Tube for axial sample injection.  
(Disc replaces quartz window)

tube. In order to overcome this problem, a precision racking device (see Plate 3.2) which allowed the capillary tube to be moved up and down inside the plasma channel and also across the base of the plasma, was constructed. This did not, however, permit any increase in the reliability of the sample injection and the best position for viewing the cadmium emission was still at one edge of the plasma. The shape of the plasma shown in Figure 3.19 may have been responsible for the difficulty involved here. The sample was shown only to enter the side of the plasma opposite the anode. The arrowed line represents the probable sample path. It was usually observed that during a given run, sample injection was reproducible, even if not efficient. However, on re-starting the arc following switch-off, re-alignment of the sample introduction tube was necessary on every occasion.

#### 3.4.10 Conclusions

The plasma was found to be very stable and operated for several hours with only slight cathode wear and negligible anode wear. Sample introduction using commercial nebulisers was unsuccessful because they operated at flow rates which were too high. The plasma tail-flame was found to be superior to the arc core for analysis, because the background emission was much lower. Integration of the transient emission signals produced more linear calibration graphs, and also solved some of the interference problems that were due to varying rates of volatilisation of the samples from the tantalum filament. Sample rejection by the plasma was thought to be responsible for the poor sensitivity. Several attempts to try and inject the sample into the centre of the plasma met with limited success.

One-shot sample introduction has been used extensively for trace element analysis<sup>(86-88)</sup>. The main advantage over

conventional nebulisation is the very low absolute detection limits often obtained. The disadvantages arise mainly from the transient nature of the signals, which require fast response recording equipment and precision is usually not better than about 5%.

The simplest method for small sample analysis (10  $\mu$ l) with a flame is that of Delves<sup>(89)</sup>, who determined lead in blood by vaporisation from a nickel crucible into a silica absorption tube placed in an air-acetylene flame. The Delves sampling technique has been applied to the analysis of antimony, bismuth, cadmium, cobalt, copper, mercury, selenium tin and zinc, all with detection limits of about  $10^{-10}$  g<sup>(90-92)</sup>. In comparison, conventional nebulisation into flames needs much larger sample volumes (approximately 2 ml) and typical detection limits are at least an order of magnitude higher, normally in the range  $10^{-8}$  -  $10^{-9}$  g. This conventional nebulisation is inefficient, only 5-10% of the nebulised sample actually reaches the flame. Plasmas, unlike flames, can only tolerate small amounts of water, therefore low sample flow rates and/or desolvation is required for continuous operation.

For cadmium the detection limit in the CAP was  $5 \times 10^{-11}$  g, this entered the plasma in approximately 0.3 seconds (i.e.  $1.5 \times 10^{-10}$  g.sec<sup>-1</sup>). With a continuous system operating at a sample input rate of 2 ml.min<sup>-1</sup> and an efficiency of 5%, the detection limit would be  $3.6 \times 10^{-8}$  g or 0.018 ppm. The calculation assumes: (i) the noise on the plasma emission background is not increased by the continuous sample; (ii) the sample experiences the same temperature, and undergoes the same processes as the one-shot sample. The detection limit of 0.018 ppm is optimistic because condition (i) will not be achieved, because small amounts of water increases the noise on the plasma background. Therefore, for

continuous sampling the calculated limit should be much lower than the experimental detection limit. The following chapter investigates continuous sample introduction, using a nebuliser constructed in the college workshops.

CONTINUOUS SAMPLE INTRODUCTION  
INTO THE CAPILLARY ARC PLASMA

CHAPTER FOUR

#### 4.1.1 Introduction

Previous work has shown that continuous sample introduction into the CAP requires a nebuliser capable of operating below  $3 \text{ l.min}^{-1}$ . The nebuliser shown in the top left of Plate 6.1 was constructed in the college workshops, and was used for the work reported in this chapter. The nebuliser design, construction and operation is discussed later in Chapter 6.

#### 4.1.2 Direct Sample Introduction

Introduction of an aerosol sample without the use of desolvator was investigated. An expansion chamber was constructed from a 500 ml polythene bottle, a drain and a  $\frac{1}{4}$  inch diameter outlet tube were fitted. The nebuliser was held in position in the bottle-neck with a rubber bung, and the chamber outlet was connected to the radial sample introduction port of the CAP. The nebuliser was operated at an argon flow of  $1.85 \text{ l.min}^{-1}$  ( $8 \text{ lb.in}^{-2}$ ) producing a sample uptake rate of  $0.4 \text{ ml.min}^{-1}$ .

#### Plasma ignition

A piece of sealed plastic sampling tube was placed over the end of the nebuliser's capillary tube to prevent air from entering the system. The plasma was ignited in the usual way, the plasma flow was set at  $1.6 \text{ l.min}^{-1}$ , and a few minutes was allowed for stabilisation. The sealed tube was then removed from the capillary tube and water was sprayed into the CAP, and during the first few minutes of operation, the aerosol began to condense in the chamber outlet tube. Eventually pulsing of the sample flow stream (caused by droplet condensation) created instability in the plasma.

#### 4.1.3 Sample desolvation

In Chapter 3, the single-shot method of sampling provided a means of desolvation of the analyte before its entry into the plasma. Other workers, notably Winefordner et al<sup>(75)</sup>, Lichte and Skogerboe<sup>(77)</sup> and Dickinson and Fassel<sup>(56)</sup> have used desolvators in conjunction with

radio frequency and microwave plasmas. The desolvators were based on the design of Veillon and Margoshes<sup>(18)</sup>. A nebuliser, operating on argon at  $50 \text{ lb.in}^{-2}$ , was inserted into the end of a heated glass chamber ( $5 \times 15 \text{ cm}$ ) and the output from the chamber was connected to a Friedrichs condenser cooled with water at  $10^\circ \text{C}$ . The excess water from the sample was condensed and collected in a liquid drain trap. The dry aerosol was transported in the stream of argon to a radio frequency plasma-torch. The efficiency of the system (percentage aspirated sample reaching the plasma) was stated to be 35%.

A similar desolvator was constructed (see Figure 4.1) for use with the CAP. It consisted of a glass chamber ( $15 \times 6 \text{ cm}$ ), a coil condenser, and a conical flask fitted with a side arm. A heating coil was wrapped around the top half of the desolvating chamber, and the temperature was controlled with an energy regulator (Sunvic Isomantle coil and energy regulator). The coil was insulated with a layer of asbestos rope. The brass nebuliser was sealed into the bottom of the heated chamber with a PTFE ring.

The efficiency of the desolvator was tested under the following conditions; argon flow rate  $1.85 \text{ l.min}^{-1}$  ( $8 \text{ lb.in}^{-2}$ ); energy regulator 100 (maximum); cooling water  $0.75 \text{ l.min}^{-1}$  at  $13^\circ \text{C}$ ; sample uptake rate  $0.41 \text{ ml.min}^{-1}$ . Water was nebulised into the desolvator for 10 minutes to ensure that the system was at an equilibrium temperature, then 2.5 ml of 10,000 ppm manganese (sulphate) was sprayed. The glassware was washed with 3 x 100 ml portions of acidified distilled water. The washings were collected and diluted to one litre, and the solution was analysed for manganese using a Varian Techtron model 1000 atomic absorption spectrophotometer. From the analysis figures, a nebuliser/desolvator efficiency of 15% was calculated.

Direct methods for measuring the efficiency were unsuccessful due to the difficulty encountered in trapping the very fine aerosol. When bubbled through a U tube containing distilled water, only a small fraction

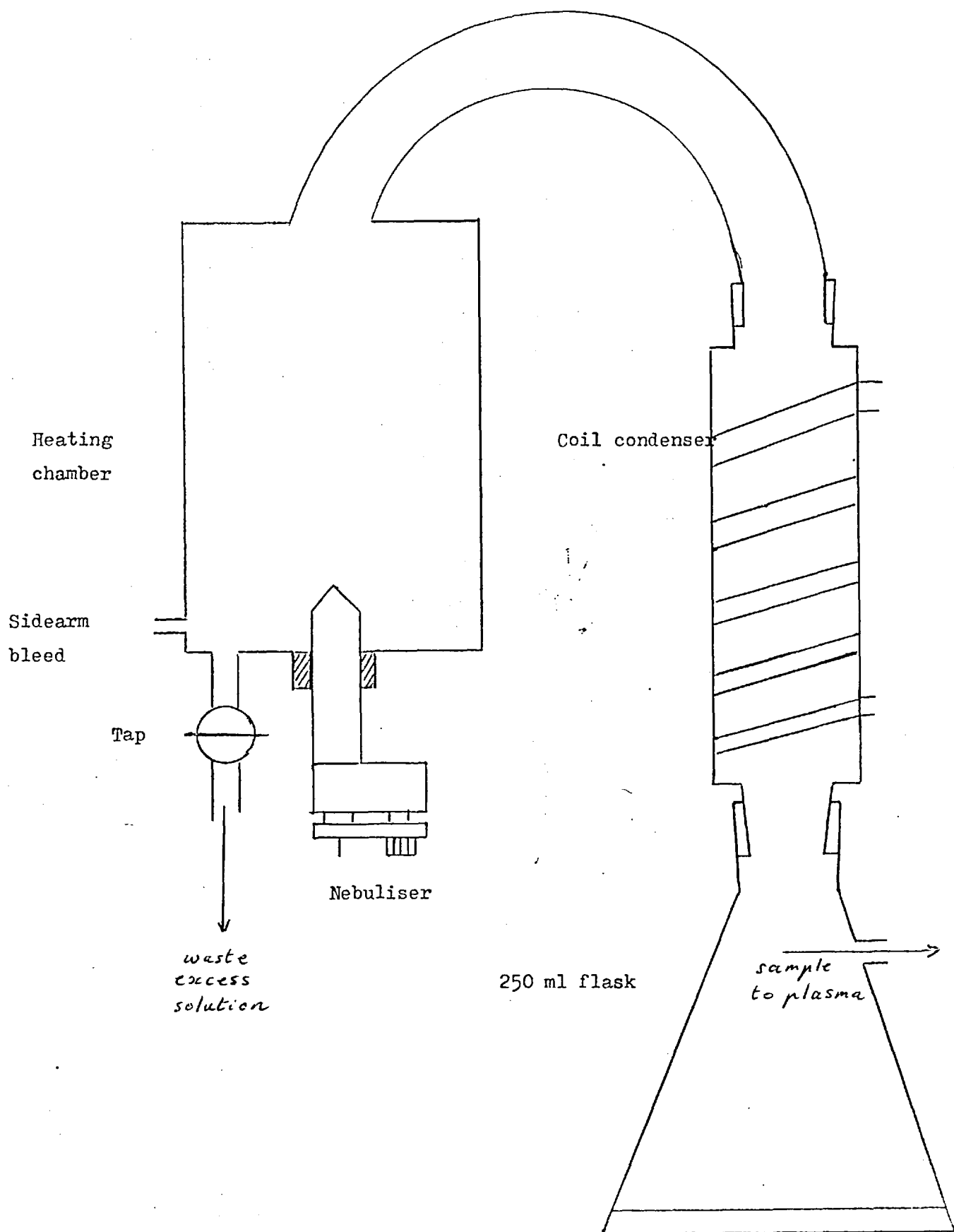


Figure 4.1. Desolvator System.

of the aerosol was removed, even traps containing glass wool, which were cooled with carbon dioxide or liquid nitrogen, failed to remove all the droplets.

#### 4.2.1 Operation of the CAP with the desolvator

The desolvator was flushed with argon for 5 minutes. The nebuliser tube was blocked with a piece of sealed plastic tubing to prevent entry of air. The plasma flow was set at  $1.6 \text{ l.min}^{-1}$  and the plasma ignited and stabilised as described previously. The arc current was set at 11 amps. The sealed plastic tube was replaced with a one inch long sample tube and water was nebulised into the plasma. The plasma tail-flame was observed to be unstable and pushed to one side of the cathode block. Stability was achieved by bleeding off some of the sample through the sidearm in the glass heating chamber, which was fitted with a piece of polythene tubing and screw clip. The clip was tightened so as to control the amount of gas lost. The flow rate could not be measured because the gas was saturated with water vapour.

A preliminary visual investigation of the tail flame was carried out by spraying sodium chloride solution. 100, 10 and 1 ppm solutions gave noisy signals, and emission could only be seen in the most diffuse (cooler) and hence noisier parts of the tail-flame. The high temperature and more stable parts of the plasma did not show any appreciable sodium emission, even at high sodium concentrations. A 1:1 image of the tail-flame was focused on the monochromator slit and emission at 589.0 nm was recorded on the Servoscribe. The recorder was damped with a 300  $\mu\text{F}$  capacitor, giving a response time of about 20 seconds for full scale deflection. Signals from samples containing 0.1 ppm sodium were easily measured, and a detection limit of about 0.02 ppm was obtained. This is very poor when compared to the detection limit obtained by flame photometry (0.00007 ppm)<sup>(93)</sup>.

#### 4.2.2 Optimisation of the CAP Operating Parameters

Cadmium was used to optimise the single-shot method of sampling and therefore it was decided to use it again for the continuous

sample introduction. 100 ppm of cadmium solution was nebulised into the CAP, and the centre of the tail-flame was viewed using a 0.1 mm spectrometer slit (i.e. spectral bandpass ca. 0.3 nm). The cadmium 228.8 nm line was scanned at a rate of  $0.5 \text{ nm.min}^{-1}$ , using the SP 900 scanning motor and the signals recorded on the Servoscribe. Only small signals were obtained.

To ascertain the optimum position for cadmium emission, the effect of height of observation in the tail-flame was investigated. A horizontal slit (1 mm x 10 mm) was constructed from a piece of aluminium, and it was placed in front of the monochromator slit. 100 ppm of cadmium solution was nebulised into the plasma, the 228.8 nm line was scanned and the signal/background ratios measured at different heights in the tail-flame. Figure 4.2 shows the maximum signal/background was reached at approximately 5 mm above the base of the tail-flame.

The effect of viewing different positions across the tail-flame was investigated by scanning the vertical slit of the monochromator across the plasma.

The bottom 2 mm of the plasma was not viewed because there was no cadmium emission from this region. The graph of signal/background against position of observation is shown in Figure 4.3 and illustrates that emission is fairly evenly distributed across the plasma. This seems to contrast, with the results obtained in Chapter 3 (Figure 3.11). However, with continuous sampling there was more noise and turbulence in the plasma which obviously resulted in better mixing of the plasma gases in the higher regions of the tail-flame. Again, cadmium emission was not observed from the high temperature zones of the plasma.

#### Plasma flow

The plasma was observed with the above viewing slit, at a height of 5 mm above the base of the tail-flame. The arc was operated at 10 amps and the nebulising argon flow was set at  $1.85 \text{ l.min}^{-1}$ , giving a sample uptake rate of  $0.57 \text{ ml.min}^{-1}$ . A 100 ppm cadmium solution was aspirated into the arc and the plasma flow rates were varied between

Figure 4.2

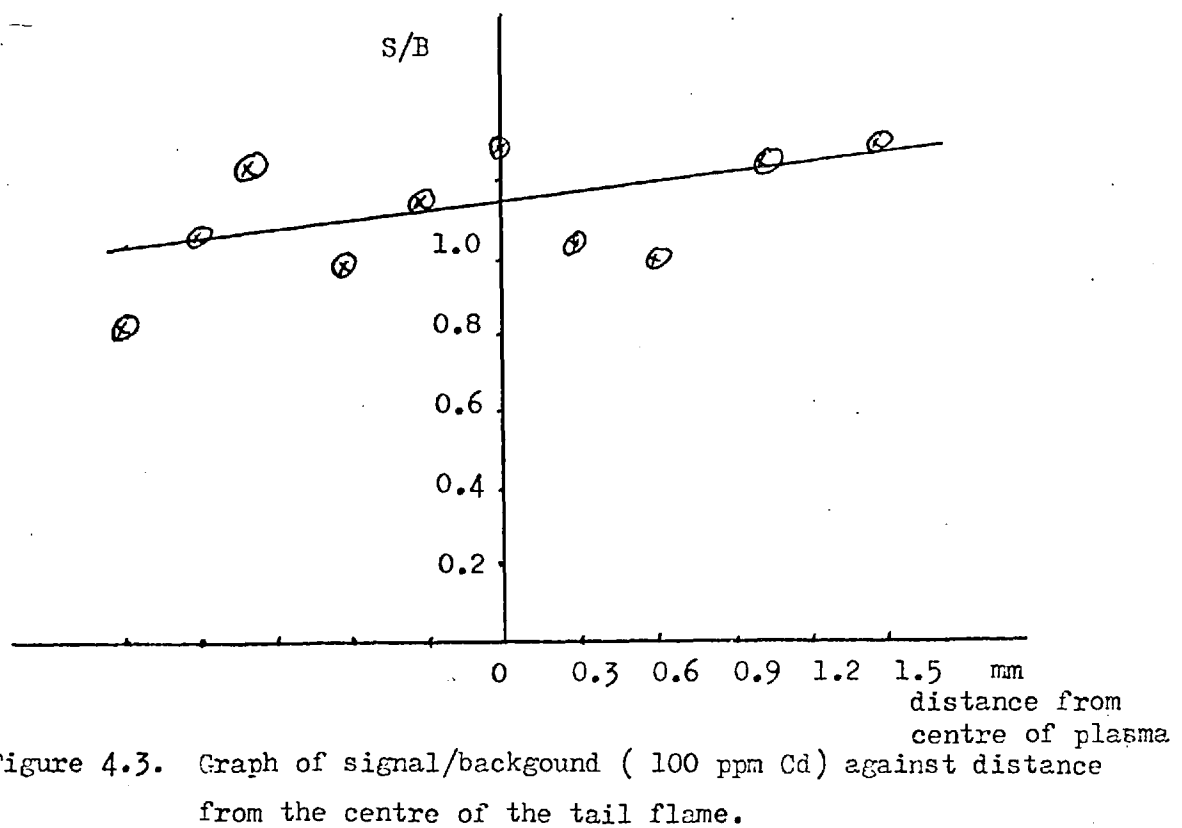
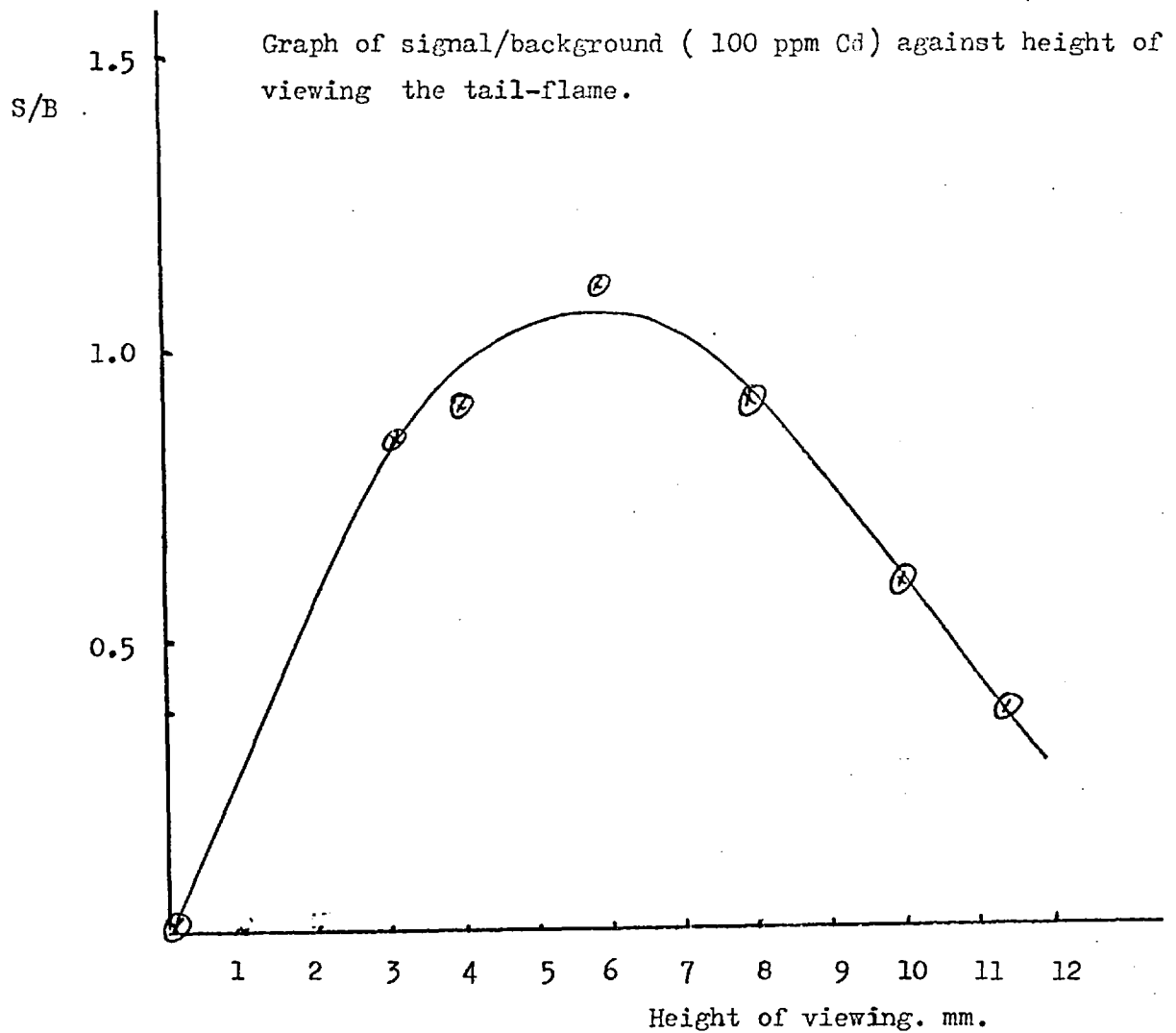


Figure 4.3. Graph of signal/background (100 ppm Cd) against distance from the centre of the tail flame.

1.35 and 0.1 l.min<sup>-1</sup>. The signals at 228.8 nm were recorded by the scanning technique and Figure 4.4 shows the graph of signal/background against plasma flow. The reduction in signal at higher flows was probably due to the dilution and decreasing residence time of the cadmium atoms in the plasma. The best signal/noise ratios were obtained at 0.25 l.min<sup>-1</sup>.

### Nebulisation rate

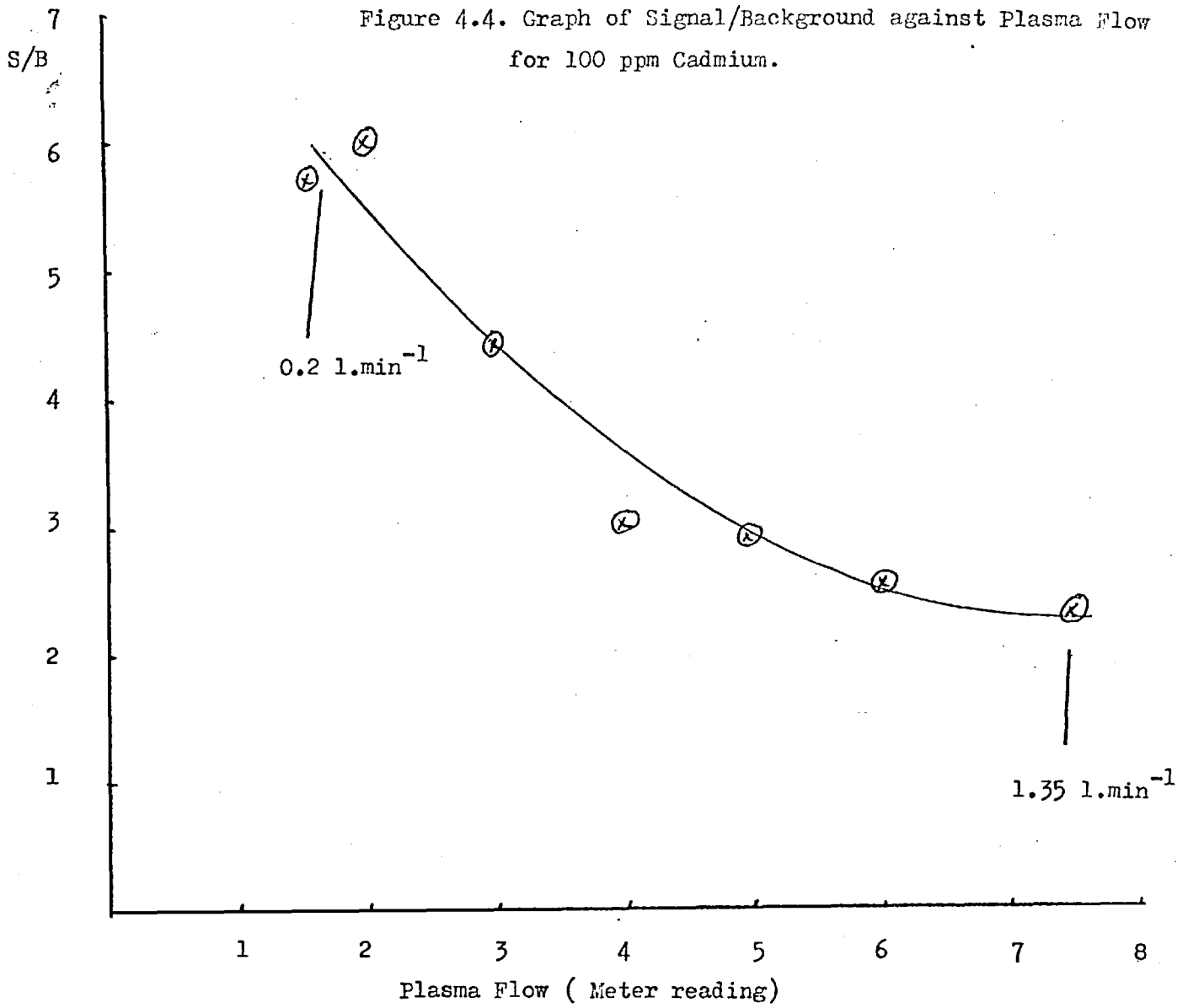
The effect of varying the nebulisation rate on the signal/noise for 10 ppm cadmium was investigated. The plasma showed instability above a nebulisation gas flow of 1.85 l.min<sup>-1</sup> and the nebuliser ceased to function below 1.3 l.min<sup>-1</sup>, therefore flow rates between the two were used. Table 4.1 shows the signal/noise, signal/background and sample uptake rates for three gas flows. The best signal/noise was recorded with a sample uptake rate of 0.41 ml.min<sup>-1</sup> and gas flow rate of 1.7 l.min<sup>-1</sup>. The detection limit for cadmium (S/N = 2) was therefore calculated to be 0.4 ppm.

| <u>Flow rate</u><br><u>l.min<sup>-1</sup></u> | <u>Signal/</u><br><u>noise</u> | <u>Signal/</u><br><u>background</u> | <u>Sample uptake</u><br><u>ml.min<sup>-1</sup></u> |
|-----------------------------------------------|--------------------------------|-------------------------------------|----------------------------------------------------|
| 1.85                                          | 20                             | 1.05                                | 0.57                                               |
| 1.7                                           | 54                             | 0.57                                | 0.41                                               |
| 1.4                                           | 18                             | 0.2                                 | 0.20                                               |

Table 4.1 - Effect of nebulisation rate on S/N for 10 ppm Cd.

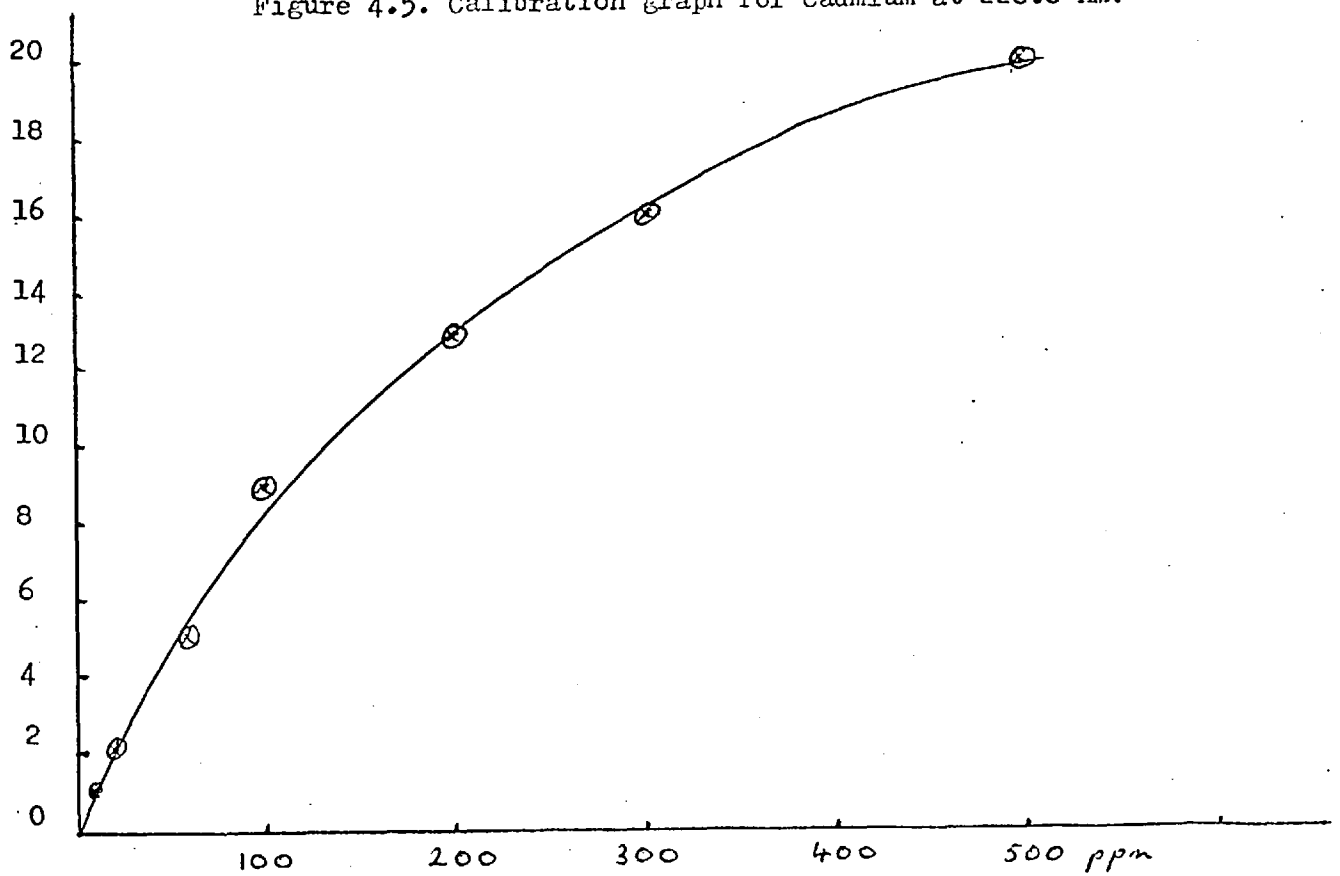
Measurement of the detection limit was made difficult by a high blank, which was initially thought to be due to cadmium particulate left behind in the desolvator. When the system was cleaned with nitric acid and distilled water, the blank was not reduced. The blank signal, equivalent to approximately 2 ppm cadmium, was therefore attributed to cadmium from the brass cathode block. Analysis of the brass by atomic absorption spectrometry showed a cadmium content of 730 ppm.

Figure 4.4. Graph of Signal/Background against Plasma Flow for 100 ppm Cadmium.



signal mV.

Figure 4.5. Calibration graph for Cadmium at 228.8 nm.



### Arc current

The arc current was varied between 8 and 12 amps, and the signals from 100 ppm cadmium were measured. No significant change in the signal/background was observed but the arc was most stable at 11 amps.

### Calibration graph

A calibration graph was constructed for cadmium at 228.8 nm, from 0 to 500 ppm. The graph (Figure 4.5) is non-linear but self-absorption was thought to play only a small part in the deviation from linearity. The main cause of the curvature was thought to be due to an increasing sample rejection factor as the concentration, and hence the size of the dry aerosol particles was increased.

### Observation at other wavelengths

No emission was observed from the cadmium ion lines at 214.4 and 257.2 nm. Small signals were observed from 20 ppm cadmium at the 361.0 and 326.1 nm atom lines.

#### 4.2.3 Effect of sodium and potassium chlorides

Zmbova and Marinkovic<sup>(21)</sup> used a gas stabilised arc for the determination of trace elements in gold. Addition of large amounts of potassium chloride decreased the detection limits by one to two orders of magnitude. The effect was attributed to more favourable conditions being attained for the entry of aspirated elements into the arc column and to the suppression of ionisation of easily ionised elements. The low temperature conditions did not decrease the detection limit for elements with high excitation potentials or for elements forming stable oxides (e.g. boron and beryllium).

Potassium and sodium (5000 ppm) were added to solutions containing 10 ppm cadmium. Both solutions were introduced into the CAP, the tail flame was viewed at several different heights, and emission from cadmium at 228.8 nm was measured by scanning the line. Signals could only be observed in the higher regions of the tail flame, and the detection limit for cadmium in the presence of sodium was

increased to 2 ppm, due to the increasing background (monochromator leakage) and noise. Therefore, it was concluded that potassium and sodium were not able to reduce the degree of sample rejection.

#### 4.3.1 Stabilisation of the tail-flame

The noise in the plasma was observed to be larger when the normal end block was replaced by the cut-away cathode block. In an attempt to reduce the noise and air entrainment, a quartz window (8 mm x 14 mm) was inserted into the cathode block (see Figure 4.6). This resulted in an increase in the length of the tail flame by about 3 mm i.e. from 7 mm to 10 mm, and reduced the noise. The increased stability of the plasma enabled the desolvator to be operated without the gas bleed. However, an increase in sensitivity was not observed.

Devitrification of the quartz window, and sample deposits, gradually reduced the intensity of the emission signal reaching the monochromator. These effects were not noticeable for operation periods of up to four hours, and for solutions with low concentrations of analyte (100 ppm). However, when solutions containing 5000 ppm of sodium were sprayed, the quartz window transmission was reduced by 10% after a period of five minutes.

#### Precision

Precision measurements were made by setting the monochromator wavelength at 228.8 nm, distilled water and 100 ppm cadmium solutions were sprayed alternately several times. The percentage relative standard deviation for 11 signals was 3.5%.

#### 4.3.2. Conclusions

Continuous sample introduction offers some advantages over the one shot technique. However, sample nebulisation/desolvation is only about 10% efficient whereas the one-shot method has sampling efficiencies approaching 100%.

Nebulisation into flames is easily accomplished because they operate at high gas flows (for air/acetylene typical flows are, air 4 l.min<sup>-1</sup>

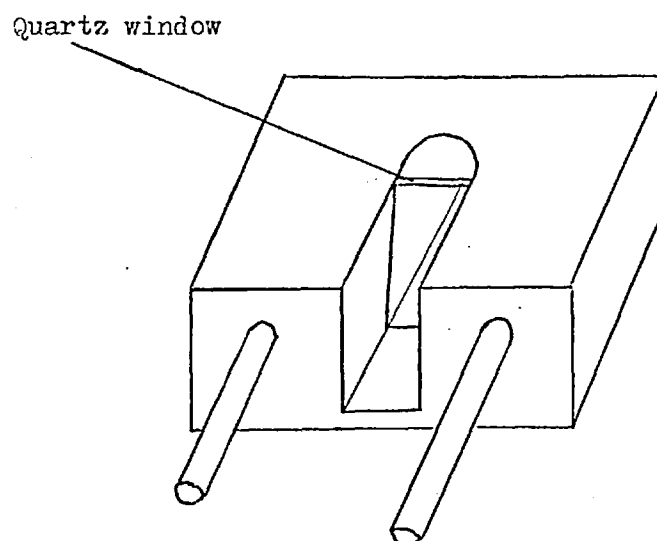


Figure 4.6. Cathode block with quartz window.

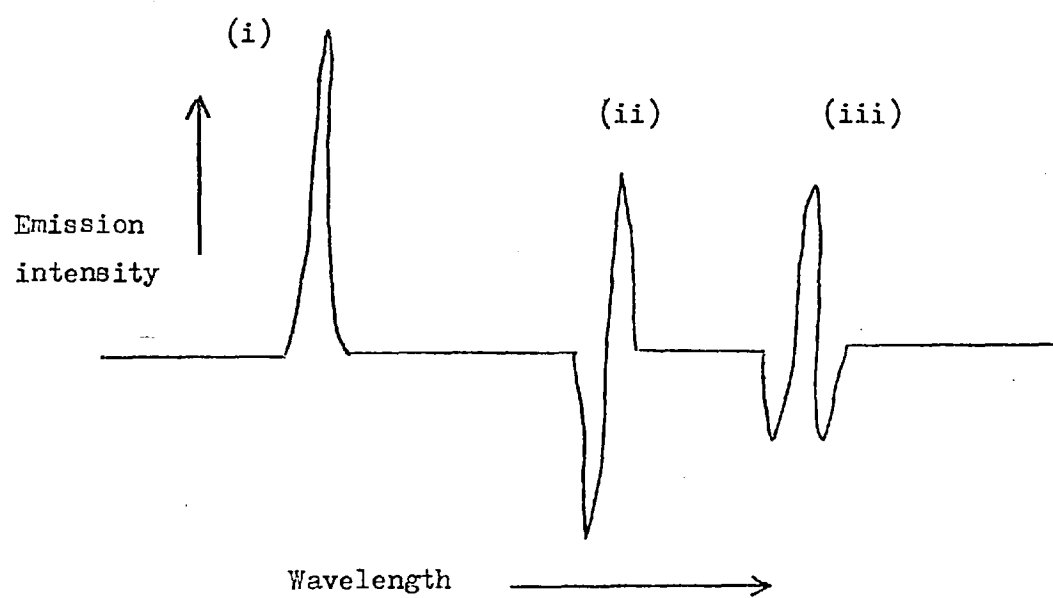


Figure 4.7. Typical emission signals

(i) Normal spectrum scan

(ii) 1st derivative

(iii) 2nd derivative

@ 30 lb.in<sup>-2</sup>, acetylene 1.5 l.min<sup>-1</sup> @ 10 lb.in<sup>-2</sup>) and can tolerate fairly large amounts of water (0.5 ml.min<sup>-1</sup>) without any appreciable drop in flame temperature or stability. Pneumatic nebulisation is therefore cheap, precise and a comparatively easy sampling technique.

Signals obtained from continuous sampling are easily monitored, using conventional amplifiers and slow response chart recorders. Precisions better than 1% may be obtained by using conventional flame photometry and atomic absorption spectrochemical analysis. Transient signals require fast response amplifiers and recorders, the precision of analysis is usually about 5%.

In emission techniques, the detection limit is determined by the signal/noise ratio, which in turn is determined by the signal and the noise on the background emission. Thus good analytical sources should produce very high signal/background ratios for the analyte element. High background interference can be overcome by the use of a high resolution monochromator or by derivative scanning methods. Several authors<sup>(94-96,78)</sup> have described derivative spectroscopy for the detection of low intensity bands and lines. The simplest technique consists of a vibrating quartz plate mounted behind the entrance slit of the monochromator, (equipped with a photomultiplier), the wavelength is scanned in the region of the line of interest. The output from the photomultiplier is fed into a phase sensitive lock-in amplifier which is tuned to the frequency of the vibrating plate. The amplifier output is fed into a chart recorder which records the first derivative of the signals with respect to wavelength i.e.  $ds/d\lambda$ . If the amplifier is tuned to twice the vibrational frequency, the second derivative  $d^2s/d\lambda^2$  is obtained, which is proportional to the analyte concentration (see Figure 4.7). Perregaux and Ascarelli<sup>(94)</sup> vibrated the quartz plate with a piezoelectric transducer and Snelleman et al<sup>(78)</sup> used a mechanical oscillator. The latter workers used their system for the flamephotometric determination

of barium in the presence of 100 fold excess of calcium, and interference effects from the CaOH band system were drastically reduced. Skogerboe and Lichte<sup>(76)</sup> applied the same processing techniques for microwave plasma emission analysis.

In the CAP, better detection limits could be obtained if derivative techniques were available. However, the main problem associated with the plasma is that of sample rejection, which does not allow the sample to experience the high dissociation and excitation temperatures available within the core. Even if derivative methods were used, interference effects (atomisation) would drastically reduce the analytical potential of the source.

USE OF THE CAPILLARY ARC PLASMA AS A HIGH  
TEMPERATURE ATOMISATION AND FRAGMENTATION  
SOURCE FOR A LOW WATTAGE MICROWAVE SOURCE

CHAPTER 5

### 5.1.1 INTRODUCTION

Chapter one includes most of the work that has been carried out on the low wattage microwave plasma. All the authors report the plasma's low tolerance for sample loading. The maximum sample introduction rate that the plasma can tolerate is about  $10^{-5}$  g.sec<sup>-1</sup>. Skogerboe<sup>(77)</sup> has modified the tuning of a  $\frac{1}{4}$ -wave cavity and reported that a stable plasma can be obtained even though the argon is saturated with water vapour.

The CAP operates at 500 watts and can tolerate quite large amounts of water vapour before it is extinguished. The high temperature properties of the CAP may therefore be suitable for the fragmentation of the nebulised samples before entry into a microwave plasma. It was proposed to use the CAP as a fragmentation source, prior to microwave excitation of the exhaust gases. Using this technique it may be possible to introduce large amounts of analyte into a microwave plasma, and thus obtain very low detection limits.

### 5.1.2 APPARATUS

For the preliminary investigations, the nebuliser/desolvator described in Chapter 4 was used. The cut-away cathode block was replaced by the normal microwave generator (Electro-Medical Supplies Ltd., Wantage, Berks.) The microwaves were transmitted along a coaxial cable to a  $\frac{1}{4}$ -wave Evenson type cavity.

### 5.1.3 PRELIMINARY INVESTIGATIONS

Initially the arc was operated on dry argon. After initiation and stabilisation of the arc (at a current of ca 10 amps) the  $\frac{1}{4}$ -wave cavity was placed 5 mm from the top of the cathode block, so that the exhaust gases from the CAP (tail-flame) followed an axial path through the cavity. During ignition (to prevent arcing) the grounded cavity was removed to a distance of at least 2.5 cm from the cathode block.

Microwave excitation of the hot plasma gases was attempted by gradually increasing the microwave power from 20 to 100 watts. However, as soon as a plasma began to appear (at about 60 watts) it was extinguished because a discharge between the large and fine tuning stubs of the cavity was formed. It was thus concluded that a microwave plasma needed to be contained inside a quartz tube.

A quartz tube 8 mm internal diameter tapering to 2 mm was cemented on the cathode block centrally above the exhaust gas orifice. The CAP was ignited and stabilised as described previously. The following gas flows were employed, cathode flush  $0.15 \text{ l.min}^{-1}$ ; plasma  $1 \text{ l.min}^{-1}$ ; sample  $2.1 \text{ l.min}^{-1}$  @  $10 \text{ lb.in}^{-2}$ . The large tuning stub of the cavity was positioned approximately 3 cm above the cathode block and 0.5 mm from the 2 mm section of the quartz tube. The microwave generator was set at 100 watts and tuning was accomplished by turning the large tuning stub until minimum reflected power (approximately 15 watts) was obtained. At the optimum tuning position, a plasma was formed in the tube without the use of a tesla coil. This indicated quite a large number of electrons and ions at this height above the tail-flame. The plasma formed in the 2 mm section of the tube was unstable, but when the cavity was lowered to the wider section of the tube (8 mm) a stable plasma was formed (at 100 watts). The tube was then replaced with a 5 cm length of 8 mm internal diameter quartz tubing. A similar plasma was obtained, which was diffuse, approximately 15 mm in length, and occupied most of the width of the tube. An image of the plasma was focused on the slit of the Unicam SP 900 monochromator using the lens set-up as shown in Figure 3.10. Solutions containing 10 ppm of mercury (nitrate) and 10 ppm cadmium (sulphate) were nebulised into the plasma system. Good emission signals at 253.6 and 228.8 nm were obtained.

### Emission from sodium

Emission from a solution containing 10 ppm of sodium (chloride) was seen visually from a plasma formed at 100 watts. However, when the microwave power was reduced to approximately 50 to 60 watts, the argon plasma was extinguished but the sodium emission was still present. When the power was gradually increased from 20 to 50 watts the sodium emission intensity was found to increase even though an argon plasma was not formed. The sodium atoms/ions produced in the CAP, were being excited without the formation of an argon plasma. Excitation of atoms/ions without the background emission of a plasma may possibly lead to very low detection limits. To test the system for excitation of other metals without the formation of an argon plasma, cadmium (10 ppm) was introduced. Emission signals were not seen at the 228.8 nm line. Therefore, it was concluded that the low ionisation potential of sodium (5.1 eV) facilitated the formation of a sodium type plasma, whereas cadmium with a high ionisation potential (8.99 eV) only emitted when an argon plasma was formed.

#### 5.1.4 MODIFICATION OF THE PLASMA CONTAINMENT TUBE

In the preliminary investigations the quartz tube was cemented (araldite) to the cathode block. During ignition of the CAP, the plasma struck on the cathode block and copper was spluttered on the inside of the quartz tubing. After two or three days of operation the tube became opaque due to copper deposits. It was decided to modify the tube assembly so that the CAP could be ignited and stabilised before the quartz tube was placed above the cathode block.

A length of quartz tube (5 cm) was cemented into the centre of a piece of tufnol plastic (42 x 42 x 3 mm). Three holes were drilled so that it fitted over the heads of the CAP polythene screws (see Figure 5.1). The new tube assembly was placed in position after

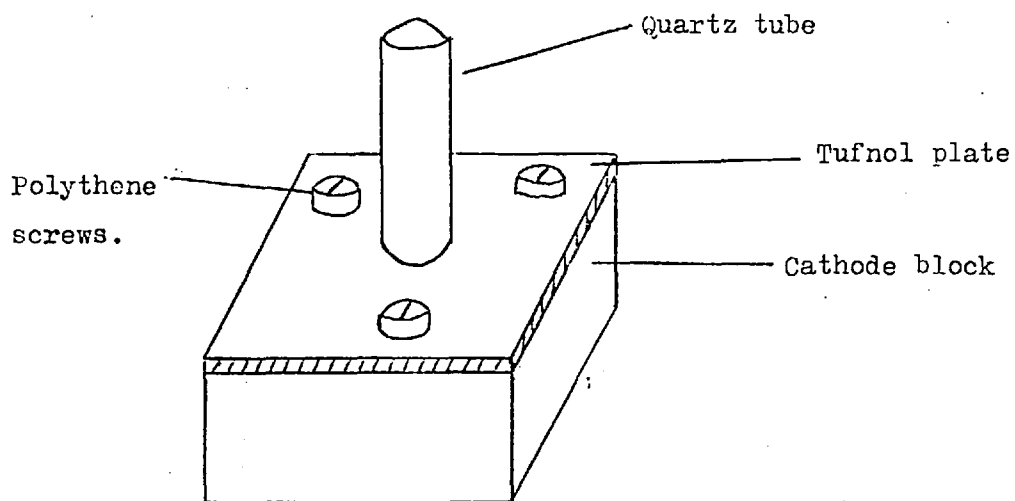


Figure 5.1.

Quartz tube assembly for the microwave excitation of CAP exhaust gases.

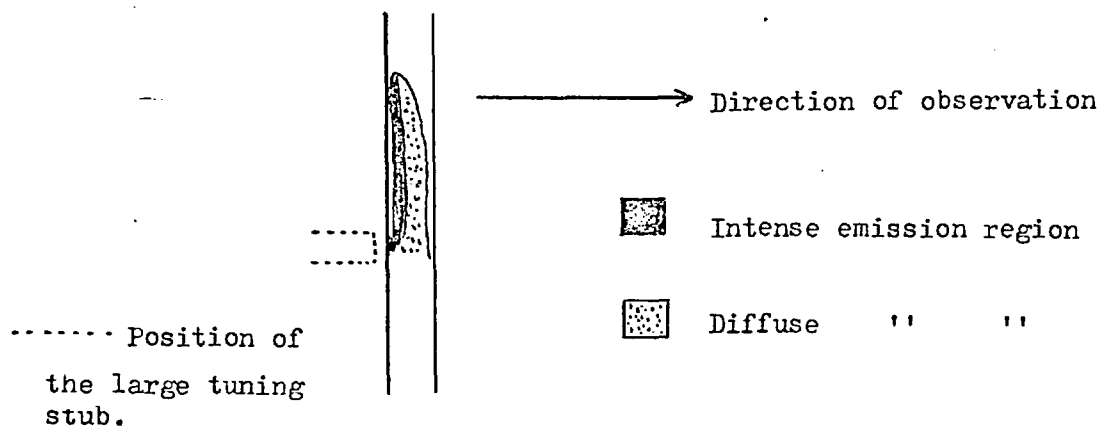


Figure 5.2. Microwave plasma formed inside the 6 mm quartz tube.

the CAP was ignited and stabilised. A microwave plasma was formed in the usual way at a generator power of 100 watts. The plasma was very stable when compared with the ones previously obtained, the increase in stability was thought to be due to the clean quartz tubing. After a few hours operation no copper could be seen on the tube, but at the side adjacent to the large tuning stub, the quartz was devitrified.

#### 5.1.5 EFFECT OF THE HEIGHT OF THE CAVITY ABOVE THE CATHODE BLOCK

10 ppm of sodium was sprayed into the system and the cavity gradually raised along the length of the quartz tubing. At a generator setting of 100 watts, a plasma was maintained for every cavity position (up to 4 cm) above the cathode block. However, when no sodium was sprayed the plasma could only be observed when the cavity was within 5 mm of the cathode block.

#### 5.1.6 PRELIMINARY ANALYTICAL INVESTIGATION

Cadmium was chosen for the initial analytical investigation. The CAP was operated at 11 amps, and the microwave plasma at 100 watts. The sample introduction rate was  $0.8 \text{ ml.min}^{-1}$  with an argon flow of  $2.9 \text{ l.min}^{-1}$  ( $12 \text{ lb.in}^{-2}$ ). The image of the microwave plasma was focused on the spectrometer slit using the lens system shown in Figure 3.10. A solution containing 10 ppm of cadmium was nebulised into the plasma and the 228.8 nm line scanned. The maximum signal/background recorded was 10, and from measurements performed at different positions across the plasma, the emission and sample seemed to be evenly distributed. However, the best emission signals were observed at the centre of the plasma. Decreasing the sample flow rate from  $0.8 \text{ ml.min}^{-1}$  to  $0.4 \text{ ml.min}^{-1}$  decreased the signal by a factor of 1.5. Increasing the microwave power from 100 watts to 150 watts increased the signal 1.5 times. A detection limit of about 0.02 ppm cadmium was obtained with this system.

During the experiments with the 8 mm quartz tubing, it was noticed that some tubing did not give a stable plasma. This problem was investigated and it was shown that the wall thickness of the tubing used was an important factor. The wall thickness of several tubes were measured with a travelling microscope, they were then used as plasma containment tubes. The experiments showed that thinner walled tubing was the most suitable for the production of a stable microwave plasma. Tubing with a wall thickness of 1.1 mm gave a stable easy to handle plasma, whereas tubing of 1.3 mm did not give a stable plasma, and tubing of 1.5 mm wall was practically useless.

#### 5.1.7 USE OF A $\frac{3}{4}$ -WAVE CAVITY

Hieftje and Layman<sup>(97)</sup> used a  $\frac{3}{4}$ -wave cavity to couple the microwave power to a plasma contained in a 8 mm quartz tube. The  $\frac{3}{4}$ -wave cavity was found to require less tuning and gave a more stable plasma than the  $\frac{1}{4}$ -wave cavity. The  $\frac{3}{4}$ -wave cavity was tested for the production of a microwave plasma above the CAP. The CAP was ignited, and the quartz tube (inserted in the tufnol plate) was placed above the cathode block. The  $\frac{3}{4}$ -wave cavity was lowered over the tube and the microwave power was switched to 170 watts (maximum output) but a plasma was not formed. It was thought that if the cavity was placed closer to the cathode block, a plasma would be easily formed. This was accomplished by removing the large tuning stub from the cavity (not critical for tuning or production of a microwave field) but again no plasma was observed.

#### 5.1.8 OPTIMISATION OF OPERATING PARAMETERS

##### Arc current

The sample flow rate was fixed at  $2.7 \text{ l.min}^{-1}$  ( $11 \text{ lb.in}^{-2}$ ) giving a solution uptake rate of  $0.58 \text{ ml.min}^{-1}$ . The microwave plasma was operated at 150 watts (12 watts reflected power) and the CAP current was varied between 8 and 13 amps. A solution containing 1 ppm

cadmium (sulphate) was nebulised and the signal/background was measured at 228.8 nm for the various CAP currents. Results indicated that changing the arc current did not significantly alter the value of the signal/background, but the microwave plasma was most stable at an arc current of 10 amps.

#### Microwave power

Runnels and Gibson<sup>(72)</sup> reported when the microwave power was increased, the length of their plasma increased, but the emission intensity from copper (observed from the lower section of the plasma) slightly decreased. Sharp et al<sup>(73)</sup> observed a similar increase in the length of the plasma and at 35 watts the length of the plasma reached 20 mm. The authors studied the effect of microwave power on the emission intensity of cadmium and found that the signals gradually increased with increasing power until the spectrometer slit was completely filled. It was concluded that increasing plasma dimensions were responsible for the increased signals and not an increase in the translational or electronic excitation temperature.

The effect of microwave power on the emission signal from 1 ppm cadmium solution was studied keeping the operating conditions the same as before. Increasing the microwave power from 120 to 170 watts increased the length of the plasma from approximately 15 mm to 20 mm, and the signal from cadmium also increased. However, signal/background measurements remained constant, which suggested that there was no increase in the excitation temperature with increasing power.

#### Sample flow rate

Sharp et al<sup>(73)</sup> operated the microwave plasma at the mouth of a 2 mm internal diameter quartz tube, using argon flows between 2.1 and 1.6 l.min<sup>-1</sup>. Runnels and Gibson<sup>(72)</sup> used lower flows (0.1-0.3 l.min<sup>-1</sup>) because their plasma was confined inside a 1 mm diameter tube. The above authors used a single shot method of sample

introduction, therefore the optimal flows were easily established. However, with the continuous system the gas flow rate was primarily dictated by the characteristics of the nebuliser used. Below  $1.6 \text{ l.min}^{-1}$  ( $8 \text{ lb.in}^{-2}$ ) the nebuliser ceased to operate, and efficient operation was only obtained at and above  $1.85 \text{ l.min}^{-1}$  ( $10 \text{ lb.in}^{-2}$ ) which gave a solution uptake of  $0.27 \text{ ml.min}^{-1}$ . Increasing the rate from  $0.27$  to  $0.92 \text{ ml.min}^{-1}$  for a  $1 \text{ ppm}$  cadmium solution increased the signal/background by a factor of two. At high flows noise became a serious problem and the optimum rate which gave the best signal/noise was found to be  $2.1 \text{ l.min}^{-1}$  ( $12 \text{ lb.in}^{-2}$ ) which yielded a solution uptake of  $0.35 \text{ ml.min}^{-1}$ .

### 5.2.1 FORMATION OF THE MICROWAVE PLASMA IN SMALLER DIAMETER TUBES

The plasma described in Section 5.1 was rather diffuse. In order to study the effect of reducing the diameter of the containment tube, various tube sizes were tried, including  $6 \text{ mm}$ ,  $4 \text{ mm}$  and  $2 \text{ mm}$ . The following sections deal with the plasmas formed inside these tubes.

#### 5.2.2 6 mm CONTAINMENT TUBE

The  $8 \text{ mm}$  quartz tube was replaced by a  $5 \text{ cm}$  length of  $6 \text{ mm}$  (internal diameter) tubing. The microwave plasma obtained was more intense than the one previously described. It was approximately  $2 \text{ cm}$  long and occupied about  $1/3$  of the tube width, the  $2 \text{ mm}$  section adjacent to the large tuning stub was more intense than the rest of the plasma (see Figure 5.2).

The full length of the plasma image was focused on the spectrometer slit and  $1 \text{ ppm}$  of cadmium solution was sprayed into the system. The emission at  $228.8 \text{ nm}$  was observed at several positions across the plasma, and signal/background measurements showed that the sample was evenly distributed throughout the plasma. The most intense signals were again observed at the centre of the discharge.

### Height of viewing

Runnels and Gibson<sup>(72)</sup> observed the best emission signals from copper, in the lower regions of their microwave plasma (bottom 2 mm). The reason for this behaviour appeared to be that the copper plated the walls of the discharge tube.

In order to study the spectral intensities along the length of the plasma, a slit was constructed from aluminium (2 x 10 mm). An approximately 1:1 image of the plasma was focused on the spectrometer slit and the aluminium slit was placed adjacent to the monochromator shutter. A 2 mm section of the plasma was viewed. A 1 ppm cadmium solution was nebulised into the plasma and emission was monitored at several heights above the base of the discharge (formed opposite the large tuning stub). Figure 5.3 shows a graph of observation position against signal/background (at 228.8 nm), the best signals were obtained in the lower few mm of the discharge.

### Microwave power

The plasma was reasonably stable above 100 watts generator output (15 watts reflected power), and therefore to study the effect of power on the plasma stability and emission characteristics a range of between 100 to 170 watts was covered. Even though larger signal/background ratios were obtained in the lower regions of the plasma, satisfactory signals were obtained when the full length of the discharge was viewed. The noise on the emission background was lowest at 150 watts, which was chosen as optimal.

### Calibration graph

A calibration graph for cadmium (228.8 nm) was obtained between 0 and 50 ppm, using the wavelength scanning technique of measurement. The curve was linear up to 10 ppm and the precision of the measured signals at the 1 ppm level was 5% and the detection limit was 0.02 ppm.

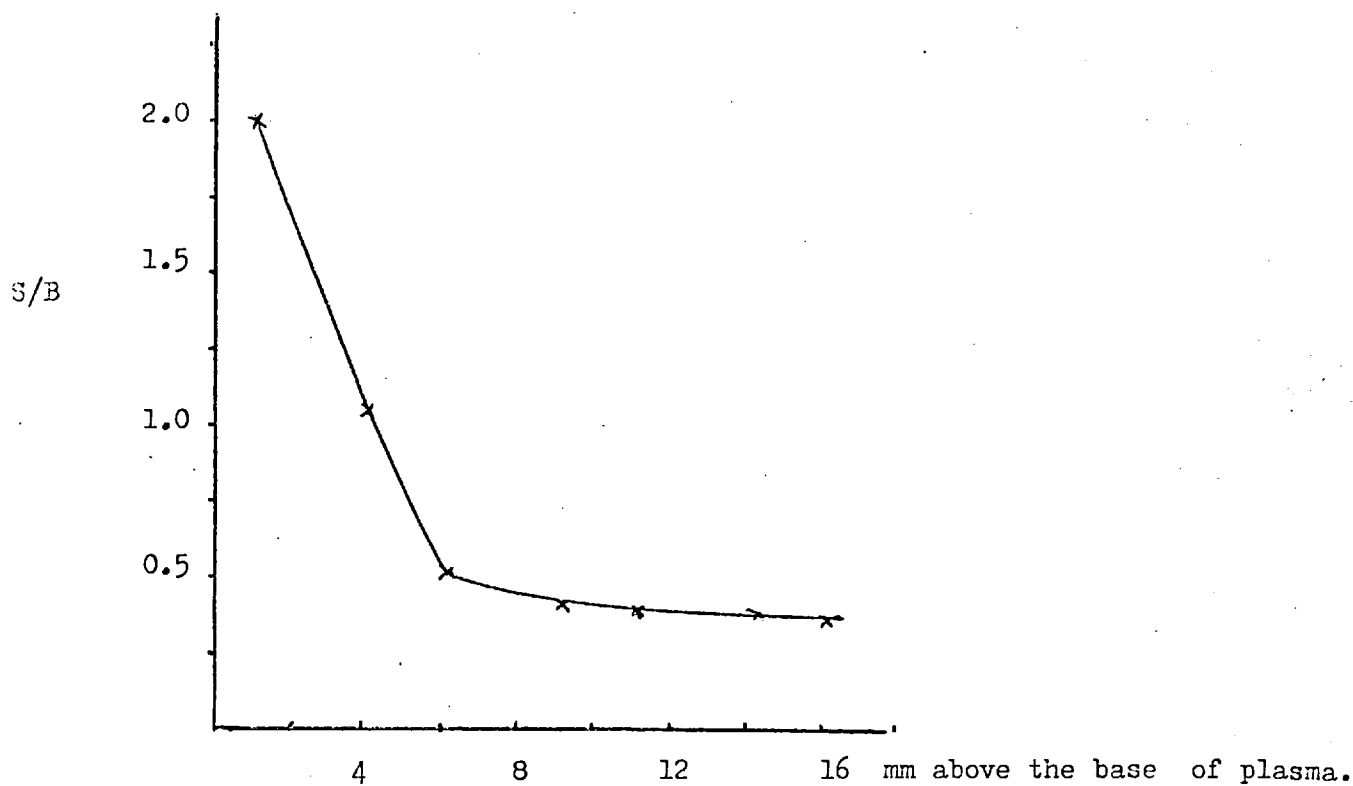


Figure 5.3. Graph of signal/background for 1 ppm cadmium observed at various heights in the microwave plasma ( 6 mm tubing).

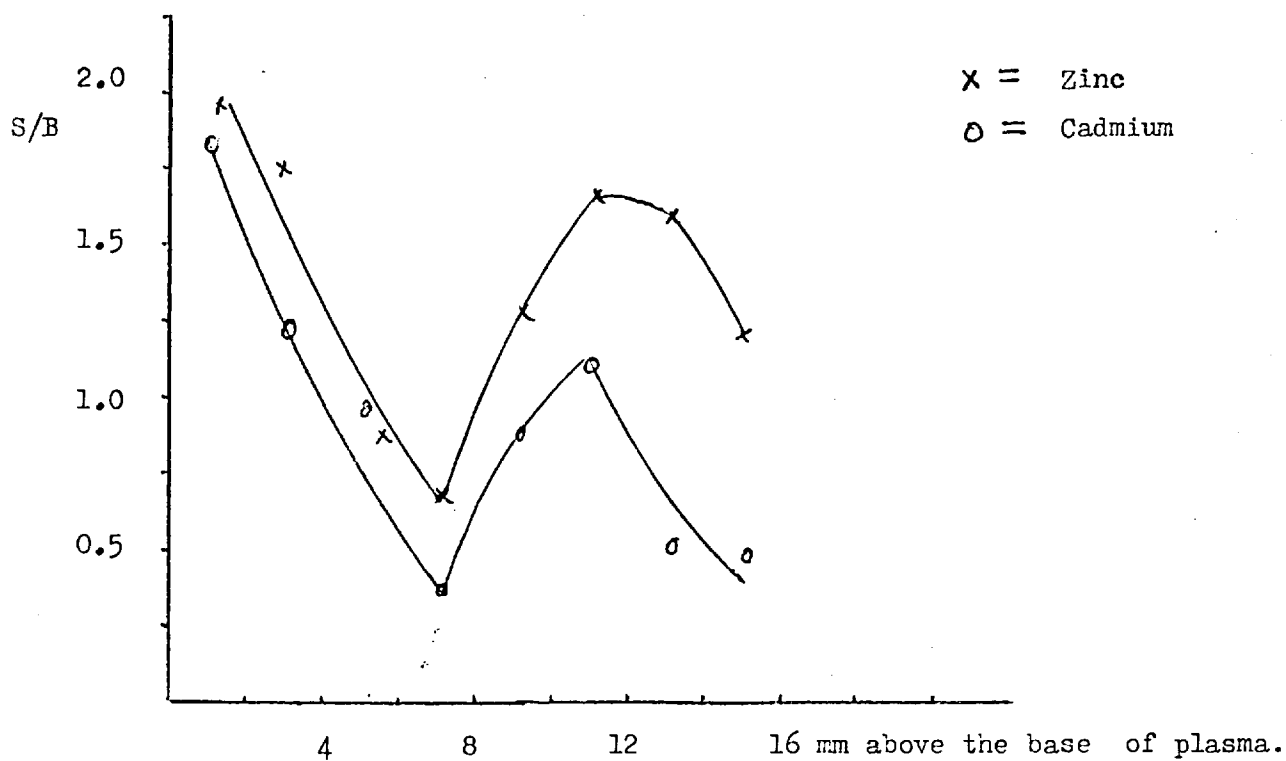


Figure 5.4. Graph of signal/background for 1 ppm cadmium and zinc vs. height of viewing in the microwave plasma. ( 4 mm quartz tubing).

### Operation of the plasma without desolvation

The use of a conventional nebuliser/expansion chamber with the CAP was not feasible when the sample was introduced radially. (See Chapter 4.) Even when the desolvator was used, the noise was known to be partially due to the method of radial sampling. It was therefore decided to introduce the aerosol with the main plasma flow. However, the plasma flow entrance channels were considered to be too narrow (sample condensation), so a new sample introduction/plasma flow system was constructed. The CAP quartz window was replaced with a tufnol plastic disc (3.7 cm diameter, 0.3 cm thick). Into the disc was cemented a copper tube ( $\frac{1}{4}$ " OD) positioned so as to protrude 2.3 cm into the CAP. The normal plasma flow entrance port was blocked with a piece of plastic tubing, and the radial sample entrance with a piece of graphite.

To establish whether this system of sampling was an improvement over the normal radial method, the nebuliser was operated without the use of a desolvator. A small expansion chamber, made from a 250 ml polythene bottle was fitted with a drain/trap. An outlet tube from the chamber was connected to the copper tube. A 1 ppm cadmium solution was nebulised into the CAP ( $1.85 \text{ l.min}^{-1}$  argon, sample uptake approximately  $0.5 \text{ ml.min}^{-1}$ ) and into the microwave plasma. Both plasmas were fairly stable, but only small signals at 228.8 nm were observed. It was concluded that this method of sample entry was not ideal, but was better than the previous method because it increased plasma stability. The axial sampling technique was tested using the desolvator system and for 1 ppm cadmium solution a signal/background of 2 was recorded. The plasmas were more stable and a detection limit of 0.005 ppm was obtained. The equipment was more economical to operate because only two gas flows were used (cathode flush and axial sample).

### 5.2.3 4 mm CONTAINMENT TUBE

The exit orifice of the CAP was approximately 4 mm in diameter. It was thought that containment of the microwave plasma inside a 4 mm tube would produce a more stable plasma, because the gas flow would not be disturbed during its passage from the CAP to the quartz tube. The cathode block was modified to accommodate the 4 mm i.d. tube by drilling along the exhaust channel to a depth of 6 mm, with a  $\frac{1}{8}$ " drill. The end of the quartz tube was ground until it fitted tightly into the cathode block. The microwave plasma was formed quite easily within the tube, it was more stable than the previous plasma, but similar in shape and colour. The bright part was situated to one side adjacent to the large tuning stub, and optimum stability was obtained at 100 watts generator output.

#### Effect of potassium chloride

Murayama et al<sup>(47)</sup> reported the enhancement effect of sodium on several elements (see Chapter 1). In order to see if similar effects were obtained with the present system, cadmium and mercury solutions (1 and 5 ppm respectively) in the presence of 10, 50, 100, 150 and 300 ppm of potassium were nebulised into the plasmas. The emission lines at 228.8 and 253.6 nm were scanned, results showed that potassium (100 ppm) increased the signal/background for both cadmium and mercury by a factor of two. The addition of potassium caused the plasma to shrink considerably, and at concentrations greater than 500 ppm the plasma was extinguished. It was concluded that the increase in the signal was probably due to the change in the plasma geometry, created by the increase in electron and potassium ion concentration. The effect of potassium on easily ionised calcium could not be studied because the monochromator did not possess sufficient resolving power to separate the calcium lines (317.9, 395.7, 397.3, 422.6) from the band and line emission of the plasma.

### Position of viewing

The centre of the plasma was focused on the spectrometer slit and emission signals from 1 ppm zinc and cadmium solutions were measured at several heights along the plasma. In both cases the best signal/background was observed in the lower parts of the plasma (see Figure 5.4) although emission was observed throughout the total length of the plasma.

The full length of the plasma was viewed and signals from zinc and cadmium were measured at several positions across the width of the discharge. Signal/background measurements suggested that the sample was evenly distributed across the plasma.

### Operation of a new nebuliser/desolvation system

The nebuliser/desolvator used in the above work was not really suitable because of the high gas flows needed for stable nebuliser operation. A stainless steel nebuliser was constructed in the workshops (see top right Plate 6.1) which operated efficiently at lower flows. ( $1.4 \text{ l.min}^{-1}$  @  $15 \text{ lb.in}^{-2}$ , solution uptake  $1.5 \text{ ml.min}^{-1}$ ). The new desolvation chamber (plate 5.1) was similar to the previous one except that the length was increased from 15 cm to 30 cm. Increasing the sample path length and using the new nebuliser reduced the noise in the plasma background and sample emission.

The microwave plasma tended to wander from side to side inside the 4 mm tube. In order to remedy this, a 4 cm long piece of stainless steel tubing (22 gauge) was fastened with nichrome wire on the outside of the quartz tube, adjacent to the large tuning stub of the cavity. The plasma stability was improved considerably. Figure 5.5 shows the base line (background emission at 213.9 nm) for distilled water and the emission signal from 1 ppm zinc solution. Approximately 60 seconds were required for the signal to reach a

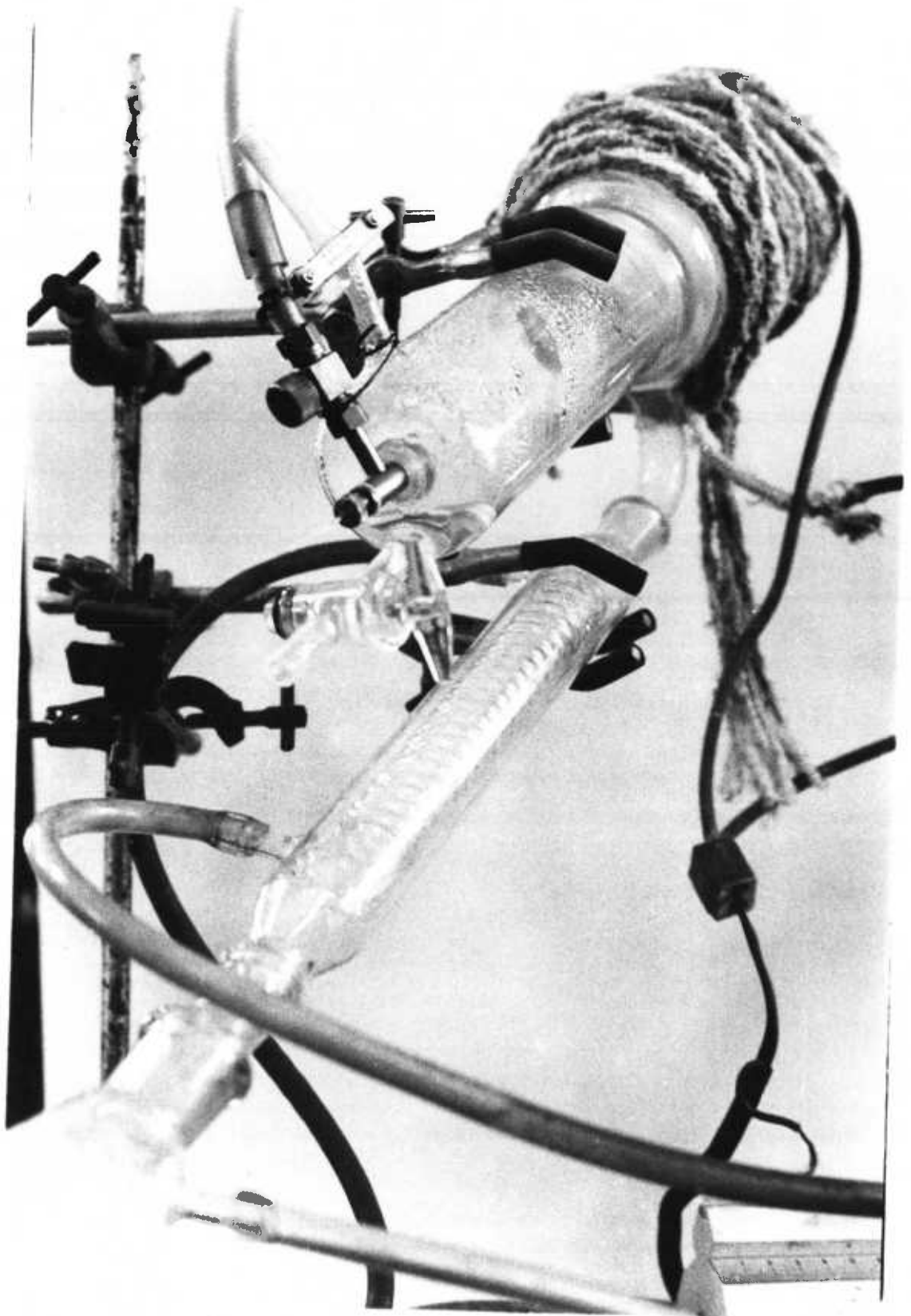


Plate 5.1 Nebuliser/desolvator

maximum, the reason being the large volume of the desolvator (900 ml), the low nebuliser flow, and the long response time of the damped recorder (approximately 20 secs).

#### Use of a low sample flow nebuliser

The long response time of the desolvator/CAP system made sampling a time consuming operation. In an attempt to discard the desolvator and increase the speed of sampling, it was decided to construct a high pressure nebuliser (see Chapter 6).

A  $\frac{3}{8}$ " hole was drilled in the centre of a tufnol plastic disc and the end of the nebuliser (venturi end-piece) was cemented in position. The disc replaced the previous sample introduction tube assembly. The nebuliser was operated between 50 and 100 lb.in<sup>-2</sup>, the sample uptake rate was 75 to 150  $\mu\text{l}.\text{min}^{-1}$  with gas flows between 1.1 and 0.7 l.min<sup>-1</sup> (measured at atmospheric pressure). The aerosol produced was extremely fine and the CAP was very stable at 10 amps. However, the microwave plasma was not fully formed and only small signals were seen from 10 ppm cadmium solution. It was concluded that desolvation was a necessary step before microwave excitation of the analyte.

#### Detection limits

The detection limits for several elements (4 mm quartz tube) are shown in Table 5.1, they were calculated from element concentrations which gave a signal/background = 1. The noise on ( $\frac{1}{2}$  peak to peak) the background emission was about 1.5%, therefore for a signal-to-noise of 2, the concentrations (that gave S/B=1) were divided by 30. Signals at five times the calculated detection limits were easily measured.

#### 5.2.4 2 mm CONTAINMENT TUBE

The development of a low gas flow nebuliser (see Plate 6.1) made the prospect of a microwave plasma, contained inside a 2 mm

quartz tube, feasible. This type of plasma should have the following advantages over the previous ones:

- (i) Greater plasma stability because the equilibrium diameter of an argon atmospheric pressure plasma is approximately 1.5 mm
- (ii) Larger emission signals, due to the more intense plasma.
- (iii) A greater proportion of the sample will be excited (in the larger tubes most of the sample passes around the microwave plasma). However, a disadvantage with a 2 mm system is the back-pressure created by the passage of hot gases through a small diameter tube, which reduces the solution uptake rate at the nebuliser.

TABLE 5.1 Calculated detection limits (4 mm tubing)

| <u>Element</u> | <u>Detection limit ppm</u> | <u>Wavelength nm</u> |
|----------------|----------------------------|----------------------|
| Ca             | 0.05                       | 422.6                |
| Zn             | 0.01                       | 213.9                |
| Hg             | 0.05                       | 253.6                |
| Pb             | 1                          | 405.7                |
| Cd             | 0.01                       | 228.8                |
| Ni             | 0.2                        | 232.0                |
| Co             | 0.2                        | 240.7                |
| As             | 0.25                       | 228.8                |
| Mg             | 0.05                       | 285.5                |
| Fe             | 0.2                        | 248.3                |

A copper insert (ring) 6 mm long, 6 mm in diameter and with a 4 mm hole was inserted into the hole previously drilled in the cathode block. An 8 cm length of quartz tube (2 mm i.d., 4 mm o.d.) was ground until it fitted into the modified exhaust orifice. The CAP was ignited and stabilised at 10 amps, then the 2 mm

tube was wedged into the cathode block. The cavity was positioned around the tube, and a stable microwave plasma was obtained at a generator power of 100 watts. It was approximately 3 cm long and was formed with the bottom of the discharge opposite the large tuning stub. With this arrangement the nebuliser did not operate smoothly below an argon flow of  $1.2 \text{ l.min}^{-1}$  ( $13 \text{ lb.in}^{-2}$ ) because of the high back-pressure created by the 2 mm tube constriction. At flow rates above  $1.45 \text{ l.min}^{-1}$  ( $16 \text{ lb.in}^{-2}$ ) the microwave plasma became noisy. In order to reduce the back-pressure the 2 mm tube was shortened to 5 cm. The nebuliser and plasma then operated smoothly at an argon flow of  $1.4 \text{ l.min}^{-1}$  with a solution uptake rate of  $1.5 \text{ ml.min}^{-1}$ .

#### Optimal microwave power

The plasma was operated between 75 (lowest power required to maintain a plasma) and 130 watts, 1 ppm zinc (sulphate) was sampled, the full length of the discharge was viewed and the signal/background and noise were measured at 213.9 nm. The signal/background slightly increased with increasing microwave power from 75 to 85 watts. Powers greater than 85 watts did not increase the signal/background, but the plasma became more stable at 100 watts. Above 125 watts the plasma became unstable, this was due to it striking below the large tuning stub and into the CAP (i.e. at high powers the plasma was beginning to form below the large tuning stub, as occurs in a conventional microwave discharge). Therefore, 100 watts were chosen as the optimal microwave power.

#### Optimal position of viewing

The plasma was operated using the conditions previously described. The centre of the microwave plasma was focused on the spectrometer slit, and the emission from 1 ppm cadmium, mercury and zinc solutions were measured along the length of the discharge. All three elements showed large emission signals from the lower regions

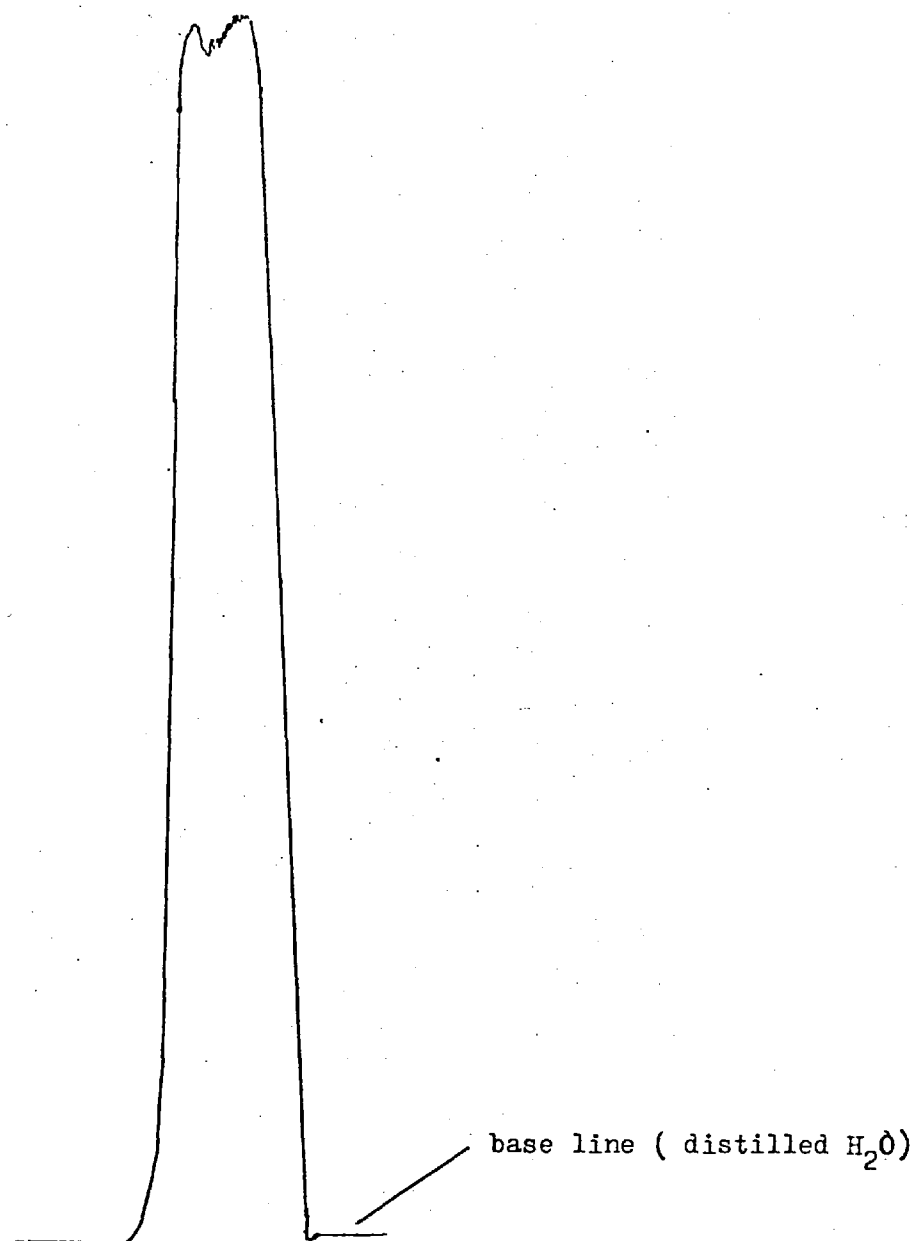


Figure 5.5. Signal obtained from 1 ppm zinc @ 213.9 nm.

of the discharge, and at heights of 1 cm and above no signals were seen for zinc or cadmium, and only very small signals were observed for mercury. Figure 5.6 shows the graphs of signal/background against height of observation for the three metals. Runnels and Gibson<sup>(72)</sup> observed larger signals in the lower regions of their plasma, due to plating of the sample on the quartz tube. However, mercury which is extremely volatile (b.p. 357C), should not plate on the hot quartz walls, and emission should be seen along the full length of the plasma. However, good signals were only obtained from the lower regions, which suggested that the microwave plasma only possessed high excitation energies in the region adjacent to the large tuning stub of the cavity. Figure 5.7 shows five repetitive samples of 1 ppm mercury solution sprayed alternatively with distilled water as a blank. The emission was measured at 253.6 nm using a spectrometer slit width of 0.05 mm (spectral band-pass of 0.15 nm) and viewing the lower 0.5 cm of the plasma.

#### Calibration graphs

Calibration graphs for zinc, cadmium and mercury were obtained from 0 to 100 ppm. The zinc and cadmium graphs were linear from the detection limits (0.01 and 0.003 ppm respectively) up to approximately 10 ppm, and the mercury graph was linear from 0.05 ppm (detection limit) up to 15 ppm. At mercury concentrations greater than 20 ppm, the system required at least ten minutes for the residual mercury to clear from the desolvator system. The less volatile zinc and cadmium did not suffer from such a large memory effect, even at concentrations of 100 ppm, only two or three minutes were required for the cleaning of the system by nebulisation of distilled water.

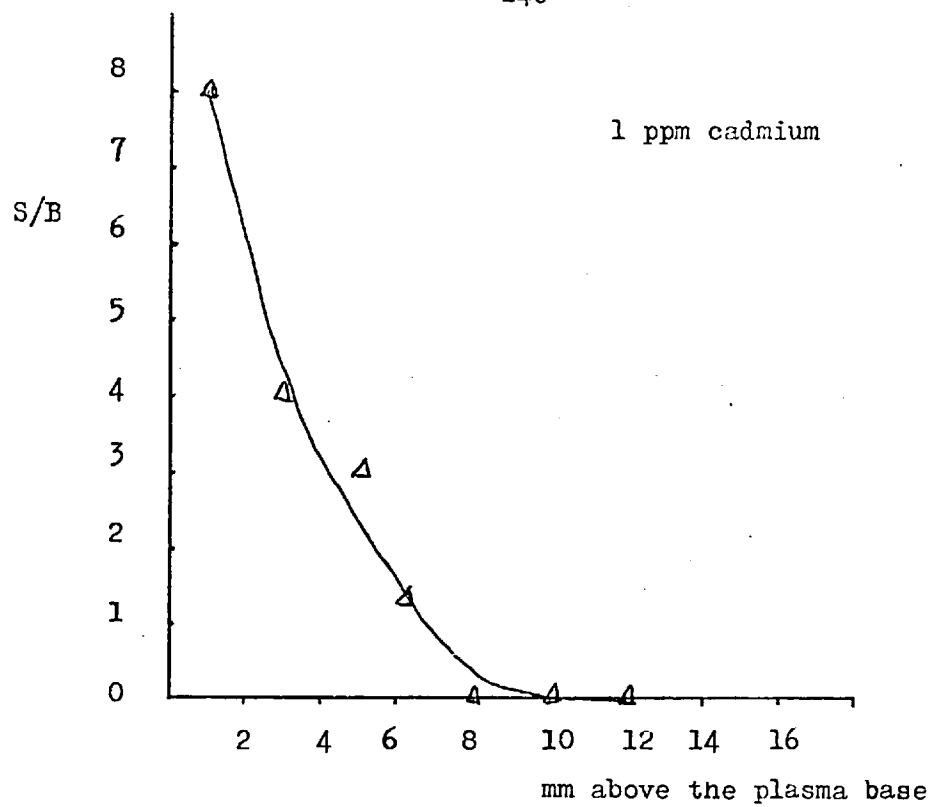


Figure 5.6 a

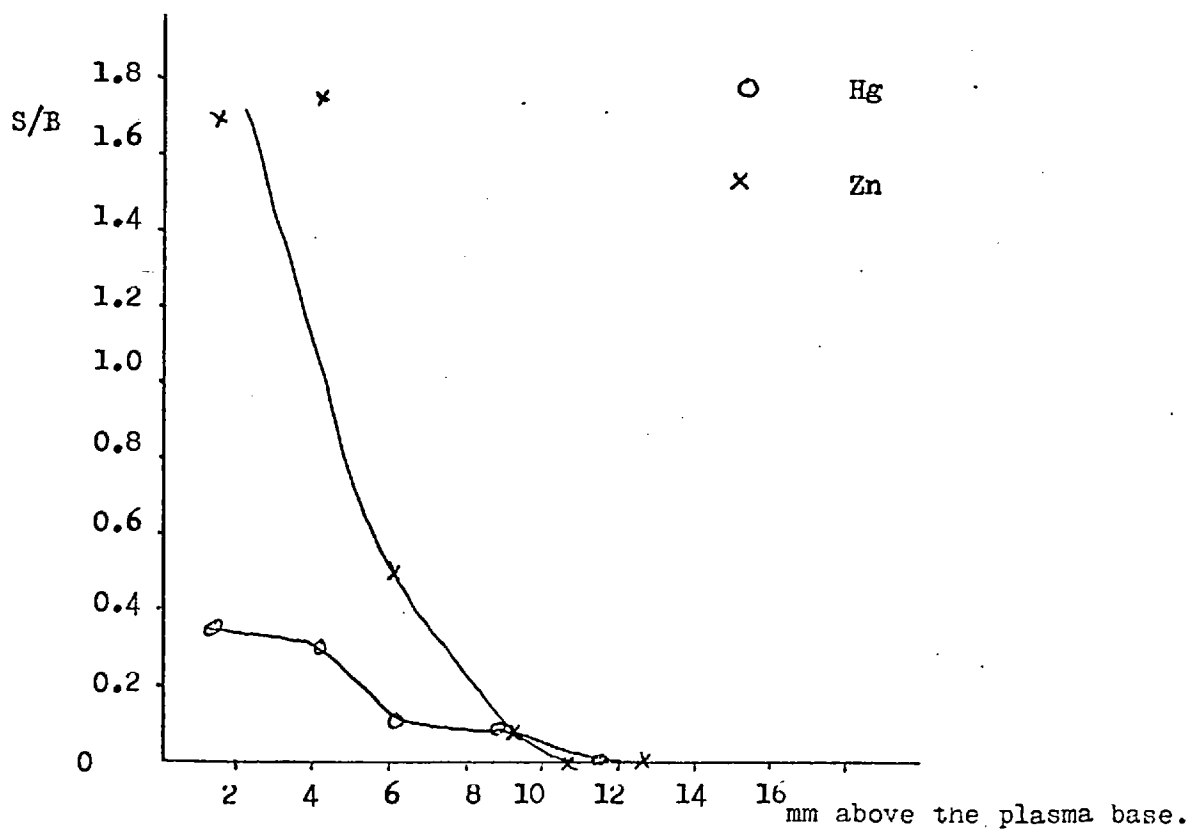


Figure 5.6 b. Graphs of signal/background for zinc, mercury and cadmium (1 ppm solutions) vs. height of viewing in the microwave plasma (stabilised, in the 2 mm quartz tubing).

## Interferences

Table 5.2 and 5.3 show the effect of several interferences (100 times excess) upon the emission signals from 1 ppm cadmium and 1 ppm zinc sulphate solutions.

TABLE 5.2 Interferences on 1 ppm cadmium

| <u>Interferent</u>                               | <u>% Interference</u> | <u>Comment</u>   |
|--------------------------------------------------|-----------------------|------------------|
| Fe as $\text{FeCl}_3$                            | 13                    |                  |
| $\text{BO}_3^{3-}$ as $\text{H}_3\text{BO}_3$    | -12                   |                  |
| As as $\text{Na}_3\text{AsO}_4$                  | 19                    | Spectral overlap |
| Sb as $\text{SbCl}_3$                            | 35                    | Spectral overlap |
| $\text{SiO}_4^{4-}$ as $\text{Na}_4\text{SiO}_4$ |                       | See text         |
| $\text{PO}_4^{3-}$ as $\text{H}_3\text{PO}_4$    | 0                     |                  |
| V as $\text{NH}_4\text{VO}_3$                    | -19                   |                  |
| Na as NaCl                                       |                       | See text         |
| Al as $\text{Al}_2(\text{SO}_4)_3$               | -70                   |                  |

TABLE 5.3 Interferences on 1 ppm mercury

| <u>Interferent</u><br>100 times excess        | <u>% Interference</u> | <u>Comment</u>                |
|-----------------------------------------------|-----------------------|-------------------------------|
| Fe as $\text{FeCl}_3$                         | 100                   | Spectral overlap Fe 253.56 nm |
| $\text{BO}_3^{3-}$ as $\text{H}_3\text{BO}_3$ | 0                     |                               |
| Al as $\text{Al}_2(\text{SO}_4)_3$            | -50                   |                               |
| V as $\text{NH}_4\text{VO}_3$                 | 0                     |                               |
| $\text{PO}_4^{3-}$ as $\text{H}_3\text{PO}_4$ | -33                   |                               |

Interferences on both cadmium and mercury were very serious. The positive interferences of arsenic and antimony on cadmium were predictable and were due to spectral overlap. However, the positive interference of iron on cadmium could not be

explained in terms of spectral overlap, and it was thought to be due to monochromator leakage of other wavelengths. The interference effects of silicate (as sodium silicate) and sodium were also difficult to study due to light leakage. In order to overcome this problem spectral scans were performed upon, sodium solution (100 ppm), cadmium solution (1 ppm) and cadmium plus sodium. The results showed that sodium enhanced the emission of cadmium by about 150%. Similar spectral scans showed that sodium silicate did not significantly reduce or enhance the emission from cadmium. This was probably due to the enhancing effect of sodium compensating for the possible interference by silicate.

#### Determination of cadmium in a copper alloy

0.2 g of a copper alloy containing 0.17% cadmium was dissolved in 5 ml of Analar concentrated nitric acid. The solution was diluted to 25 ml, filtered and then made up to 100 ml (solution X). The solution was nebulised into the plasma and the emission at 228.8 nm was measured. A calibration graph was constructed using cadmium sulphate standards containing 0.1, 1, 3, 5, 10 and 15  $\mu\text{g} \cdot \text{ml}^{-1}$ . Direct measurement of cadmium in the sample using the calibration graph gave a low result (0.05%) for the cadmium concentration. Therefore the method of standard addition was used for the analysis and the solutions were made up as follows:

5 ml of solution X was diluted to 10 ml

5 ml of solution X plus 20  $\mu\text{g}$  Cd was diluted to 10 ml

5 ml of solution X plus 40  $\mu\text{g}$  Cd was diluted to 10 ml

The cadmium emission from the three solutions was measured, and a graph was plotted (see Figure 5.8) to obtain the cadmium concentration in solution X. The cadmium content of the sample was calculated to be 0.165%. To check the result, the cadmium content of the solution was determined by atomic absorption using an air-acetylene flame on a

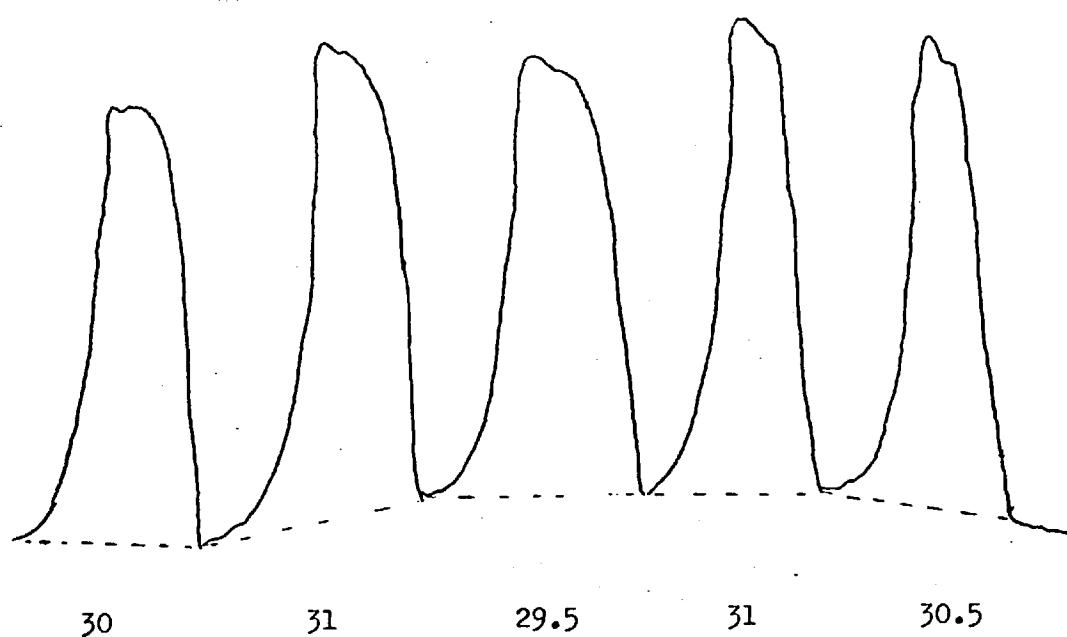


Figure 5.7. Five samples of 1 ppm mercury sprayed alternately with distilled water.

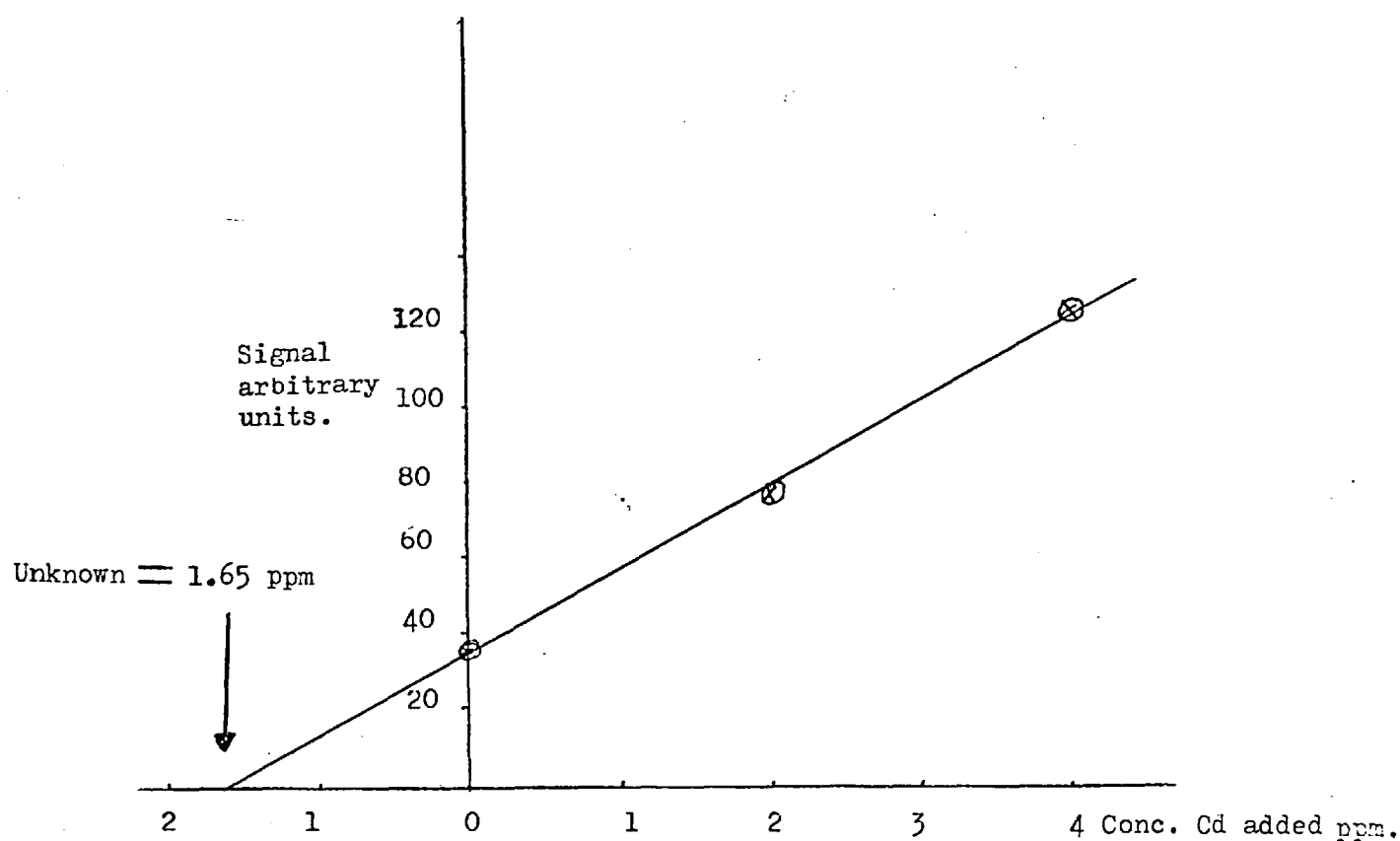


Figure 5.8. Standard addition graph for cadmium determination in a copper alloy.

Varian Techtron '1000' spectrophotometer. The cadmium content was found to be 0.17%. Nebulisation of the copper alloy solution gradually reduced the emission intensity transmitted through the quartz, due to plating of copper on the walls. After ten minutes of operation the intensity of the cadmium was reduced by about 5%, this effect limited the number of standard additions (made to solution X) to two.

#### 5.2.5 AXIAL OBSERVATION OF THE MICROWAVE PLASMA

The transparency of the plasma containment tube changed significantly with time and it was thought than an end-on optical arrangement would solve the problem. However, a normal end-on view was not suitable because the large background emission from the CAP was also observed. In order to view the microwave plasma and not the CAP, a bent tube arrangement was made (see Figure 5.9). A stable plasma was obtained at powers from 40 to 150 watts, the image was focused on the spectrometer slit, and 1 ppm on mercury solution was sampled. Smaller signal/background ratios were obtained because all of the plasma was viewed, and only the lower 0.5 cm emitted strong mercury signals. The detection limit was calculated to be 0.1 ppm, which was twice the previous limit. It was concluded that this arrangement was the best so far, but the positions of the bent quartz tube and  $\frac{1}{4}$ -wave cavity were difficult to align to give a stable plasma.

#### 5.2.6 FORMATION OF THE MICROWAVE PLASMA IN A 2 MM CUT-AWAY QUARTZ TUBE

A microwave plasma was formed at the end of a 2 mm piece of quartz tubing, the lower 0.5 cm (opposite the large tuning stub) being contained within the tube; this region has been shown to be only part of the plasma useful for analytical signals. Any attempt to form the plasma nearer the mouth of the tube resulted in an air plasma forming between the large and small tuning stubs. In order to view the lower portions, the quartz tube was cut away as shown in

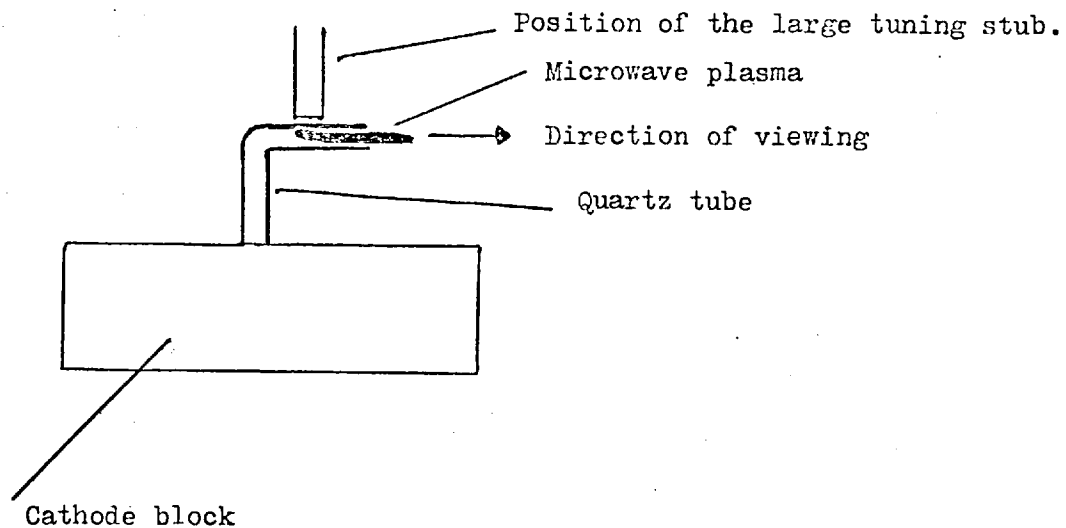


Figure 5.9. Tube arrangement for axial viewing of the microwave plasma.

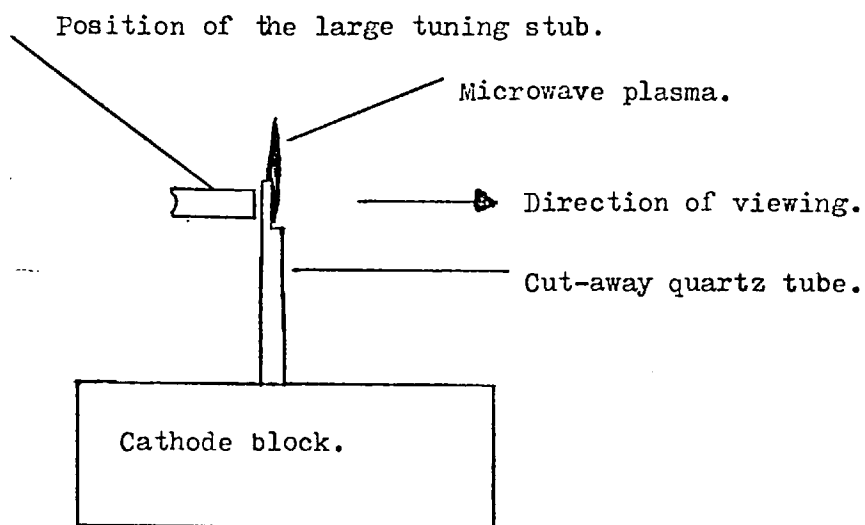


Figure 5.10. Cut-away quartz tube assembly, for viewing the lower portions of the microwave plasma.

Figure 5.10. The plasma obtained varied in length from 1 cm (60 watts) to 2.1 cm (150 watts) and was most stable at a generator power of 90 watts (15 watts reflected power). The lower 0.5 cm of the plasma was focused on the spectrometer slit, very good signals were obtained from 0.1 ppm zinc solution at 213.9 nm, and a detection limit of 0.003 ppm was calculated. This system was quite stable, good emission signals were obtained, and the previous problem associated with the varying transparency of the quartz tube was eliminated.

#### Optimisation of plasma parameters

The plasma was most stable at 90 watts, the optimal nebuliser gas flow was found to be  $1.3 \text{ l.min}^{-1}$  ( $15 \text{ lb.in}^{-2}$ ) which gave a sample uptake rate of approximately  $1 \text{ ml.min}^{-1}$ . In an attempt to reduce the noise due to the nebuliser, a double-pass desolvator was constructed, (see Figure 5.11) the purpose of the central tube being to separate the forward and reverse aerosol flows. The latter are produced as a result of the low pressure in the region of the high aerosol velocity<sup>(98)</sup>. The new chamber did not significantly reduce the noise on the signals from 1 ppm solutions of cadmium and zinc, but it was decided to keep this desolvator in the system.

The 'Sunvic' energy regulator setting, which controlled the temperature of the desolvator heating tape, seemed to affect the noise on the emission signals. To optimise the heating temperature, 1 ppm cadmium solution was nebulised into the microwave plasma, the lower emission zone was viewed, and the signal, plasma background, and noise were measured for several temperatures. The desolvator was allowed to stabilise for fifteen minutes between each temperature setting, and water was nebulised continuously between the samples. The temperature of the heating tape was monitored using

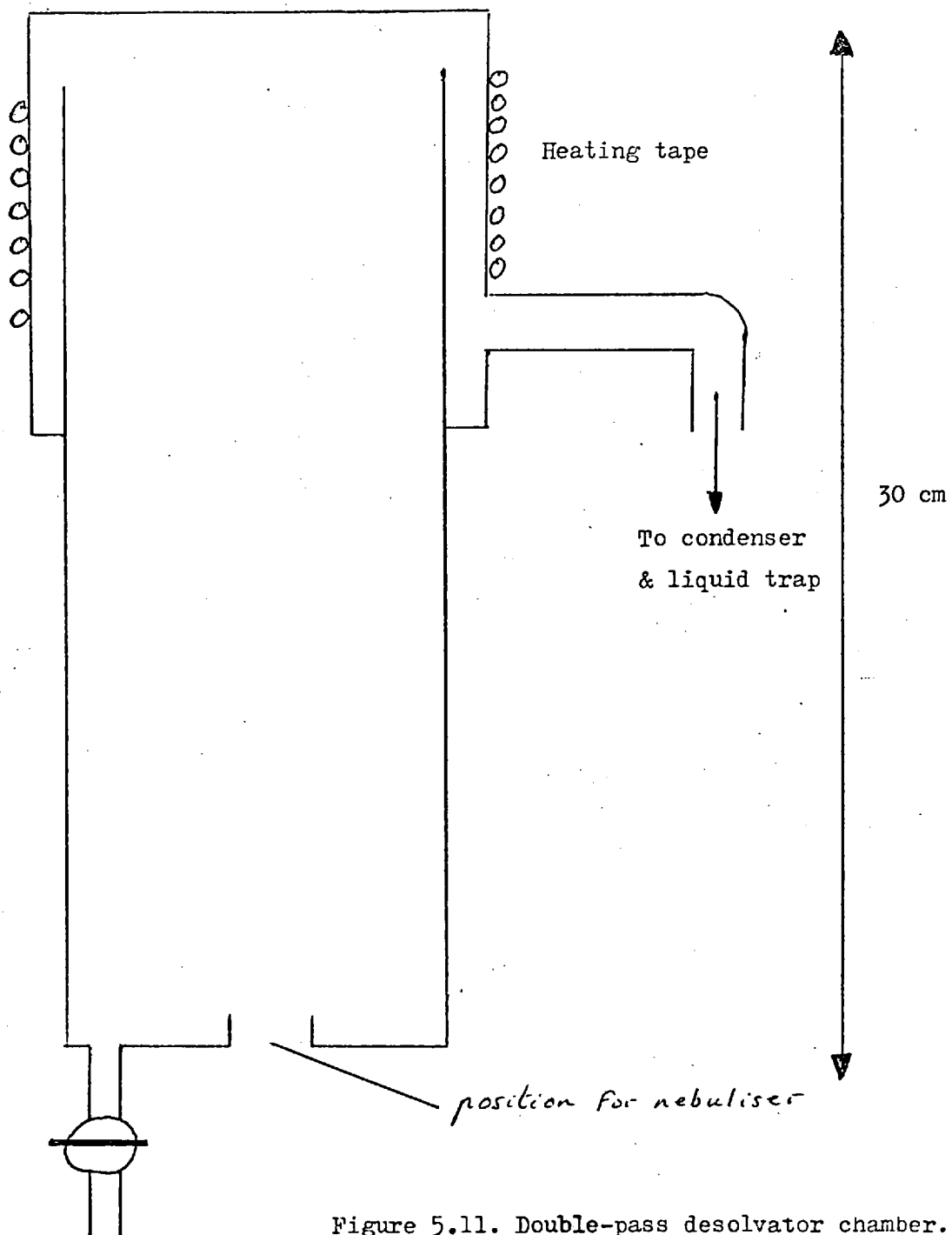


Figure 5.11. Double-pass desolvator chamber.

an iron-constantine thermocouple connected across a Servoscribe potentiometric recorder. Table 5.4 shows the signal (mV), the heater setting with the corresponding temperature, and the noise on the signal. The signal reached a maximum at a heating temperature of 470°C, and noise was minimised at 560°C.

TABLE 5.4 Effect of the heating temperature on the cadmium emission signal

| <u>Heater setting</u> | <u>Temperature °C</u> | <u>Signal mV</u> | <u>Noise on signal %</u> |
|-----------------------|-----------------------|------------------|--------------------------|
| 50                    | 320                   | 12.4             | 5                        |
| 60                    | 333                   | 12.5             | 5                        |
| 70                    | 400                   | 15.0             | 4                        |
| 80                    | 470                   | 18.5             | 4                        |
| 85                    | 560                   | 18.5             | 2                        |
| 90                    | 620                   | 18.0             | 3                        |
| 100                   | 630                   | 18.0             | 3                        |

### Calibration graph

The lower 5 mm of the plasma was viewed and calibration graphs were constructed for zinc and cadmium from 0 to 100 ppm. Curvature became quite noticeable for both elements above the 10 ppm concentration range, and the detection limits were 0.003 and 0.003 ppm respectively.

### 5.3.1 ANALYSIS OF OTHER ELEMENTS

The SP900 monochromator was only suitable for elements with strong spectral lines below 250 nm, because of its poor resolving power. The study of interferences was made difficult by monochromator light leakage. A Techtron model AA4 grating monochromator (fitted with a R.C.A. 1P.28 photomultiplier tube) with a reciprocal linear dispersion of 3 nm.mm<sup>-1</sup> was employed in the study of elements with lines above 250 nm.

### Aluminium

The use of the CAP for molecular fragmentation before the microwave plasma should enable aluminium (forms a stable refractory oxide) to be determined. A 100 ppm aluminium (sulphate) solution was nebulised into the plasma, the lower 1 cm was focused on the spectrometer slit and emission observed at the following aluminium wavelengths; 309.27, 308.21 and 394.40 nm. The first wavelength was unsuitable because of the high OH band emission and the only wavelength that gave reasonable signals was the resonance line at 396.15 nm. A signal/background of 1 was obtained at 50 ppm, from which a detection limit of 1.5 ppm was calculated. A calibration graph was plotted between 10 and 500 ppm (signals and graph shown in Figure 5.12), the curvature was too great to be entirely due to self absorption and was probably due to inefficient atomisation of the sample particles. This may be due to the formation of larger aerosol particles (at higher aluminium concentrations) which have difficulty in entering the plasma.

### Barium

In order to establish the most suitable emission line for barium, 100 ppm (as the chloride) was nebulised into the plasma system and emission was observed at 307.158, 553.548, 350.11 and 577.76 nm using a spectrometer slit of 0.025 mm. The 553.548 and 350.11 lines gave signal/background ratios of 8 and 0.25 respectively, no emission was seen from the other lines. A detection limit of 0.3 ppm was calculated from the signal and noise obtained from a 5 ppm solution. A calibration graph was constructed between 0 and 200 ppm, linearity was observed up to 100 ppm.

### Calcium

Several calcium lines were observed and Table 5.5 shows the signal/background ratios obtained from 1 ppm calcium (chloride) solution. The best line was the resonance atom line at 422.6 nm.

Signals from various aluminium concentrations.

Recorder sensitivity 5 mV for all the measurement

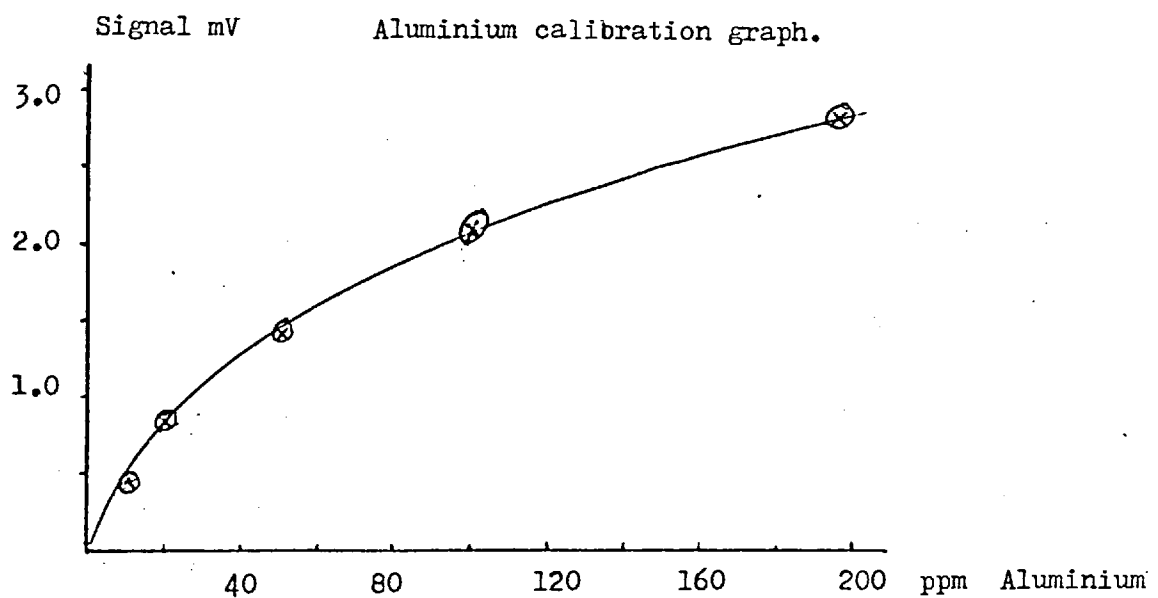
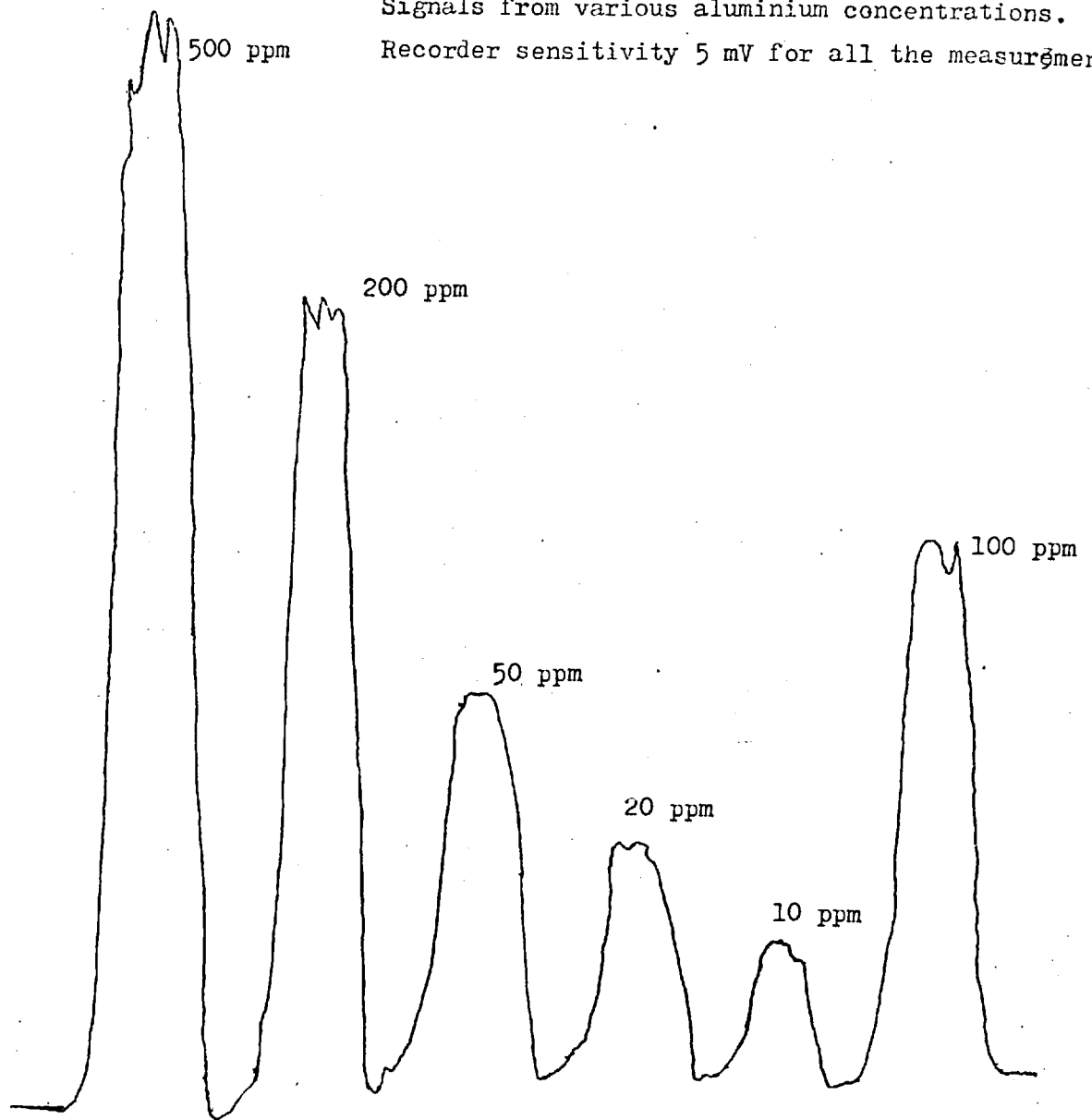


Figure 5.12. Signals and calibration graph for aluminium.

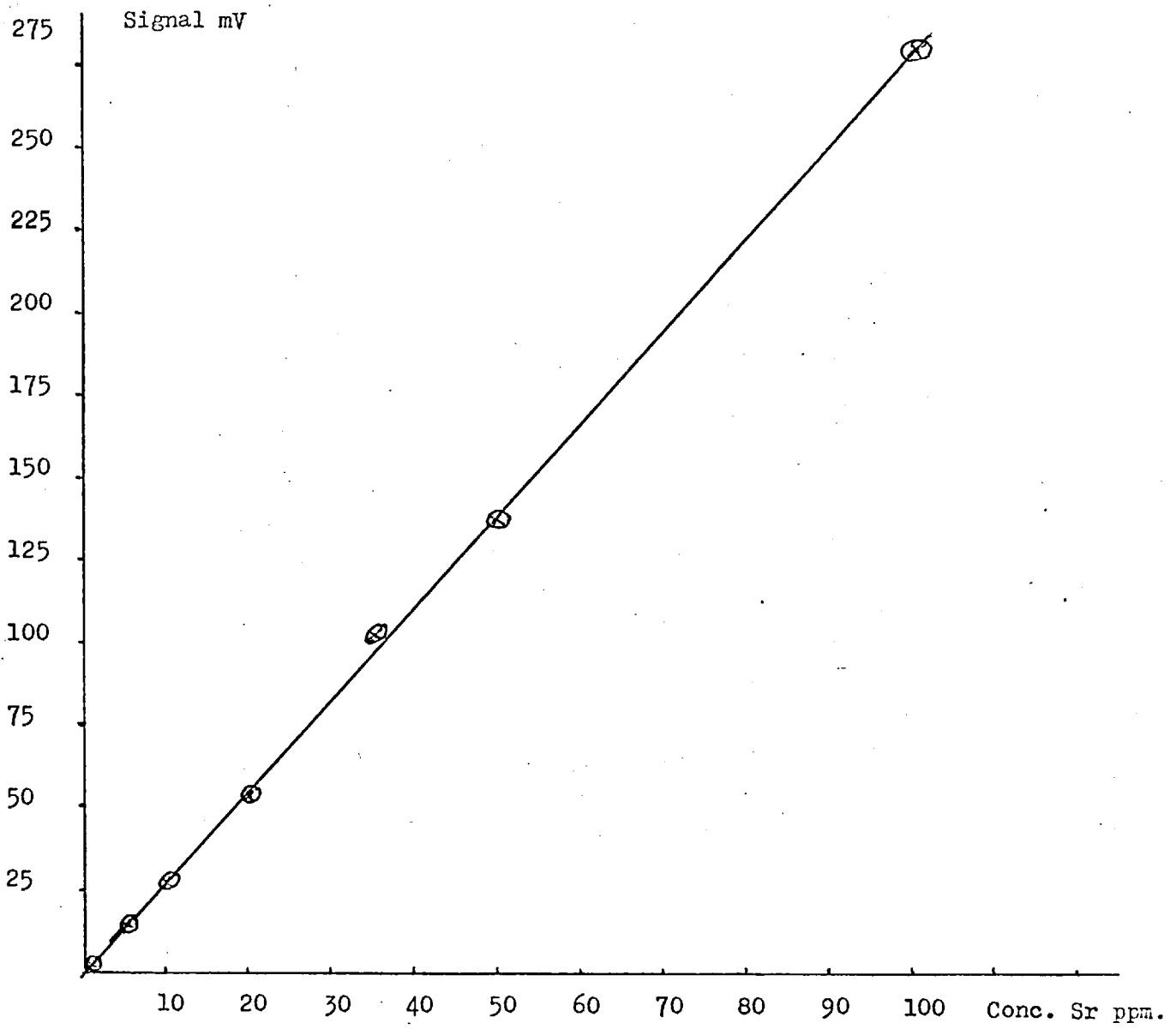


Figure 5.13 calibration graph for strontium.

The resonance ion line (Ca II) at 393.37 was also quite strong, which showed that the calcium atoms were appreciably ionised.

TABLE 5.5 Signal/background ratios for 1 ppm calcium solution

| <u>Wavelength nm</u> | <u>S/B</u> | <u>Line type</u> | <u>Comment</u>  |
|----------------------|------------|------------------|-----------------|
| 422.6                | 4.5        | I R              |                 |
| 393.37               | 4.0        | II R             |                 |
| 317.93               | 0          | II R             | High background |
| 445.59               | 0.1        | I NR             |                 |
| 445.48               | 0          | I NR             |                 |

Key: I atom line; II ion line; R resonance line; NR non-resonance line

A calibration graph (422.6 nm) was plotted between 0 and 100 ppm. It was linear up to 25 ppm and measurements were easily performed on samples containing 0.05 ppm. However, the distilled water used in the background measurements was found to contain 0.07 ppm calcium (Atomic Absorption) which increased the background. A corrected signal/background ratio for 1 ppm calcium (422.6) was calculated to be 5, and from this a detection limit of 0.006 ppm was obtained.

## Interferences

The interference of phosphate on calcium in flame atomic emission and absorption spectroscopy is well documented<sup>(99-101)</sup>.

This interference was studied using 1 ppm calcium solutions, in the presence of 100, 1000, and 10,000 ppm phosphate.

Table 5.6 shows the magnitude of the interferences.

TABLE 5.6 - Phosphate interference on 1 ppm calcium

| <u>Interference %</u> | <u>Conc. phosphate ppm</u> |
|-----------------------|----------------------------|
| 0                     | 100                        |
| -35                   | 1000                       |
| -70                   | 10,000                     |

Several other anions and cations were tested for interference effects upon the 1 ppm calcium. Table 5.7 shows the interferents and interferences.

| <u>Interferent</u>                            | <u>Conc. ppm</u> | <u>Interference %</u> |
|-----------------------------------------------|------------------|-----------------------|
| Na as NaCl                                    | 100              | -25                   |
| Al as $\text{Al}_2(\text{SO}_4)_3$            | 100              | -95                   |
| K as KCl                                      | 100              | -15                   |
| $\text{BO}_3^{3-}$ as $\text{H}_3\text{BO}_3$ | 100              | 0                     |
| Cu as $\text{CuSO}_4$                         | 1000             | -70                   |
| $\text{SO}_4^{2-}$ as $\text{H}_2\text{SO}_4$ | 100              | 0                     |

Aluminium caused severe depression of calcium signals, probably due to the formation of mixed oxides of low volatility<sup>(102)</sup>.

Sodium and potassium, which it was thought might enhance the emission from the calcium atom line also showed negative interferences. These results showed that even relatively volatile metals created serious interferences.

## Strontium

Strontium proved an interesting element, yielding a good detection limit of 0.001 ppm at the resonance ion line 407.77 nm. The signal was equivalent to the background at 0.04 ppm and analytical measurements were easily made at 0.005 ppm. The calibration graph (Figure 5.13) was linear from 0 to 100 ppm, which represented a linear range of over 4 orders of magnitude. The low detection limit combined with the linearity of calibration suggested efficient sample atomisation. Emission was also measured at 460.73 (resonance Sr I) and 421.55 (resonance Sr II) and the detection limits were calculated from signal/background ratios to be 0.003 and 0.005 ppm respectively. Precision measurements were made on 11 solutions containing 1 ppm and the percentage relative standard deviation on the signals was 2.1%.

## Interferences

As with calcium, the interferences were serious and Table 5.8 shows the effects caused by 100 fold excess of foreign ions on 1 ppm strontium.

TABLE 5.8 Interferences on 1 ppm strontium

| <u>Element</u>                                | <u>Conc. ppm</u> | <u>Interference %</u> |
|-----------------------------------------------|------------------|-----------------------|
| Al as $\text{Al}_2(\text{SO}_4)_3$            | 100              | -100                  |
| Fe as $\text{FeSO}_4$                         | 100              | - 80                  |
| Na as NaCl                                    | 100              | - 80                  |
| $\text{BO}_3^{3-}$ as $\text{H}_3\text{BO}_4$ | 100              | 0                     |
| $\text{SO}_4^{2-}$ as $\text{H}_2\text{SO}_4$ | 100              | - 10                  |
| $\text{Cl}^-$ as HCl                          | 100              | - 25                  |
| $\text{PO}_4^{3-}$ as $\text{H}_3\text{PO}_4$ | 100              | - 12                  |
| Cu as $\text{CuSO}_4$                         | 100              | - 60                  |

Nickel

The best line for nickel was found to be the non-resonance line at 341.477 nm which gave a detection limit of 0.3 ppm. The resonance line at 232.003 and the non-resonance line at 352.454 gave smaller signal/background ratios and the detection limits were calculated to be 0.6 and 0.8 ppm respectively. Calibration graphs were plotted from 0 to 100 ppm for the non-resonance (341.477) and resonance lines and in both cases, curvature towards the concentration axis became noticeable in the 30 ppm range. The effect therefore was not due to self absorption, which is only applicable to resonance line emission, but was probably due to the change in the sample atomisation efficiency when the concentration and the size of the desolvated particles was increased.

Several other elements were also determined and Table 5.9 gives the detection limits, the wavelengths of measurement and the linear calibration range.

TABLE 5.9 Detection limits

| <u>Element</u> | <u>Detection<br/>limit ppm</u> | <u>Wavelength<br/>nm</u> | <u>Linear<br/>range ppm</u> |
|----------------|--------------------------------|--------------------------|-----------------------------|
| Ag             | 0.05                           | 338.289                  | 0-50                        |
|                | 0.08                           | 328.068                  |                             |
| Mn             | 0.1                            | 279.827                  | 0-20                        |
|                | 0.2                            | 403.307                  |                             |
|                | 0.16                           | 403.449                  |                             |
|                | 0.12                           | 403.076                  |                             |
| Co             | 0.3                            | 240.725                  | 0-35                        |
|                | 1.2                            | 345.351                  |                             |
| Cu             | 0.25                           | 324.751                  | 0-20                        |
|                | 0.3                            | 327.396                  |                             |
| Cr             | 0.4                            | 359.349                  | 0-100                       |
|                | 0.4                            | 427.48                   |                             |
|                | 0.7                            | 425.435                  |                             |
|                | 0.6                            | 360.533                  |                             |
| Mg             | 0.02                           | 285.213                  | 0-20                        |
|                | 0.25                           | 277.983                  |                             |
| Pb             | 0.2                            | 405.78                   | 0-40                        |
| Mo             | 5                              | 390.296                  | 0-1000                      |
| V              | 1.5                            | 437.924                  | 0-1000                      |
|                | 3                              | 440.85                   |                             |
|                | 4.5                            | 446.029                  |                             |
| Zn             | 0.003                          | 213.9                    | 0-8                         |
| Hg             | 0.05                           | 253.652                  | 0-10                        |

### 5.3.2. Conclusions

The CAP was partially successful in its role as an atomisation source. The electrons in the tail-flame were responsible for initiation and stabilisation of the low wattage microwave plasma. Of the various tubes used to contain the plasma, the 2 mm cut-away tube was found to be

the most suitable. Elements which were easily volatilised gave quite good detection limits, i.e. Hg, Zn, Cd, Sr and Ca. Those notable for refractory oxide formation gave poor detection limits (V, Al, Mo). The precision of measurement at 100 times the detection limit was approximately 2% for all of the elements studied, and the linear calibration range was about three orders of magnitude, only in the case of strontium was the linear range over four orders.

Most of the interferences due to diverse ions were negative, which suggested that complete vaporisation of the dried aerosol particles was not taking place. Aluminium as expected, was a serious interferent on signals from cadmium, calcium and strontium. The interference of phosphate on calcium emission was not too severe in comparison with flame atomic absorption and emission spectrometry<sup>(103)</sup>. The magnitude of the interferences, and the small linear calibration range for most elements make the system unsuitable for simultaneous multi-element analysis.

SAMPLE NEBULISATIONCHAPTER 6

### 6.1.1 Introduction

The function of nebulisers in analytical spectroscopy is to produce a uniform and efficient supply of sample solution to the atom cell. Aerosol production for conventional atomic absorption and emission is easily accomplished by the use of pneumatic nebulisers which operate at high gas flows (approx.  $8 \text{ l.min}^{-1}$  @  $30 \text{ lb.in}^{-2}$ ) and solution uptake rates of  $2\text{-}4 \text{ ml.min}^{-1}$ . The flame can tolerate large amounts of water ( $0.5 \text{ ml.min}^{-1}$ ) without stability being affected. However, plasmas generally have a low tolerance for sample loading, and special nebulisers have been constructed which produce smooth aerosol flows with low gas and sample flow rates. Chapter 6 briefly reviews sample nebulisation techniques and discusses the operating parameters of several nebulisers constructed during the course of the work.

### 6.1.2 Pneumatic nebulisation

Mechanism - Figure 6.1 shows the construction of a typical concentric nebuliser. Compressed gas is forced out between the solution capillary tube and the nebuliser aperture (venturi) a pressure drop is produced at the end of the capillary tube and atmospheric pressure forces the sample solution up the capillary and into the high velocity gas stream, where it is broken up into tiny droplets. The aerosol is then transported to the atom cell.

The best commercial nebulisers used in conjunction with spray/expansion chambers show a maximum efficiency of about 10% because only the small droplets (below  $2\mu$ ) eventually reach the atom cell<sup>(104)</sup>. Impact beads which are placed in front of the nebuliser to break up the liquid droplets have been shown to reduce the mean droplet size from 12 to  $9\mu$ <sup>(105)</sup> and increase the total weight of sample carried from the spray chamber to the atom cell.

### Nebuliser calculations - Solution sample uptake

rates can be calculated if the dimensions of the nebuliser are known. The pressure drop at the venturi end of the nebuliser capillary can be approximately calculated from Bernoulli's equation<sup>(106)</sup>.

$$\frac{1}{2}\rho V_1^2 + P_1 = \frac{1}{2}\rho V_2^2 + P_2 \quad 6.1$$

where  $\rho$  is the gas density ( $\text{g.l}^{-1}$ ),  $V_1$  and  $V_2$  are the gas velocities ( $\text{m.sec}^{-1}$ ) in the nebuliser body and in the venturi respectively,  $P_1$  is the gas pressure around the venturi (atmospheric) and  $P_2$  is the pressure experienced at the end of the capillary tube (see Fig. 6.2).

Equation 6.1 can be re-arranged in the form:

$$\Delta P = \frac{\rho}{2}(V_2^2 - V_1^2) \quad 6.2$$

where  $\Delta P$  is the pressure drop (1 bar = 1 atmosphere).  $V_2 \gg V_1$ , therefore  $V_1^2$  can be neglected, so equation 6.2 can be rewritten:

$$\Delta P = \frac{\rho}{2} V_2^2 \quad 6.3$$

$V_2^2$  is calculated from the flow rate of the nebuliser gas, and the dimensions of the venturi. Therefore, the pressure drop can be calculated for a series of gas flow rates and venturi sizes. Solution uptake rates can then be determined using Poiseuille's Equation:

$$Q = \frac{\pi R^4 \Delta P}{8 \eta L} \quad 6.4$$

where  $Q$  is the flow rate ( $\text{ml} \cdot \text{sec}^{-1}$ ),  $R$  is the capillary radius (cm),  $\Delta P$  is the driving pressure ( $\text{dynes cm}^{-2}$ ),  $\eta$  is the liquid viscosity, and  $L$  is the tube length (cm).

A computer was programmed by J Goulter to calculate sample uptake rates for various capillaries, venturis and gas flows. Table 6.1 shows typical sample uptake rates that were calculated for a 22 gauge capillary tube (o.d. 0.712 mm, i.d. 0.420 mm) with several venturis and gas flow rates varying from 0.75 to 2.0  $\text{l} \cdot \text{min}^{-1}$ .

Liquid droplet-size - The mean drop size of a spray produced from a concentric nebuliser can be calculated approximately from the empirical equation of Nukiyama and Tanasawa<sup>(107)</sup>.

$$d_o = \frac{585}{(u-v)} \left[ \frac{\gamma}{\rho} \right]^{0.5} + 597 \left[ \frac{\eta}{\gamma \rho} \right]^{0.5} \left[ 10^3 \frac{Q_L}{Q_G} \right]^{6.5}$$

where  $d_o$  = mean diameter ( $\mu$ )

$u$  = velocity of gas  $\text{m} \cdot \text{sec}^{-1}$

$v$  = velocity of liquid  $\text{m} \cdot \text{sec}^{-1}$

$\gamma$  = surface tension  $\text{dyne} \cdot \text{cm}^{-1}$

$\rho$  = density  $\text{g} \cdot \text{cm}^{-3}$

$\eta$  = viscosity  $\text{g} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$

$Q_L$  = liquid flow rate  $\text{ml} \cdot \text{min}^{-1}$

$Q_G$  = flow rate of gas  $\text{ml} \cdot \text{min}^{-1}$

For a typical nebuliser ( $u = 333 \text{ m} \cdot \text{sec}^{-1}$ ,  $v = 1 \text{ m} \cdot \text{sec}^{-1}$  and  $Q_G = 8.5 \text{ l} \cdot \text{min}^{-1}$ ) the value of the mean droplet diameter can be calculated to be  $13\mu$ . Other workers have investigated the mechanism of droplet production<sup>(108-109)</sup> but no universally acceptable theory has been proposed.

### 6.1.3 Droplet-size measurement

Dean and Carnes<sup>(110)</sup> measured droplet size distributions using an impact technique. The droplets were impacted on a glass slide which had been coated with magnesium oxide (from burning magnesium ribbon) and the diameter of the holes produced were measured with a microscope. The true droplet size was calculated from the ratio of the true droplet size to the impression size (0.86), established previously by Nukiyama and Tanasawa<sup>(107)</sup>. Koirtyohann and Pickett<sup>(111)</sup> used the same technique to measure the mean droplet diameter ( $8.6\mu$ ) of sample reaching the flame of a Perkin-Elmer 290B atomic absorption spectrophotometer. However, May<sup>(112)</sup> reported the method unsuitable for droplet measurements below  $10\mu$ . Therefore the measurements of Koirtyohann and Pickett give a false impression of the mean droplet diameter.

Willis<sup>(104)</sup> used Watson's method<sup>(113)</sup> to measure the size of droplets eventually entering the flame of a Techtron atomic absorption spectrophotometer. The nebuliser, spray chamber and burner were surrounded by a 'hot-box' maintained at  $60^{\circ}\text{C}$  by means of a 1 kW electric radiator and fan. A 0.5% aqueous solution of methylene blue was aspirated and the solid particles formed were sampled by means of a 'Casella' thermal precipitator. The particles were sized by microscopic examination and the diameters of the drops were calculated. A mean diameter of  $2\mu$  was obtained.

### 6.1.4 Simple nebulisers

Figure 6.3 shows an angle nebuliser where the liquid and aspirating gas passes through two perpendicular tubes. This method of aerosol production is not very efficient because a large portion of the gas stream sweeps unused past the orifice of the solution capillary tube. However, the nebuliser has one advantage over the concentric type because it is easily constructed from two capillary tubes.

TABLE 6.1 (Calculation of sample uptake rates (22 gauge capillary tube))

| Venturi mm | GAS FLOW RATE L MIN <sup>-1</sup> (air) → |        |        |        |        |        |        |        |        |        |
|------------|-------------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|            | 0.7500                                    | 0.9500 | 1.0000 | 1.1500 | 1.2500 | 1.3500 | 1.5000 | 1.5500 | 1.7500 | 2.0000 |
| 0.9906     | 0.0027                                    | 0.0043 | 0.0043 | 0.0064 | 0.0075 | 0.0088 | 0.0108 | 0.0116 | 0.0147 | 0.0193 |
| 0.9652     | 0.0034                                    | 0.0054 | 0.0060 | 0.0079 | 0.0094 | 0.0109 | 0.0135 | 0.0144 | 0.0184 | 0.0240 |
| 0.9398     | 0.0043                                    | 0.0069 | 0.0077 | 0.0101 | 0.0120 | 0.0140 | 0.0172 | 0.0184 | 0.0234 | 0.0306 |
| 0.9144     | 0.0016                                    | 0.0090 | 0.0100 | 0.0132 | 0.0156 | 0.0182 | 0.0225 | 0.0240 | 0.0306 | 0.0400 |
| 0.8890     | 0.0076                                    | 0.0122 | 0.0135 | 0.0179 | 0.0211 | 0.0246 | 0.0304 | 0.0325 | 0.0414 | 0.0540 |
| 0.8382     | 0.0159                                    | 0.0256 | 0.0284 | 0.0375 | 0.0443 | 0.0517 | 0.0638 | 0.0681 | 0.0868 | 0.1134 |
| 0.8128     | 0.0258                                    | 0.0415 | 0.0459 | 0.0608 | 0.0718 | 0.0837 | 0.1034 | 0.1104 | 0.1407 | 0.1838 |
| 0.7874     | 0.0478                                    | 0.0766 | 0.0849 | 0.1123 | 0.1327 | 0.1548 | 0.1911 | 0.2040 | 0.2601 | 0.3397 |
| 0.7366     | 0.4809                                    | 0.7715 | 0.8549 | 1.1306 | 1.3358 | 1.5581 | 1.9235 | 2.0539 | 2.6181 | 3.4196 |

Solution uptake rates ml min<sup>-1</sup>

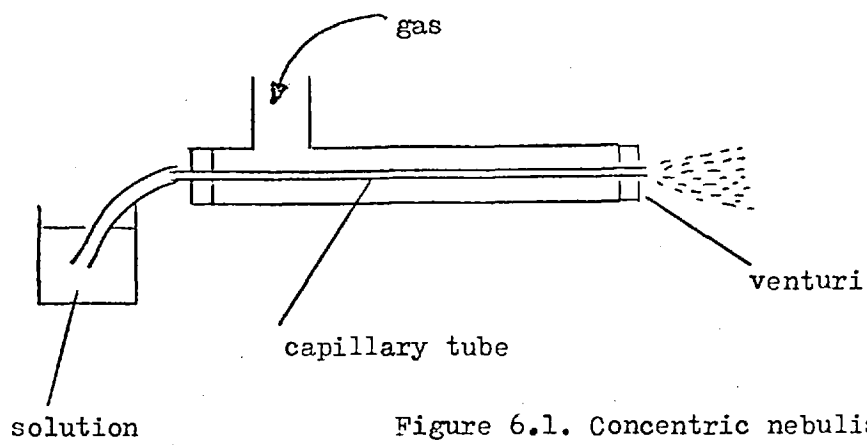


Figure 6.1. Concentric nebuliser

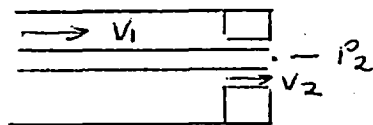


Figure 6.2.

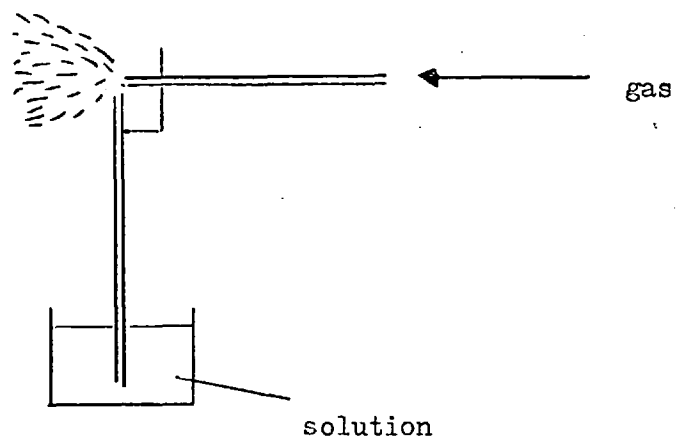
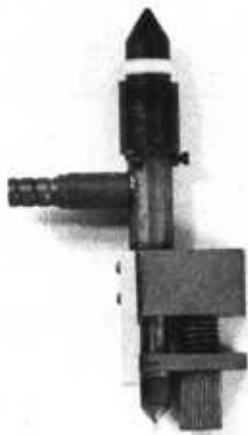
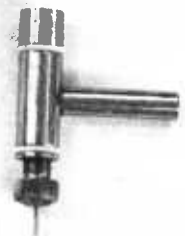


Figure 6.3. An angle nebuliser.



Brass nebuliser



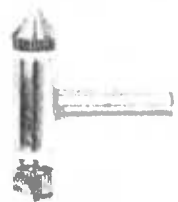
Stainless steel nebuliser

2"

Stainless steel nebuliser with copper seals



Plate 6.1



High pressure nebuliser

## Stainless steel nebuliser

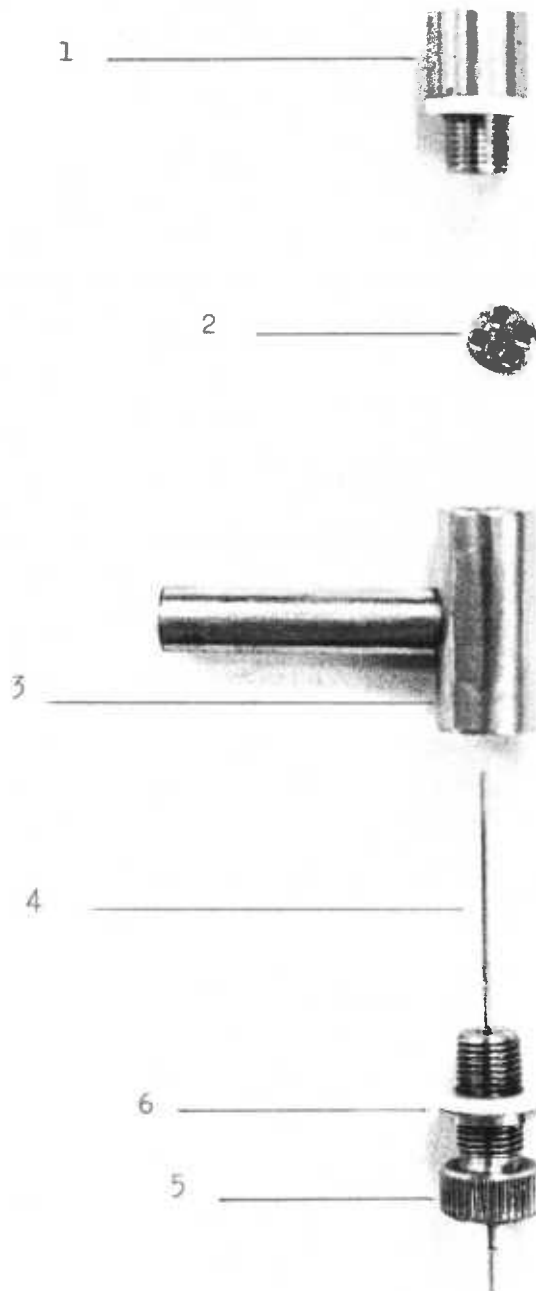


Plate 6.2

Plates 6.1, and 6.2 show various concentric nebulisers and components constructed in the College workshops. For the work described in Chapter 5, the nebuliser in Plate 6.2 was found to be the most suitable.

### 6.2.1 Ultrasonic nebulisation

Wood and Loomis<sup>(114)</sup> first reported aerosol generation by ultrasonic means. Other workers have attempted to elucidate the mechanism of droplet formation<sup>(115-116)</sup> but only approximate theoretical explanations have been suggested.

Gerken et al<sup>(117)</sup> used a velocity transformer or a focussing bowl transducer to couple ultrasonic energy to solution samples (see Figure 6.4).

West and Hume<sup>(43)</sup> and Fassel et al<sup>(56)</sup> used similar arrangements for aerosol production. Constant pressure devices were used to provide a steady feed of solution sample to the nebulisers, to maintain a uniform aerosol production rate. The above methods were not convenient because they required large volumes of solution (ca 25 ml).

A pulse ultrasonic nebuliser, which operated on small sample volumes (less than 0.2 ml) was described by Denton et al, for use with conventional flame atomic absorption<sup>(118,119)</sup>. The system enabled convenient and reproducible analysis of 25  $\mu$ l samples with a typical relative standard deviation of about 2%.

### 6.2.2 Droplet size

Lang<sup>(115)</sup> and Robinson et al<sup>(120)</sup> postulated that standing waves were formed on the surface of the liquid and sections of the surface bounded by the nodal lines were ruptured to form droplets. Equation 6.6 was deduced from this postulate:

$$d = (\pi\gamma)^{1/3} / (4\rho F^2)^{1/3}$$

6.6

where  $F$  = frequency of ultrasound

$d$  = mean diameter of the droplets.

Factors such as the viscosity and ultrasonic power appeared to affect the rate of nebulisation rather than the droplet size.

Denton and Swartz<sup>(118)</sup> operated their one-shot ultrasonic nebuliser between 700 kHz and 3MHz. The aerosol was found to contain 90% of its droplets between 4 and 6 $\mu$  at 1MHz, whilst at 3MHz 80% of the droplets were between 1 and 3 $\mu$ . Stupar and Dawson<sup>(121)</sup> operated their ultrasonic nebuliser between 70 kHz and 115 kHz (at powers from 8-15 W) and they showed ultrasonics to be efficient at producing uniform aerosols. The authors concluded that ultrasonics (70-115 kHz) did not possess any advantages over conventional nebulisation, except at higher powers and frequencies (>500 kHz).

### 6.3.1 Nebuliser design and construction

Mavrodineanu<sup>(105)</sup> has summarised pneumatic methods of introducing samples into flames. Veillon and Margoshes<sup>(18)</sup> designed a high pressure nebuliser (Fig. 6.5) and desolvation system ideally suited for use with an R.F. plasma. Stupar and Dawson<sup>(121)</sup> and Willis<sup>(104)</sup> used Techtron nebulisers with replaceable venturis and capillary tubes in their studies.

The first nebuliser constructed in the college workshop was made from brass, (top left plate 6.1 and Fig. 6.6) fitted with a 22 gauge (i.d. 0.34 mm, o.d. 0.74 mm) 10.5 cm length of stainless steel capillary tube. The venturi was 0.787 mm in diameter and the gas stream was converged at an angle of 30°. The nebuliser operated quite well for continuous sample introduction into the CAP and at an argon flow of 1.85 l.min<sup>-1</sup> @ 8 lb.in<sup>-2</sup> pressure

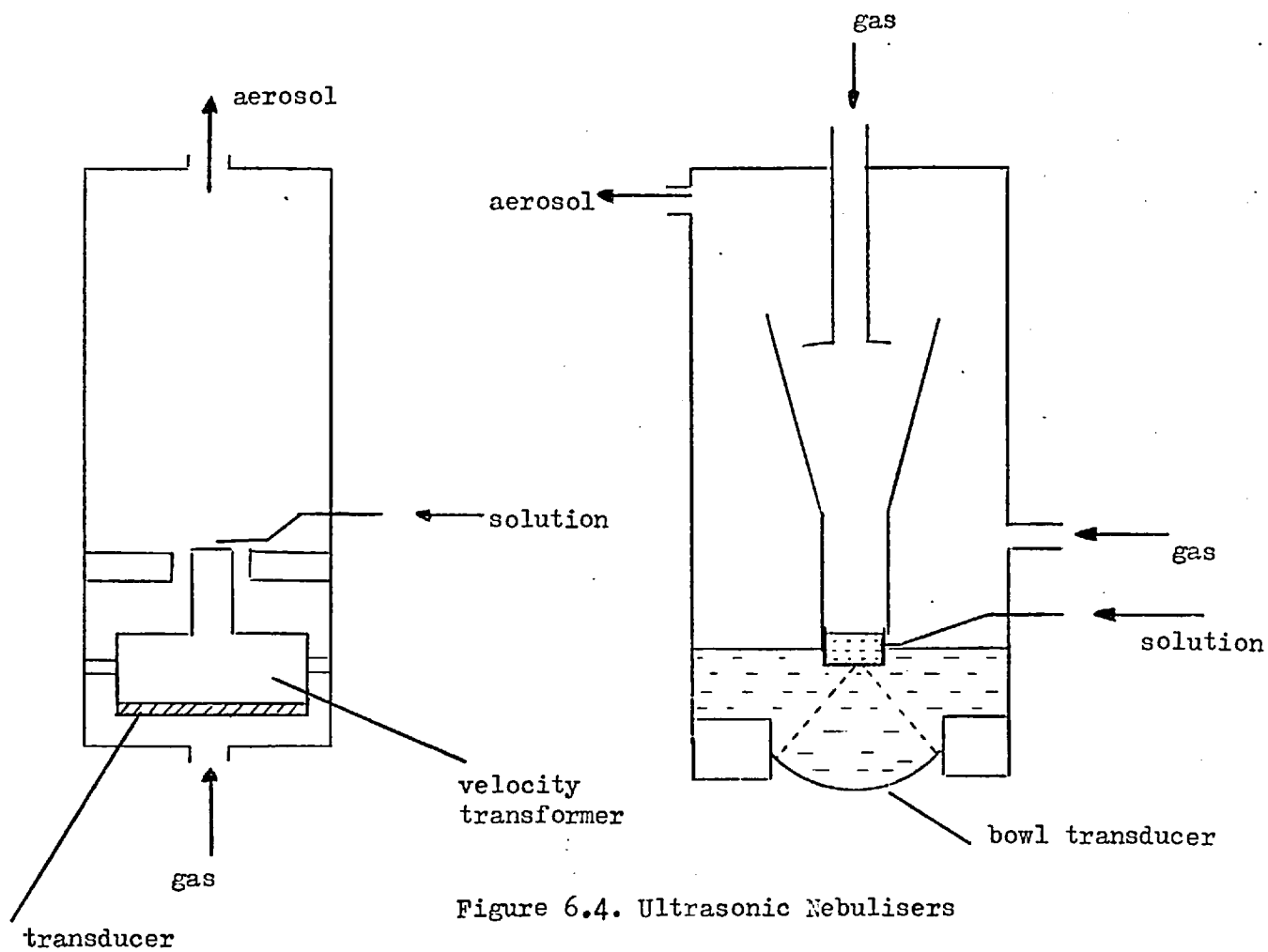


Figure 6.4. Ultrasonic Nebulisers

→ || ← 0.78mm orifice

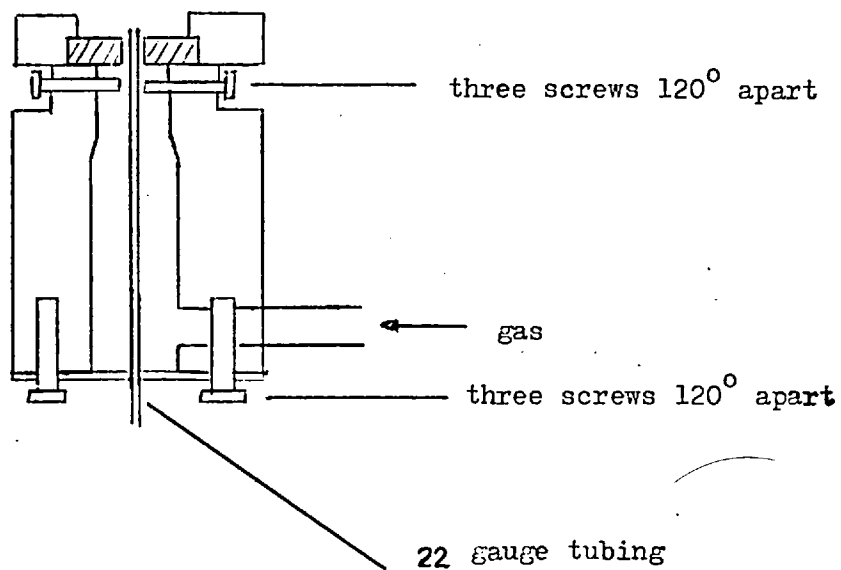


Figure 6.5. Veillon and Margoshes type nebuliser.

a solution uptake rate of  $0.4 \text{ ml.min}^{-1}$  was obtained. However, when it was used in the CAP/microwave system where low gas flows were required, very little sample was nebulised. It was unsuitable due to the large back-pressure created by the constriction of the gas flow through the microwave containment tube.

Another nebuliser (top right Plate 6.1) was constructed from stainless steel because this material is not so prone to chemical attack. It was fitted with the same gauge tubing (4.9 cm long) and venturi as the brass nebuliser. Several types of venturis were constructed and tested (see section 6.3.2). Plate 6.2 shows the various parts of the nebuliser. Part No.1 is the venturi end-piece and teflon washer, No.2 is the centering disc which screws into the nebuliser body (part No.3) and holds the capillary tube (No.4) in the centre of the venturi. The capillary tube is soldered into part No.5 which screws into the body and is locked in position by a locking screw (No.6) and teflon washer.

A high pressure, low sample uptake nebuliser was constructed (Plate 6.1 bottom right) on the same design as the above nebuliser. It was fitted with a capillary tube 5 cm long (0.14 mm i.d., 0.304 mm o.d.) and a 0.35 mm venturi.

Finally, in an attempt to simplify nebuliser design and to reduce gas leakage soft copper compression rings were substituted for the teflon seals. The locking screw (part No.6) was discarded and part No.5 was constructed like a venturi end-piece (see bottom left Plate 6.1).

### 6.3.2 Nebuliser tuning

The capillary tube of the brass nebuliser was lowered into water (air supplied at a pressure of  $10 \text{ lb.in}^{-2}$ ) and the capillary tube gradually moved towards the venturi by tuning the adjusting screw (see Plate 6.1 and Fig. 6.6). Before the

capillary tip reached the venturi, air was blown back through the water to be aspirated. As the capillary approached the venturi a neutral point was reached where no sample was nebulised and blow-back ceased. When the tube was moved further from this point water aspirated at an increasing rate. Maximum sample was aspirated with the capillary tip positioned slightly below the venturi tip. The conical shaped droplet cloud was produced at an angle of about  $20^{\circ}$  to the nebuliser body. The cloud was not homogeneous, very large droplets were produced from one side of the venturi and very fine droplets from the opposite side. This was a result of the capillary lying to one side of the venturi. To remedy this fault, three centering screws were inserted through the nebuliser body (Fig. 6.6). Fine adjustment of the screws enabled the capillary tube to be centred, which resulted in a more uniform spray. Finally the capillary tubes (venturi end) were electrolytically polished in a chromic oxide ( $\text{CrO}_3$ )/glacial acid medium to remove any rough edges produced during cutting.

The stainless steel nebuliser was tuned in a similar manner, however, two tuning positions were found. One position was as above and the other was with the capillary tip protruding from the venturi. The advantages of tuning the nebuliser this way were

- (i) a more homogeneous spray was produced
- (ii) sample only made contact with the capillary tube, this prevented excessive wear and blockage of the venturi
- (iii) tuning was more easily accomplished.

### 6.3.3 Nebuliser operating parameters

#### Introduction

Winefordner and Latz<sup>(122)</sup> studied the quantitative factors affecting sample introduction into flames. They showed that the simple Poiseuille equation for liquid flow did not accurately

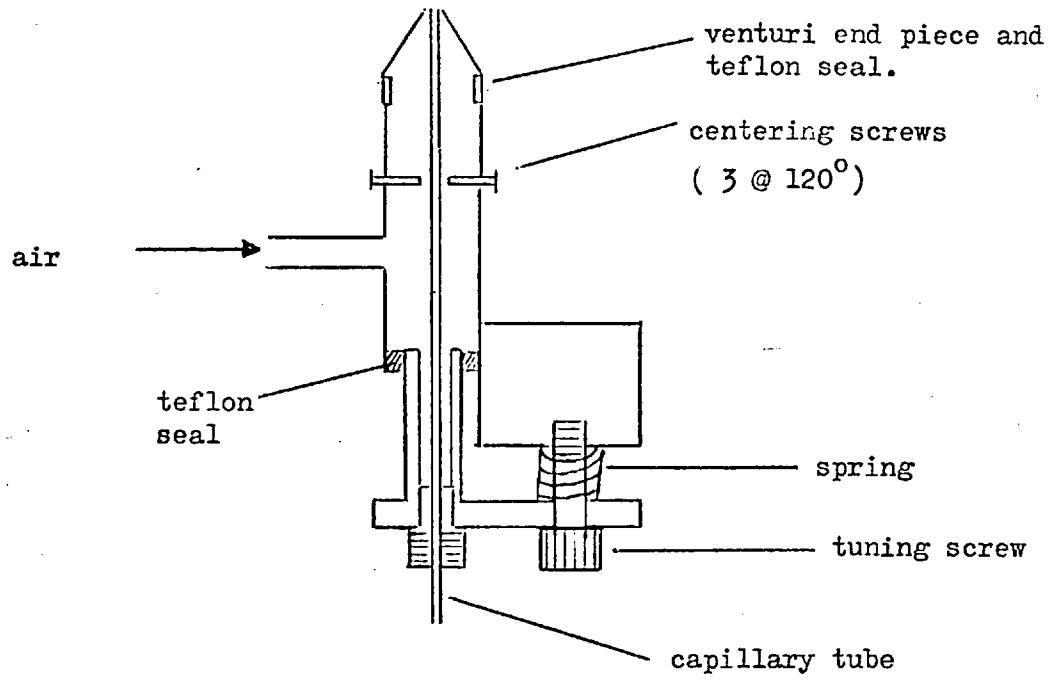


Figure 6.6. Brass nebuliser.

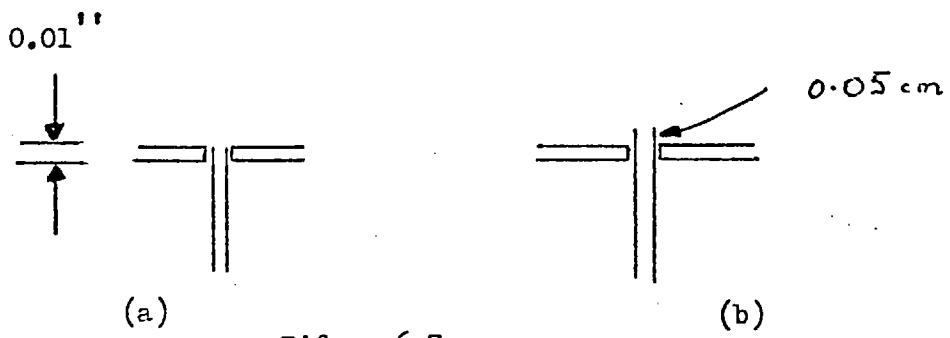


Figure 6.7

describe the type of flow encountered in nebuliser capillaries.

The nebuliser studied in this work was constructed to operate at low sample uptake rates and at low gas flow rates. Particular attention was paid to nebuliser tuning and venturi end-piece construction. Sample uptake rates were measured for various venturis and the nebulisers were finally tested in a simple flame photometer.

### Comparison of venturis

Fig. 6.7 shows two tuning positions initially employed in the stainless steel nebuliser. The length of capillary protruding from the venturi was measured using a travelling microscope. The two tuning positions were compared by measuring the sample uptake rates at various air pressures and flows. A graph (Fig. 6.8) of sample uptake rate ( $\text{ml.min}^{-1}$ ) against air flow rate ( $\text{l.min}^{-1}$ ) and gas pressure ( $\text{lb.in}^{-2}$ ) shows that the tuning position as in Fig. 6.7(b) is far superior. Graph (a) shows that sample uptake rates predicted from Table 6.1 compare reasonably well only at low sample flows. Below  $1.3 \text{ l.min}^{-1}$  the nebuliser ceased to operate because the pressure drop at the capillary venturi was insufficient to overcome the force of gravity, viscous resistance and other factors<sup>(122)</sup>. From the graphs 6.8 and 6.9 an approximately linear relationship between air flow/pressure was obtained for all three venturis, indicating that the Poiseuille equation was partially obeyed.

To study the effect of increasing the venturi length, one was constructed with a  $\frac{3}{8}$ " long orifice (Fig. 6.10). The nebuliser was easier to tune and produced a more even spray than the previous  $1/100$ " orifice. However, quite a large pressure was required to force the gas through the longer venturi. In an effort to retain all the advantages of a long orifice, but reduce

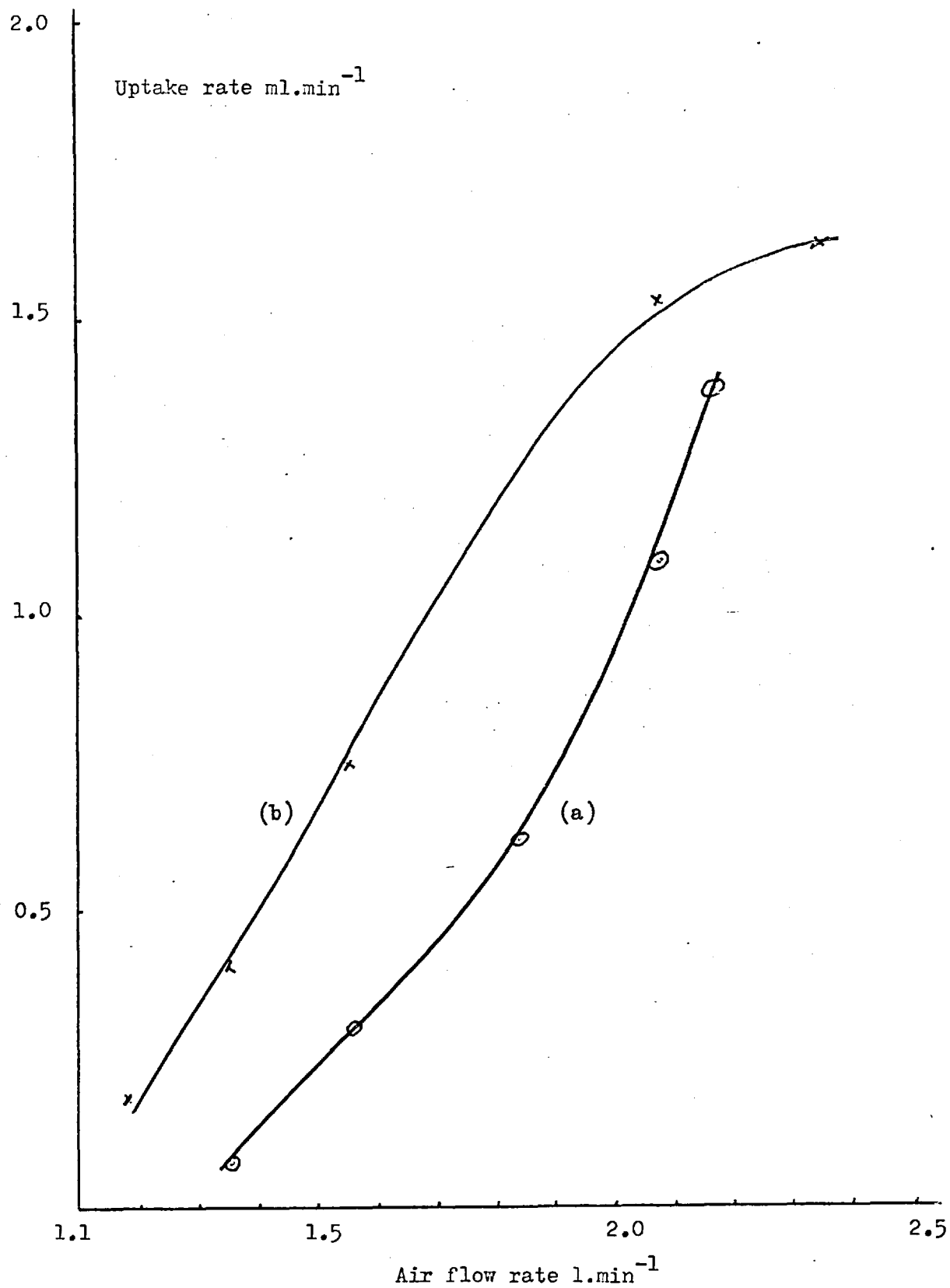


Figure 6.8.

Graph of air flow rate vs. solution uptake rate.

(a) capillary level in orifice

(b) capillary protruding 0.05 cm.

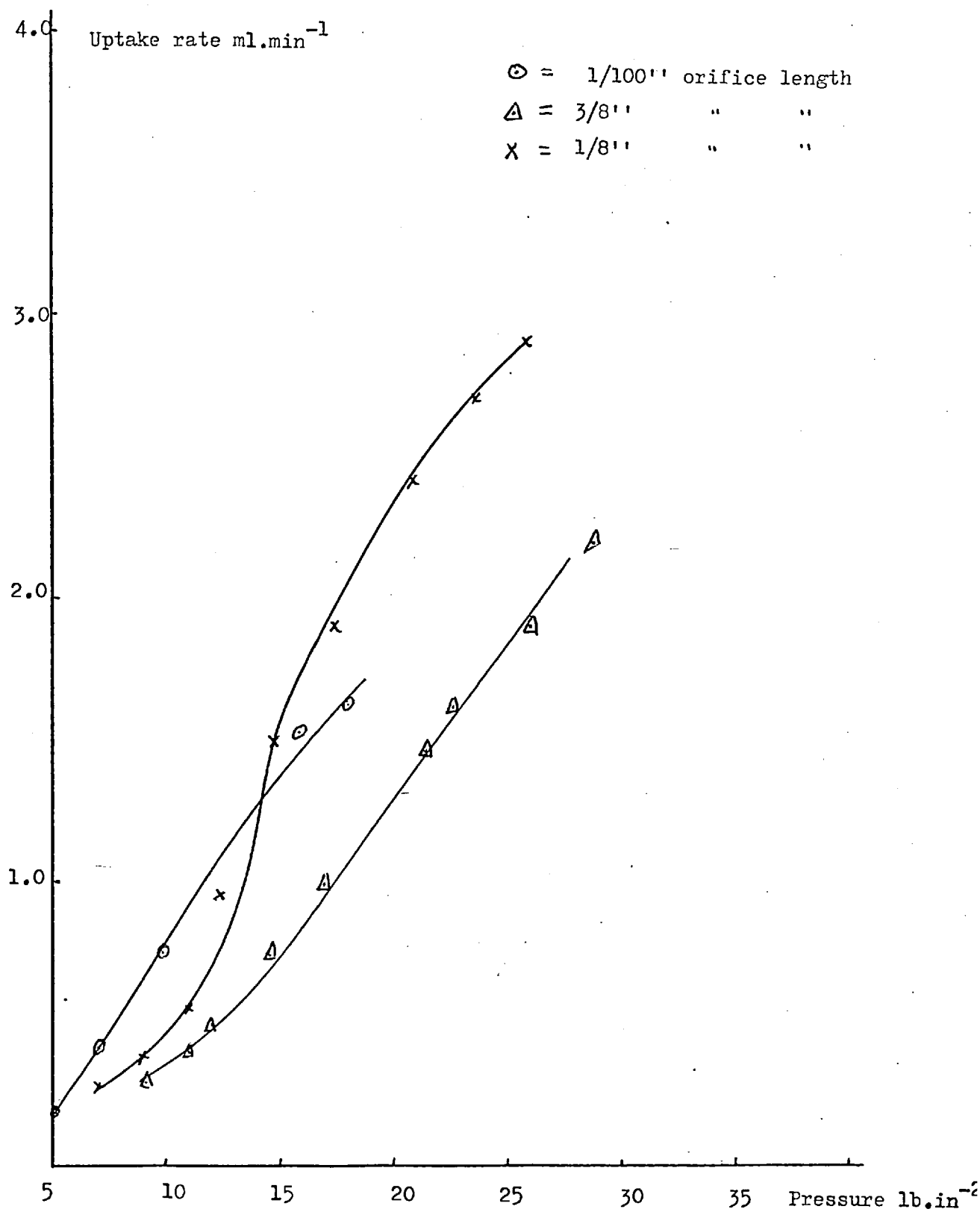


Figure 6.9. Graph of gas pressure vs. sample uptake rate for three venturis.

the operating pressure, one was constructed with a length of  $\frac{1}{8}$ ".

The pressure vs sample uptake graphs (Fig. 6.9) suggests that at low flows the  $\frac{1}{100}$ " orifice gives the best sample uptake rates. When the volume of gas flowing is taken into consideration the  $\frac{1}{8}$ " venturi has a greater sample/gas volume ratio as shown in Table 6.2. This venturi was therefore used for the nebuliser desolvator system described in Chapter 5.

TABLE 6.2 - Sample/gas volume ratios (air) for 3 types of venturi

| <u>Solution<br/>flow<br/>ml.min<sup>-1</sup></u> | <u>Air flow 1.min<sup>-1</sup><br/>corrected to<br/>Ats.</u> | <u>ml solution/<br/>litre air</u> |
|--------------------------------------------------|--------------------------------------------------------------|-----------------------------------|
| (i) <u><math>\frac{1}{8}</math>" orifice</u>     |                                                              |                                   |
| 0.290                                            | 1.77                                                         | 0.164                             |
| 0.380                                            | 2.00                                                         | 0.19                              |
| 0.547                                            | 2.41                                                         | 0.227                             |
| 0.97                                             | 2.74                                                         | 0.354                             |
| 1.496                                            | 3.23                                                         | 0.465                             |
| 1.985                                            | 3.84                                                         | 0.518                             |
| 2.43                                             | 4.60                                                         | 0.53                              |
| 2.74                                             | 5.16                                                         | 0.53                              |
| 2.91                                             | 5.98                                                         | 0.486                             |
| (ii) <u><math>\frac{3}{8}</math>" orifice</u>    |                                                              |                                   |
| 2.21                                             | 5.16                                                         | 0.428                             |
| 1.91                                             | 4.46                                                         | 0.428                             |
| 1.62                                             | 3.70                                                         | 0.437                             |
| 1.48                                             | 3.37                                                         | 0.440                             |
| 1.09                                             | 2.70                                                         | 0.405                             |
| 0.75                                             | 2.36                                                         | 0.318                             |
| 0.51                                             | 1.93                                                         | 0.264                             |
| 0.41                                             | 1.73                                                         | 0.237                             |
| 0.316                                            | 1.58                                                         | 0.200                             |
| (iii) <u><math>\frac{1}{100}</math>" orifice</u> |                                                              |                                   |
| 0.07                                             | 2.03                                                         | 0.0345                            |
| 0.31                                             | 2.68                                                         | 0.115                             |
| 0.63                                             | 3.81                                                         | 0.165                             |
| 1.18                                             | 5.53                                                         | 0.213                             |
| 1.39                                             | 6.31                                                         | 0.221                             |

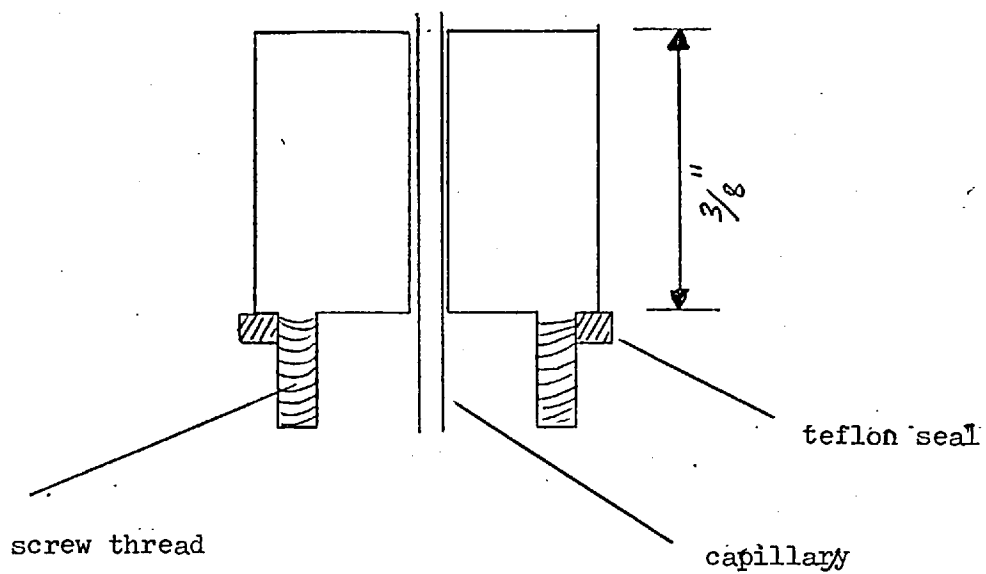
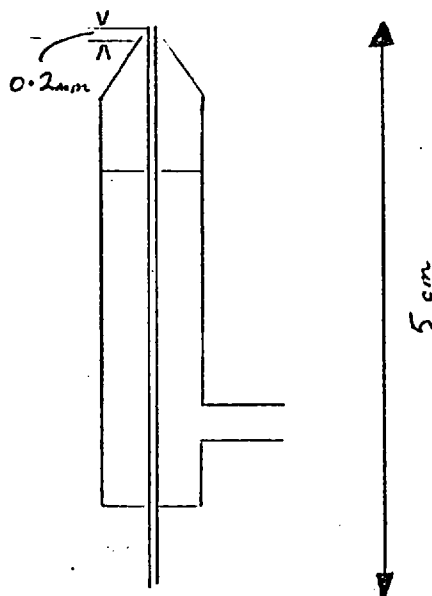


Figure 6.10.  $\frac{3}{8}$ " orifice venturi.



Capillary O.D. 0.304 mm  
I.D. 0.140 mm

venturi diameter = 0.35 mm  
venturi length =  $\frac{1}{100}$

Figure 6.11 High pressure nebuliser.

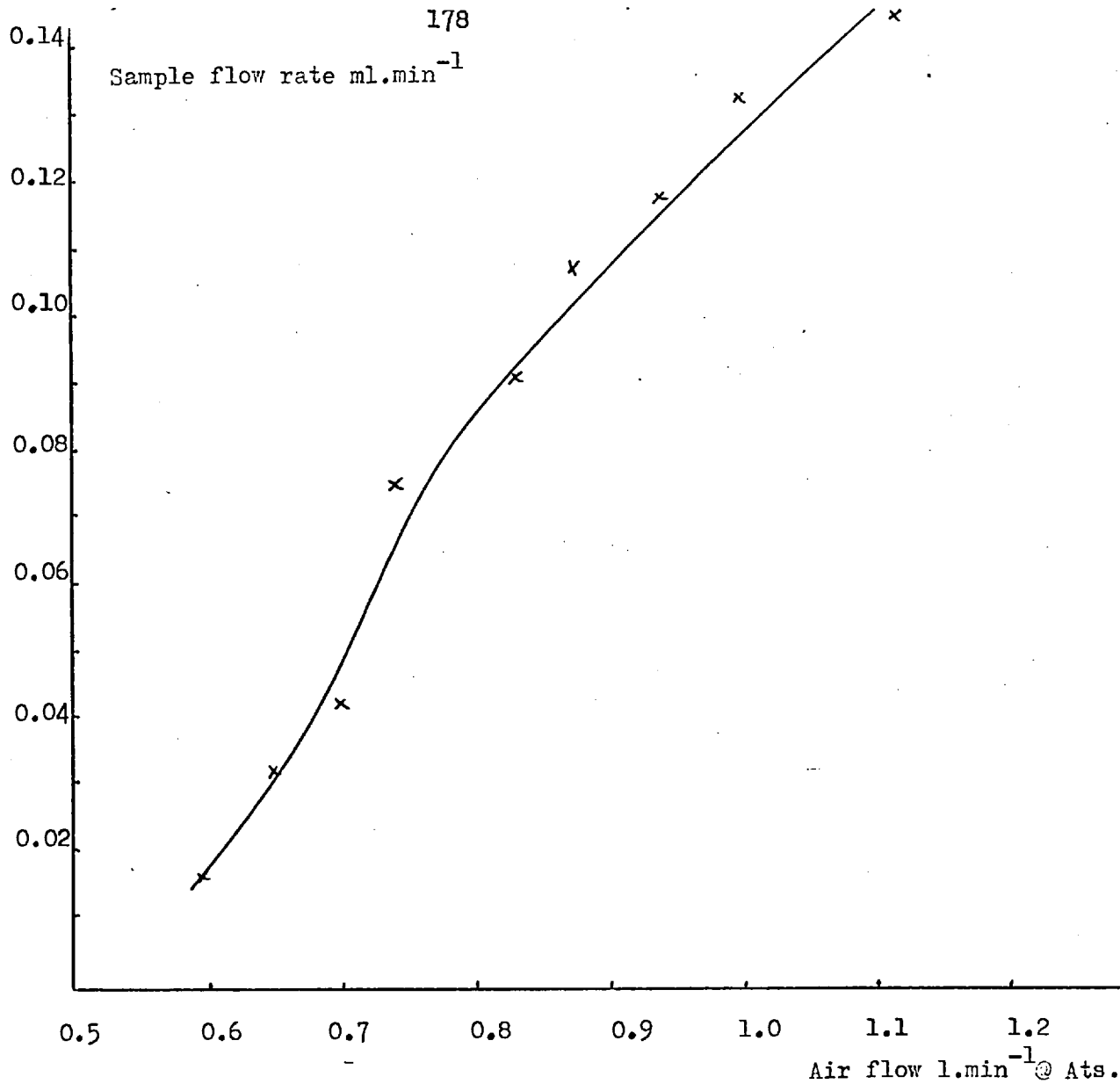


Figure 6.12 (a) Graph of sample uptake vs. air flow rate for the high pressure nebuliser.

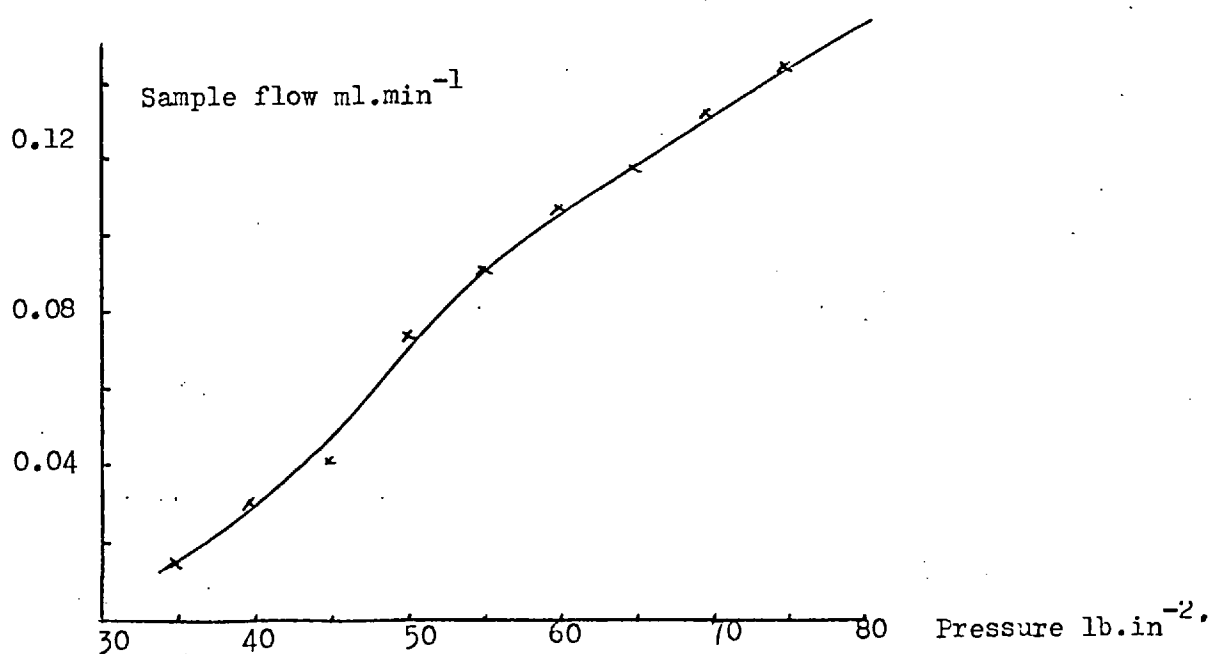


Figure 6.12 (b) Graph of sample uptake vs. air pressure

### High pressure nebuliser

In an attempt to eliminate the desolvation system for the CAP/microwave plasma (see Chapter 5) a high pressure low sample uptake nebuliser was constructed. The same type of body, centering disc and venturi as the previous nebuliser was used. The capillary and venturi dimensions are given in Fig. 6.11. The nebuliser was operated at pressures between 35 and 75 lb.in<sup>-2</sup> (0.6 to 1.12 l.min<sup>-1</sup> <sup>atmospheric pressure</sup> corrected to  $\wedge$ .) with sample uptake rates of 0.016 to 0.146 ml.min<sup>-1</sup> (see Fig. 6.12).

#### 6.3.4 Protection of stainless steel capillary tubes

Pt/Ru has been used for capillary tubes because of its resistance to acids. The tubing is expensive, therefore the possibility of coating stainless steel capillaries with 'teflon' was investigated. The coating was introduced as an aerosol and then dried at 360 C for two hours. The teflon did not adhere to the stainless steel surface. The tubes were then etched with hydrofluoric acid (50%), washed, dried, coated with 'teflon' and placed in the oven. The tubes were apparently coated but they were only partially resistant to 6M hydrochloric acid.

#### 6.3.5 Comparison of nebulisers, using a simple flame photometer

Fig. 6.13 shows a diagram of a simple flame photometer set-up used for comparing the nebulisers. The meker burner/expansion chamber was that of a Southern Analytical A1740 flame photometer, which was modified to accept the nebulisers. An auxillary air tube was introduced into the expansion chamber for use with the low flow rate and high pressure nebuliser. The monochromator (Hilger & Watts D292) was fitted with an RCA 1.P. 28 photomultiplier (PMT) powered by a Brandenburg EHT supply. The PMT output was fed across a Servo-scribe potentiometric recorder.

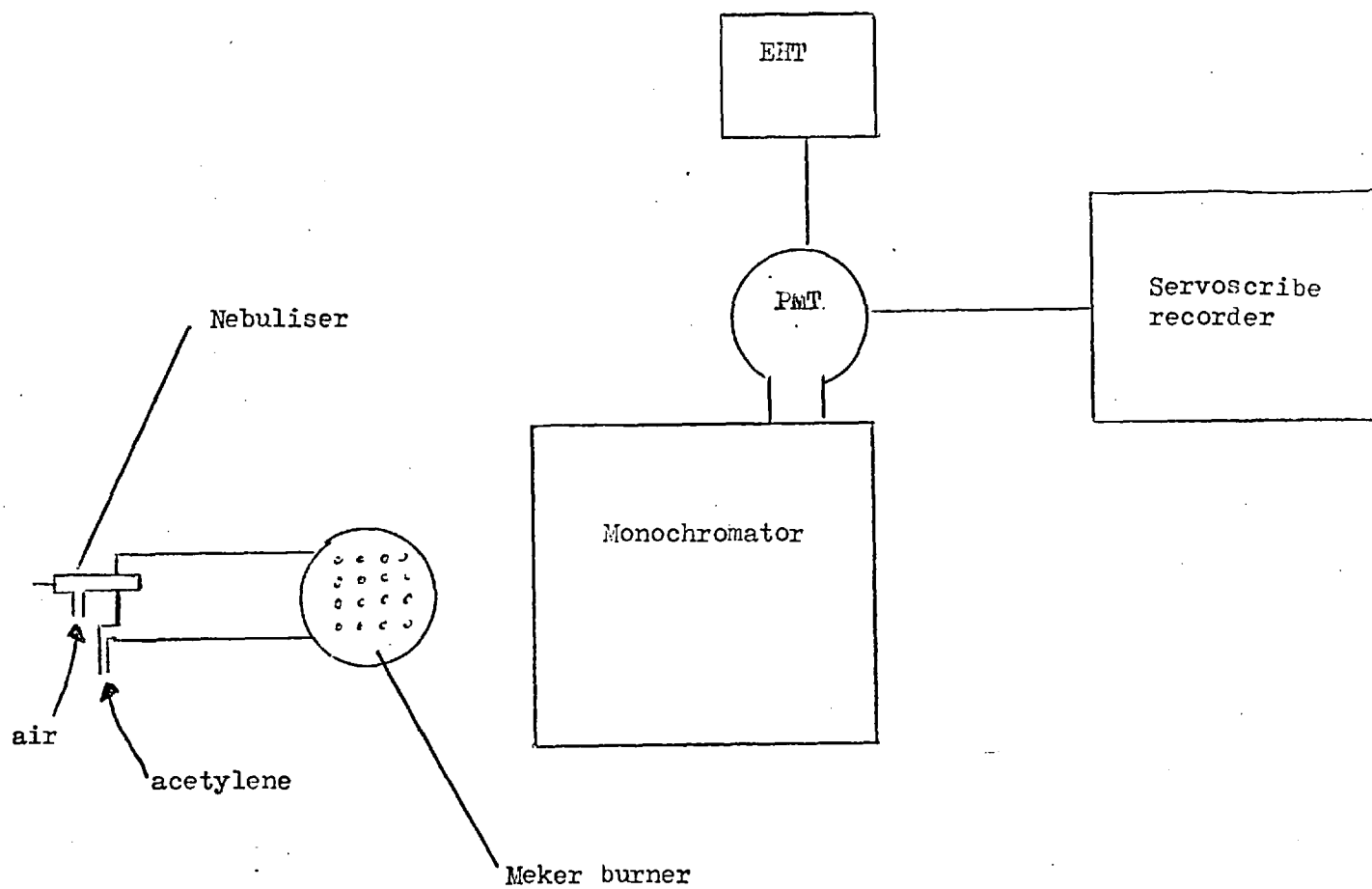


Figure 6.13 . Simple Flame Photometer.

The high pressure nebuliser was operated with air at  $100 \text{ lb.in}^{-2}$ , the brass and stainless nebuliser ( $\frac{1}{8}$ " orifice) operated at  $40 \text{ lb.in}^{-2}$ . Acetylene was fed to the burner at  $1.5 \text{ l.min}^{-1}$  and the auxillary air flow was adjusted to provide the same total air flow. Under these conditions the average solution uptake rates were  $2.84 \text{ ml.min}^{-1}$  for the brass nebuliser,  $2.24$  for the  $\frac{1}{8}$ " orifice nebuliser, and  $0.03 \text{ ml.min}^{-1}$  for the high pressure nebuliser.

Calcium (10 ppm) was sprayed into the flame using all three nebulisers. The best response (422 nm) was received from the  $\frac{1}{8}$ " orifice nebuliser (1.5 times the brass nebuliser) and a signal was not observed when the high pressure nebuliser was used. Measurable signals were only obtained with concentrations greater than 30 ppm. When an impact bead was placed in front of the brass nebuliser the calcium signal was increased approximately 1.3 times. However, the impacting bead had very little effect upon the signals from the other two nebulisers. A possible explanation may be that the brass nebuliser produces relatively large droplets which are subsequently broken up by impacting. This produces an aerosol with a greater proportion of small droplets and it is known<sup>(104)</sup> that only the small droplets eventually reach the flame.

### 6.3.6 Conclusions

Continuous sample introduction into flames and plasmas is easily accomplished by conventional pneumatic nebulisers. Even though ultrasonic nebulisers are extremely efficient at producing very fine aerosols they are still not widely used because they require large volumes of solution, constant head/pressure and pump devices.

Commercially manufactured nebulisers are designed to operate at high gas flows ( $8 \text{ l.min}^{-1}$  @  $30 \text{ lb.in}^{-2}$ ) with solution uptake rates of  $3\text{--}4 \text{ ml.min}^{-1}$ . High gas flow rates were shown to be unsuitable for the CAP. Initially a brass nebuliser was constructed, it had a solution uptake of  $0.4 \text{ ml.min}^{-1}$  at a gas flow of  $1.85 \text{ l.min}^{-1}$  @  $8 \text{ lb.in}^{-2}$ . It was suitable for nebulisation into the CAP but unsuitable for sampling into the CAP/microwave plasma. The gas flow was constricted by the microwave containment tube, therefore a nebuliser operating at lower gas flows was needed. A stainless steel nebuliser was constructed and experimentation with venturi design and tuning positions produced a nebuliser capable of producing a fine aerosol with a large solution/gas flow ratio. It was successfully used in a desolvator system for sampling into the CAP/microwave plasma.

In an attempt to eliminate the large desolvator a high pressure, low sample uptake nebuliser was constructed. It was used to inject solution directly (axial mode) into the argon stream of the CAP/microwave system. Both the microwave and the dc plasma were stable, showing that the nebuliser provided a suitable solution flow. However, poor emission signals were obtained from the CAP/microwave plasma, this was thought to be due to rejection of the aerosol by the plasma. It was concluded that for the best emission signals the analyte needed to be desolvated, i.e. an extremely fine aerosol was required to penetrate the dc plasma.

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