

MICROWAVE EXCITED ATOMIC SPECTRAL SOURCES

by

MICHAEL DAVID SILVESTER, B.Sc.

A Thesis submitted for the Degree of Doctor of
Philosophy in the University of London

November 1971

Chemistry Department
Imperial College of Science and Technology
London, S.W.7.

ABSTRACT

This Thesis describes:

(i) A preparative scheme for the production of microwave excited electrodeless discharge lamps for use as atomic spectral sources in atomic fluorescence spectrometry, which enables the fill gas pressure, the applied microwave power and the lamp mounting configuration to be predicted.

(ii) A comparison between various microwave cavities and antennas when used as microwave coupling devices.

(iii) The use of a microwave power attenuator to decrease EDL source noise.

(iv) The development of three new microwave excited atomic spectral sources, especially designed for elements that rapidly attack the quartz walls of EDLs.

(v) The development and optimisation of two new methods of modulating the resonance radiation emitted from microwave excited EDLs, and a comparison of these two methods with that previously used.

(vi) The theoretical derivation of an expression for the frequency of minimum noise for atomic fluorescence spectrometry, when using a constant relative bandwidth amplifier/phase sensitive detection measurement system.

(vii) The optimisation of the operating frequency and amplifier parameters for atomic fluorescence spectrometry, using modulated EDLs as sources and a tunable constant relative bandwidth amplifier/phase sensitive detection measurement system.

ACKNOWLEDGEMENTS

The majority of the work in this thesis was carried out in the Chemistry Department of Imperial College of Science and Technology, London, U.K. between October 1969 and October 1971. A small part of the work in Chapter II was carried out in the Chemistry Department of West Virginia University, West Virginia, U.S.A. under the guidance of Dr. W.J. McCarthy between June 1968 and October 1969. The work is entirely original except where due reference is made and no part of it has been submitted for any other degree.

The author takes this opportunity to acknowledge those persons who, in various ways, have contributed something of themselves not only to his thesis but also to his professional aptitude and welfare. The many who are not singled out by name are no less appreciated. This includes the numerous members of staff and friends (no sharp distinction implied) from who I have sought and received advice while conducting this research.

By name, I wish to express my gratitude to my supervisors, Professor T.S. West and Dr. R.M. Dagnall, for their advice and encouragement. I am also especially grateful to Mr. D. Alger for the patience he showed while explaining many electronic intricacies to me. Finally, I would like to thank the SRC for the award of a research studentship in support of this work.

CONTENTS

	<u>Page</u>
Abstract	1
Acknowledgements	2
Chapter I Introduction	4
Chapter II Electrodeless Discharge Lamps	19
Chapter III Atomic Spectral Sources for alkali and alkaline earth elements	88
Chapter IV Source Modulation	118
Chapter V Noise	149
Bibliography	167

CHAPTER I

INTRODUCTION

1.1. Uses and Requirements of Atomic Spectral Sources

The atomic spectroscopist has many uses for atomic spectral sources; they include: interferometry, wavelength calibration, spectral structure elucidation, optical pumping, atomic absorption spectrometry (AAS), and atomic fluorescence spectrometry (AFS). The analytical chemist's main interest in atomic spectral sources centres around the last two of these applications, AAS and AFS. Both AAS and AFS require an external source of radiation to excite the analyte atoms in the flame cell or atom reservoir. For a source of excitation to be analytically useful in atomic fluorescence measurements it must be extremely intense over the centre of the analyte atom's absorption line; that is to say, it must be intense and must exhibit as little self-reversal as possible (1). In addition, the source should be stable, cheap and adaptable to a variety of elements. The ideal source for AFS would actually have much in common with the ideal source required for optical pumping experiments, because both techniques involve the optical excitation of an atomic resonance level. Budick et al. (2) have summarized the ideal source requirements for optical pumping experiments as follows:

(1) The total optical output in the resonance line of interest should be in the range of $10^{15} - 10^{18}$ photons per second (1 milliwatt to 1 watt for ultraviolet lines). The lower output is suitable for fully allowed transitions, whereas the higher output is required for partially forbidden transitions.

(2) The spectral line must be free of self-reversal.

Only the radiation in the centre of the line is useful for producing fluorescence. Light in the wings of the line contributes to the scattering background and noise but not to the useful signal.

(3) The source should require a minimum of sample material.

(This is probably the least important requirement; nevertheless, this is a practical requirement if it is necessary to construct sources of rare elements or radioactive isotopes.)

(4) The lamp fluctuations must be minimal. Short term noise should be small, for example, less than one part in 10^5 , and long-term drifts should be minimal, for example, less than one part in 10^3 . (For AFS these fluctuations can fortunately be much larger because of high noise levels associated with the flame cell or atomic reservoir.)

(5) The source should be adaptable to a wide variety of elements.

Unfortunately, no single source type to date meets all of the above mentioned requirements. In AAS hollow cathode discharge lamps (HCL) are available for most elements in the periodic table. Because absorption measurements do not require sources of extreme intensity, the HCLs operating at low currents are quite adequate for most metals. AFS, nevertheless, has been fortunate in one respect, namely that there has been a concurrent search under way among physicists for better sources to use in optical pumping and related experiments (2-6). The

analytical spectroscopists interested in AFS, however, has slightly different goals in mind than the physical spectroscopist carrying out resonance radiation experiments. The analyst, first of all, is nearly always interested in being able to measure several elements within a short time period. Therefore, he is much more concerned with features such as cost, simplicity, interchangeability and duplicity than is the physicist. This is especially true if an instrument manufacturer is to place the technique into the hands of the average analyst or technician. Secondly, the demands of the analyst usually are not as severe with regard to stability, material requirements, self-reversal and spectral line widths.

As stated previously, the intensity of sources for AAS is not of prime concern because the sensitivity and the limit of detection are independent of the source intensity. A source is adequate for AAS provided it is capable of producing a sufficient signal from the photodetector, after its radiation has passed through a fairly high resolution monochromator. HCLs have been found to be suitable sources for the AAS of most elements. Thus, this thesis is mainly concerned with the development of atomic spectral sources for AFS; however, mention of their use in AAS will be made.

The intensity of the fluorescence signal at low atomic concentrations is directly proportional to the source radiation intensity (7,8) and hence the limit of detection and the sensitivity will be proportional to the intensity of the

primary excitation source. The quality of the atomic line emission is not so important for AFS as for AAS, because unlike in AAS the source is not viewed directly. However, it is still desirable for the atomic spectral lines not to be self-reversed and for them to be as narrow as possible, so that the maximum irradiating power is available at the wavelength of maximum absorption.

The absorption of radiation by atoms occurs over a very narrow frequency interval called the atomic absorption line (9, 10, 11). The absorption line profile and half-width are determined by broadening parameters. The absorption of radiation results in the electronic activation of an atom from the ground (sometimes from metastable states above the ground state) electronic state to an upper excited state. The excited atom remains in the upper level for a short time period, for example 10^{-8} seconds, and then undergoes either a non-radiational deactivation, for example by a collision with flame gas molecules, or a radiational deactivation (atomic fluorescence). The intensity of radiation transmitted through an atomic vapour of absorbers (I_ν) varies with the frequency and is related to the incident intensity, I_ν^0 , at the same frequency, ν , and to the product of the atomic absorption path length, L , in centimeters and the atomic absorption coefficient, k_ν , in cm^{-1} . The expression relating I_ν to the above factors is given by:

$$I_\nu = I_\nu^0 \exp (-k_\nu L) \quad (1)$$

The broadening of spectral lines results in the absorption

(and emission) of radiation by atoms over a finite frequency interval rather than an infinitely narrow frequency interval. The half-width, $\Delta \nu$, of an atomic absorption line is defined as the half-width of the plot of k_ν versus ν . Therefore, it is the width of the absorption line profile at $k_{\max}/2$, where $k_{\max}$ is the maximum atomic absorption coefficient. The major causes of spectral line broadening of atoms in flame, or for that matter in atomic spectral sources, are:

(1) Natural broadening.

The natural broadening of spectral lines is associated, from a quantum electrodynamic viewpoint, with the degree to which energy levels are broadened. This broadening of the energy levels occurs as a result of the finite lifetime, τ , of the levels between which a transition takes place. The natural width of a resonance line, $\Delta \nu_N$, can be defined as:

$$\Delta \nu_N = 1/2\pi\tau \quad (2)$$

and is of the order of $10^{-4}\text{\AA}$.

(2) Doppler broadening

Doppler broadening is associated with the random thermal motion of the emitting or absorbing atoms relative to the observer. As a result of the motion of an atom at a velocity in the line of sight, the observed frequency of absorption or emission by the atom is displaced. The Doppler half-width, $\Delta \nu_D$, of a spectral line is equal to:

$$\Delta \nu_D = 2 \frac{\nu_0}{c} \sqrt{2 \ln 2 \cdot \frac{RT}{M}} \quad (3)$$

where T is the temperature in degrees Kelvin, M is the atomic weight of the emitting or absorbing species, ν_0 is the frequency of maximum absorption or emission, R is the gas

constant, and C is the velocity of light in a vacuum. For temperatures between 500 and 3000°K, the Doppler half-width for most lines (12) of most elements is of the order of 0.003 to 0.09 Å.

(3) Lorentz broadening

Lorentz broadening is due to the perturbation of the absorbing or emitting atoms by foreign gas molecules. The Lorentz half-width of a spectral line, $\Delta \nu_L$, is equal to:

$$\nu_L = 2 \times 6.02 \times 10^{23} \sigma^2 P \sqrt{\frac{2}{\pi RT} \left(\frac{1}{M} + \frac{1}{M_F} \right)} \quad (4)$$

where P is the pressure of the foreign gas whose molecular weight is M_F and σ^2 is the effective cross-section for collision between the emitting or absorbing atom and the foreign gas molecules. For most resonance lines of most atoms, the Lorentz half-widths are between 0.01 and 0.1 Å (12) for analytical flames at one atmosphere pressure.

(4) Resonance broadening

Resonance broadening is similar to Lorentz broadening except that the perturbation is produced by the same atomic species as is emitting or absorbing. The equation for the Resonance half-width, $\Delta \nu_R$, is exactly the same as the equation for the Lorentz half-width except that M_F is replaced by M , which gives:

$$\Delta \nu_R = 2 \times 6.02 \times 10^{23} \sigma^2 P \sqrt{\frac{4}{\pi RM}} \quad (5)$$

Resonance broadening is negligible in flames because of the low concentration of the analyte; however, in atomic spectral

sources the resonance broadening can be quite large, especially in sources like the high pressure mercury arc where the mercury pressure can be as high as 100 atmospheres.

(5) Stark and Zeeman broadening

Stark and Zeeman broadening are due to the splitting of atomic lines by electrical and magnetic fields respectively. In flames both of these broadening processes are negligible; however, Aldous (63) has stated that they can become important in electrically or magnetically excited atomic spectral sources, such as HCL and electrodeless discharge lamps (EDLs). Recently Bruce and Hannaford (156) have measured the broadening processes in a HCL and have found Stark and Zeeman broadening to be negligible.

Neglecting Stark and Zeeman broadening, the total half-width, $\Delta\nu$, of the absorption or emission profile is related to the half-widths caused by the broadening process by the following equation:

$$\Delta\nu = \sqrt{\Delta\nu_D^2 + (\Delta\nu_L + \Delta\nu_R + \Delta\nu_N)^2} \quad (6)$$

This total half-width, $\Delta\nu$, is the half-width of the absorption or emission line profile and thus governs the amount of light that is absorbed by an atomic vapour of absorbers (see equation 1). As both AAS and AFS rely on an absorption process, the sensitivity and limit of detection of these two methods will depend on the source emission line profile and the analyte absorption profile. Thus a knowledge of the effects of these line profiles, or half-widths, on the sensitivity of AAS and AFS is important. In

general the narrower the line profiles the more sensitive will be these two methods. The full implications of the effects of line profiles on AAS and AFS have been very fully derived and discussed elsewhere (7-9, 13-15), and the author feels that no useful purpose will be served by further repetition.

1.2 Sources

Several sources types have been utilized as primary sources in analytical atomic spectroscopy; a brief description of them and their operation follows:

(1) Metal-Vapour Arc Lamps.

The Osram and Phillips metal-vapour arc lamps were the first source type to be utilized in atomic fluorescence flame spectrometry (16), and they have been used by several workers since (17-22). These are similar to the original Pirani and Houtermans lamps which are described by Mitchell and Zermansky (9). They consist of a sealed tube containing the metal and an inert gas at a low pressure (usually 1-10 torr); there is an oxide-coated filament at each end of this tube. The tube is surrounded by an evacuated jacket so that a sufficiently high vapour pressure of the metal is maintained. The lamp is started by sending a current of a few amperes through both the filaments until they are red hot; at this time the filament current is terminated and an alternating voltage is applied across the two filaments, producing an arc which keeps the filaments hot and the metal partially vapourized.

Commercial metal-vapour arc lamps have been used extensively for the production of AF of zinc, cadmium and thallium. Although these sources are available for other metals, only these three are analytically useful. All of these lamps, especially those of mercury and the alkali metals, suffer from self-reversal and resonance broadening (16, 17, 18). The indium and gallium lamps emit extremely weak radiation and are therefore essentially unusable (18).

In operation, the lamps must be carefully thermostated in order to preserve stability and to minimise self-reversal. Mansfield et al. (18) did this by optimising and monitoring the operating current. Dagnall et al. (19) effected the same thing by directing a controlled air stream upon the lamp.

Recently, Budick et al. (2) have re-examined the Cario-Löchte-Holtgreven lamp (9), which is another variety of metal-vapour arc lamp, for use in optical pumping experiments. This lamp operates with a continuous flow of gas which carries the metal discharge and directs it away from the viewing window. While this type of lamp is very efficient for exciting resonance radiation of the more volatile metals, it requires an extensive installation for operation and is thus inconvenient for analytical use.

(2) Hollow Cathode Discharge Lamps (HCLs).

The present HCLs are second generation developments of the Paschen lamp (23) and the Schüller tube (24, 25). These earlier models are described in detail by Mitchell and Zermansky (9)

and Tolansky (26). Most of the HCLs used today are modifications of the design by Walsh and co-workers (27, 28), although variations of the Schüller tube are still in use (2).

In the HCL, a hollow cylinder is used to make up the cathode. This cylinder is usually machined out of the metal whose spectrum is desired; or, in some cases, the cylinder is made from aluminium or another metal, and the desired metal is placed or plated inside this cylinder. Positive ions of the inert gas filler (usually neon or argon) bombard the cathode and sputter excited metal atoms from its surface. If the lamp is constructed with the proper geometry and inert gas pressure, the discharge is confined to the inside of the hollow cathode. Hollow cathode lamps have been constructed for virtually every metal and are available commercially. They are used almost exclusively in AAS (29) because of the narrowness of the spectral lines that they emit.

Dinnin (37), Dinnin and Heltz (30, 38), and Rossi and Omenetti (39) have used demountable HCLs in their atomic fluorescence investigations. While these lamps are somewhat elaborate in construction detail, they have the desirable feature that the cathodic material is interchangeable. Thus, one lamp lends itself to several elements. Using the demountable HCL, reasonably low limits of detection have been obtained for the atomic fluorescence of gold, silver, nickel, bismuth, lead, copper, magnesium, thallium, gallium, indium, manganese, cobalt, iron, palladium, titanium, zirconium,

chromium and aluminium. From this sampling of elements, one must conclude that this source type certainly offers the universality that is desired in AF applications.

Unfortunately, HCLs fall short of being the ideal source in one respect, namely intensity. They are generally operated at low currents, about 10 milliamps; under such conditions they are stable and long-lived, but lack the intensities necessary for atomic fluorescence applications (31). At higher currents, very little useful line intensity is gained, since metal is sputtered from the cathode at too fast a rate. This high sputter rate produces self-reversal, resonance broadening and instability of the resonance lines as well as window blackening and cathodic deterioration.

Sullivan and Walsh (32) have overcome some of the drawbacks of higher intensity operation of HCLs with their high intensity HCL. These are similar to the conventional HCL, except that an auxiliary pair of electrodes are mounted in front of the hollow cathode. The atomic vapour sputtered from the primary cathode is further excited in the positive column of the auxiliary electrode discharge. An additional power supply is required for the added electrodes, making lamp operation less straightforward and more expensive.

The recently developed shielded HCL (33, 34) now manufactured by Westinghouse and Perkin-Elmer gives a similar intensity to the high intensity HCL (35) while not requiring a secondary power supply.

Another modification of HCLs, which gave increased intensity without appreciable broadening, was described by Van Gelder (36). This novel design is similar to the high intensity HCL but has the added advantage of being capable of optical modulation (see Chapter IV).

For a review of the use of HCLs as primary excitation sources in AFS see Chapter III, section 3.5.

(3) Continua

In his original paper on AAS (40) Walsh expressed doubt in the use of spectral continua as sources in AAS; however, recent work has been published where a Xenon arc (41, 42), a 650 watt tungsten lamp (42), and a hydrogen arc (41) have been used as continuous sources for AAS in conjunction with high resolution monochromators.

Because of the theoretical superiority of the continuum as a source for AFS, several workers have evaluated its performance (43, 44, 45), although none of them have nearly reached the theoretically predicted limits of detection. Interference studies in AFS using a continuum source (a 500 watt Xenon arc) have been reported (46, 47) and limits of detection for thirteen elements have been given (46). The possibility of increasing the light output of xenon arcs by using a 2 kilowatt d.c. lamp or a lamp pulsed to 11 kilowatts (48) may improve the sensitivity of AFS.

A xenon arc is one of the brightest and most powerful continuous sources of ultra-violet radiation. The emission

from such a source is approximately continuous because of the resonance and Doppler broadening of the spectral lines. The lamp consists of a low voltage high current arc struck between two electrodes in a high pressure atmosphere of xenon.

(4) Miscellaneous Primary Sources

Strasheim (49) has demonstrated the feasibility of using an electrical discharge as a source for AAS. He used a time resolved system in which the detector only sees the emission from the discharge when the spark ceases. He obtained good sensitivity probably because of the reasonably narrow line profile. In a recent paper (50) Strasheim and Human reported the determination of copper, calcium, magnesium, and zinc using this method. The precision of this method was found to be very poor, which was especially unfortunate because of the convenience of this source for simultaneous multielement analysis. This source also suffers from a lack of intensity and is therefore unlikely to be suitable for AFS.

A gas stabilised d.c. arc (51) has been used as a primary source for AAS. Nitrogen gas was used to nebulise a solution containing the elements of interest; this gas was then used to stabilise the d.c. arc, which excited the resonance lines of the nebulised elements. This device offered the same convenience as the time resolved spark for multielement analysis and the precision obtained was as good as with a HCL as a primary source.

A high frequency plasma has been used as a primary source

of radiation in AAS (52) and in AFS (53). When solutions containing the elements of interest were sprayed into the plasma intense resonance line emission was produced; their line profiles were fairly narrow (half-widths of about $0.05\text{\AA}$).

Rann (54) has investigated the use of a flame, into which a solution containing the element or elements of interest was sprayed, as the radiation source for AAS. From both a theoretical and an experimental treatment he concluded that the sensitivity was reduced by a factor of two if a flame replaced the HCL source. Because of the low intensity of this source it is unlikely that it would be suitable for AFS.

(5) Electrodeless Discharge Lamps (EDLs)

The most effective and intense source presently available for AFS is the electrodeless discharge lamp. From the standpoint of simplicity and cost EDLs would appear to be the ideal source. They consist of a sealed-off reservoir of glass or most usually quartz containing a few torr of an inert gas and a small amount of the metal or metal salt whose spectrum is desired. EDLs are operated at RF or microwave frequencies by suitable antennas or wave-guide cavities. The absence of any internal electrodes leads to long lifetimes as no electrode burn-away occurs and there are no quartz to metal seals which are very prone to gas leaks. The real potential of EDLs as primary sources in AFS and AAS was realised by Dagnall et al. (55-60) and Winefordner and co-workers (61, 62); they have described the preparation of EDLs for several elements.

Aldous (63) has further extended this work to enable EDLs to be made for over sixty elements. However, EDLs have come in for much criticism (64-66) concerning their stability and lifetimes. Most of the studies on the preparation and operation of EDLs have been lacking in depth of investigation.

The author feels that with much more "in depth" study EDLs will prove to be the ideal source for AFS and very suitable sources for the AAS of certain elements for which only unsatisfactory HCLs are available. The bulk of the investigation work carried out in this thesis concerns the optimisation of EDLs and other electrodeless microwave excited discharges as sources for AFS.

CHAPTER II

ELECTRODELESS DISCHARGE LAMPS (EDLs)

2.1 Introduction

EDLs have been used very extensively as sources in atomic fluorescence spectrometry (21, 55, 60-62, 93-94) because of the sharp, intense spectral lines that they emit. From the standpoint of cost and simplicity they are very attractive because they only consist of a sealed-off reservoir of glass or quartz containing a few torr of an inert gas and a small amount of the metal (or metal halide) whose spectrum is desired. These lamps are operated at radio or microwave frequencies in conjunction with antennas, loading coils or wave-guide cavities as coupling devices. The absence of electrodes leads to a long lifetime of an EDL and an emitted spectrum which is uncontaminated by the spectrum of the electrode material.

2.2 Historical Development

Radio frequency and microwave excited EDLs have been used for a long time, dating back to Jackson (67), who used an EDL operated from a 10 MHz oscillator to obtain the arc spectrum of caesium in order to study its hyperfine structure. EDLs have been used since then in numerous spectroscopic applications, although most of the earlier applications did not require either intensity or stability. (The early applications were mainly studies of spectral structure utilising photographic plate detectors where the only really important criteria for the sources were sharpness of the spectral lines and purity of spectra). A renewed interest in EDLs was kindled in the

late nineteen forties when Meggers (68-70) carried out his wavelength studies of artificial mercury 198 in search of an ultimate standard of length. This work inspired further development of these sources for other spectral studies, especially spectral analysis of the lanthanide and actinide elements and their isotopes (71-77). By the early nineteen sixties, EDLs had been constructed for nearly every chemical element, and microwave cavities for the operation of these lamps had undergone considerable development (78,79).

In recent years, experimentation with optical pumping, sensitised fluorescence, and other related phenomena has created even more interest in EDLs (2-6, 80,81); researchers in these areas have been striving to obtain high intensity and stability from these sources without sacrificing the line sharpness or the spectral purity already characteristic of EDLs.

EDLs have been used for the excitation of atomic resonance fluorescence of the alkali metals (6, 82). A raman source, consisting of microwave (2450 MHz) excited sodium and mercury EDLs, has been described by Ham and Walsh (83). Microwave excited EDLs, filled with argon, hydrogen, krypton and xenon, have been used as continuous sources of radiation in the vacuum ultraviolet (84-89). Vaughan (90) was able to increase the sharpness (i.e. decrease the half-width) of the spectrum emitted by a helium EDL by cooling it in liquid helium.

Until recently there has been little work on the production

of EDLs solely for use as sources in atomic absorption and atomic fluorescence spectrometry, for which intensity and stability are of paramount importance. Ivanov et al. (91) have reported the use of high frequency excitation of EDLs as sources in atomic absorption, and Goodfellow (21) has carried out some interference studies for atomic fluorescence using microwave excited EDLs. An unsealed microwave excited continuous flow EDL system has been proposed as a spectrometric source by Richards (22). Winefordner and co-workers (16, 18) have carried out some atomic fluorescence studies using commercially available microwave excited EDLs (Opthos Instrument Co., Rockville, Maryland, U.S.A.) with rather poor results, probably because these lamps were designed for interferometry and wavelength calibration where high intensity and stability are not the prime concern. Since 1966 Winefordner and co-workers (61, 62, 92) and West and co-workers (55, 60, 93-96) have examined the effects of various parameters on the operation and use of EDLs as sources for atomic fluorescence flame spectrometry.

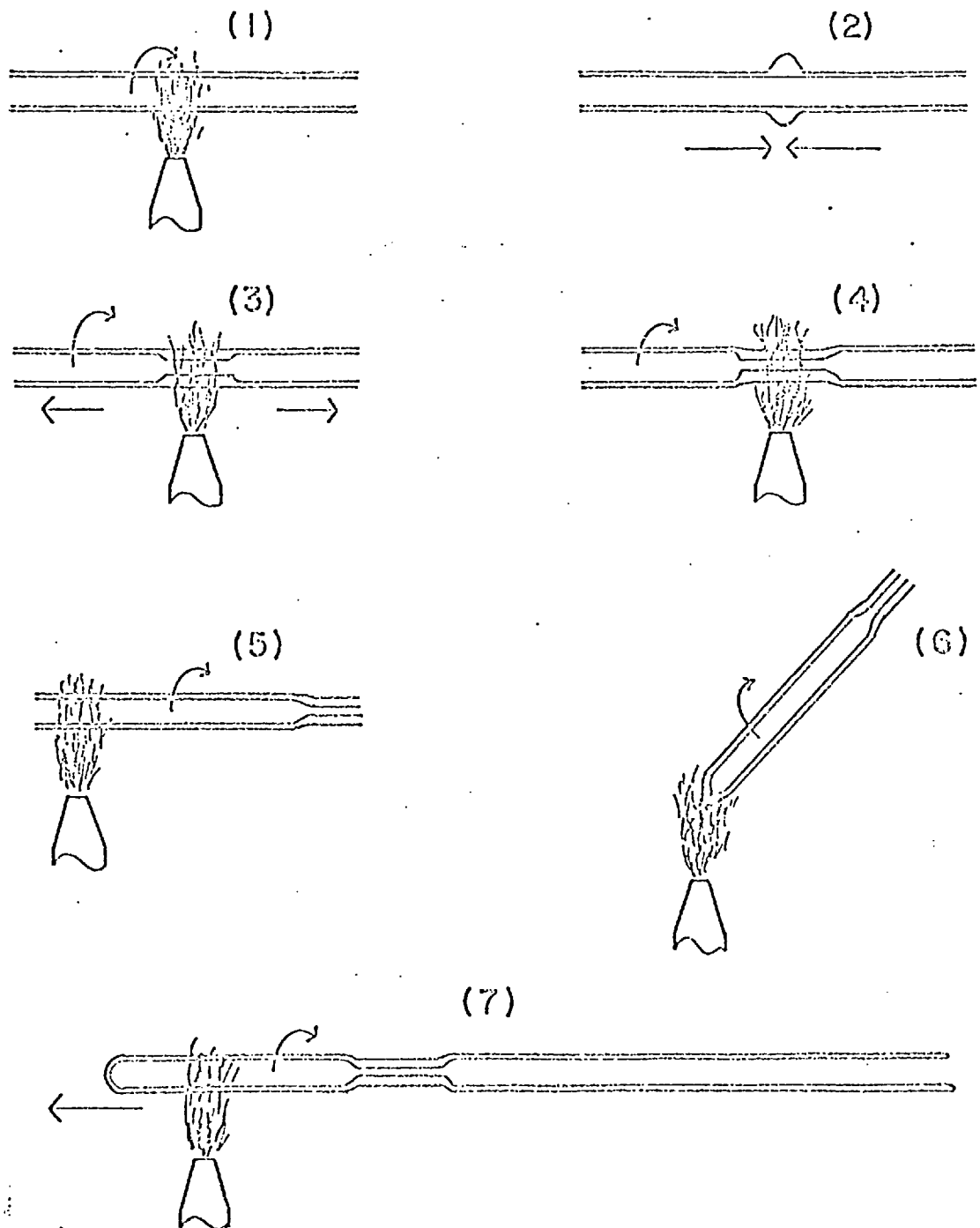
The author has investigated several of these parameters (prepreparation of the quartz EDL blank, nature of fill gas, pressure of fill gas, size of quartz EDLs, nature and weight of material introduced into the lamp, applied microwave power and choice of microwave coupling device) more systematically and to a much greater depth than previous workers (55, 61, 62, 92-96).

2.3 Preparation of EDLs

(a) Lamp construction

The lamps were made from transparent quartz tubing, of several different internal diameters, with wall thicknesses of 1 m.m. (Thermal American Fused Quartz Co., U.S.A., and Jencons Limited, England). The lamp blanks were easily made with only the use of an oxygen/coal gas torch and a minimum of glass blower's tools. Because it is easier to clean the open-ended quartz tubing than the finished lamp blank, it is recommended that the appropriate lengths of tubing be cleaned prior to lamp fabrication and that clean handling procedures be used from that point. The importance of using clean quartz tubing for lamp manufacture cannot be over-emphasised (69). The best cleaning procedure has been found to be treatment with hot chromic acid, 20% hydrochloric acid, followed by a thorough washing with distilled-deionised water (92).

Figure 1 shows the steps in construction of a lamp blank. A short section was softened, by rotating the quartz tube in the flame (step 1), and was forced into a bulge (step 2). This bulged section was then softened and drawn out slowly so that a thickened constriction was produced (steps 3 and 4). This thickened constriction facilitated the rapid and easy sealing of the lamp, which avoided reaction of the fill material with the quartz that can occur if the whole of the lamp bulb is heated to red heat (as sometimes occurs when the sealing is difficult and prolonged). The quartz tubing was then cut



EDL Construction Process

Figure 1

with the torch, at the required position (step 5), and the closed end rotated in the flame and blown out to a smooth test tube end (step 6). This step is important to avoid partial trapping of the EDL fill material, which can occur if a pointed end is left on the EDL. Finally, the entire bulb was rotated rapidly while being passed through the flame (step 7). This last step insured that most of the minute cracks and seams in the lamp walls were closed and that any cristobalite (a devitrified form of silica) formed during the lamp construction was driven out of the bulb.

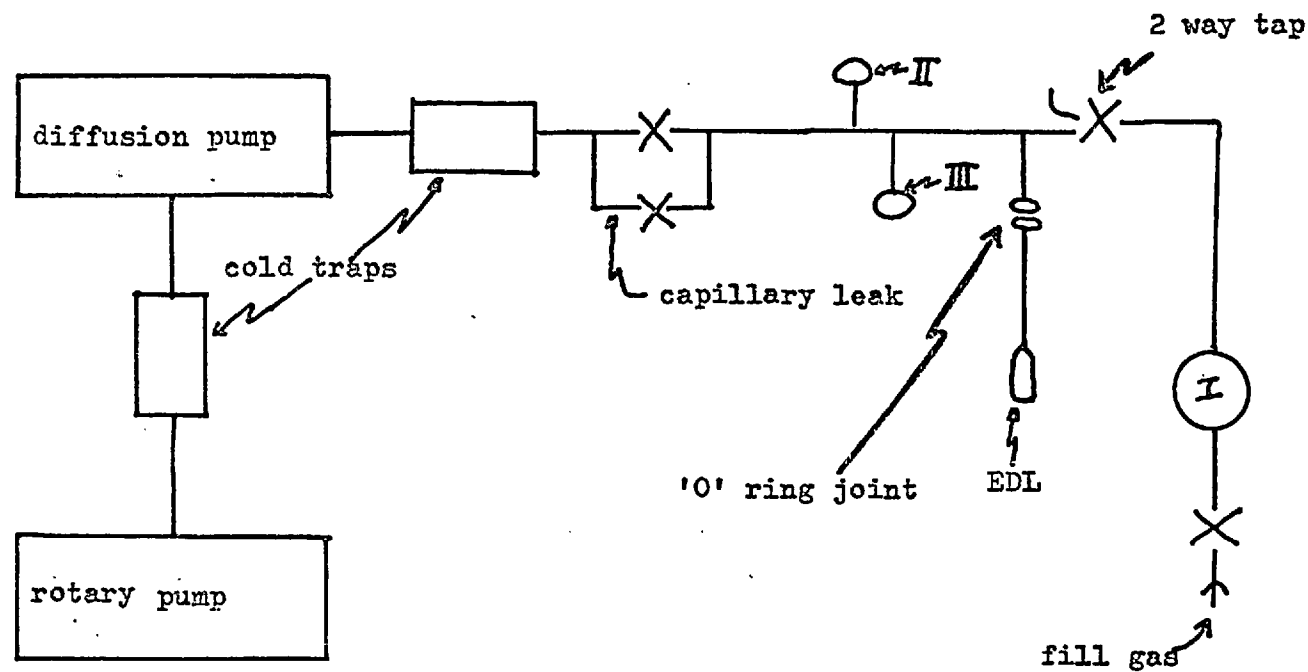
(b) The vacuum system.

The vacuum system used, in this study, for lamp preparation was capable of producing a minimum pressure of 5×10^{-6} torr, and is shown schematically in Figure 2.

(c) Production of finished lamp.

Although there were minor variations in the procedure used for making various lamps, the basic procedure was the same, and consisted of the following:-

The vacuum line was set in operation, both cold traps were filled with liquid nitrogen and the system was pumped down to about 10^{-5} torr. The EDL blank was connected via medium pressure tubing to an 'O' ring socket, which was then attached to the 'O' ring outlet on the vacuum system. The whole system was then pumped down to 10^{-5} torr, the fill gas was introduced into the system from its reservoir, and then re-evacuated to the same pressure. The EDL was baked out at



- I fill gas reservoir
- II thermistor pressure gauge
- III ionisation pressure gauge

Figure 2

Schematic diagram of the vacuum system
used in EDL preparation.

a temperature just below its softening point for about 2½ minutes, using an oxygen/propane hand torch. The EDL was allowed to cool under vacuum and then removed from the vacuum system. A few milligrams of the required substance were introduced into the bulb and the EDL was reconnected to the vacuum system.

Cooke et al. (97) have found that the amount of substance used in an EDL is important for fairly volatile compounds, when operated in a $\frac{\lambda}{4}$ Broida type microwave cavity. However, when using an 'A' type antenna Mansfield (92) found that the optimum amount of substance is not critical if the charge is smaller than 5 milligrams. The author's results tend to suggest that the optimum weight of substance is between 1.0 and 2.0 milligrams, when using an 'A' type antenna. Too small a charge weight (less than 0.1 milligrams) led to a short EDL lifetime, because of the clean up of the material on the quartz walls. Too large a charge weight (more than 5 milligrams) caused instability and plating out of the material on the quartz walls during operation of the lamp.

The lamp was then evacuated to 10^{-5} torr, flushed twice with the fill gas and then re-evacuated to 10^{-5} torr. The substance was then sublimed up the lamp blank, about 1 centimetre, to drive off any moisture and occluded gases, with mild heat from a micro-burner. After three flushings with fill gas the pressure in the system was adjusted to the required pressure and the constriction was sealed, as quickly as possible, with an oxygen/propane torch.

2.4 Lamp Operation

Radio and microwave frequency electromagnetic fields are very efficient for accelerating electrons and thereby maintaining a gaseous glow discharge, even in the absence of internal electrode contact with the plasma. It is difficult to define these discharges by equivalent electrical circuitry (4); consequently the experimental approach in optimising these discharges has been largely empirical. A concise review of instrumentation applicable to electrodeless discharges has been presented by Hollahan (100). The electrodeless discharge lamp containing metal vapours has been used by many spectroscopists because it offers a means of obtaining, when operated correctly, a stable, intense source of spectral lines, largely free of self-reversal, which often plagues arc discharges. This is due to the ability of such a discharge to achieve a skin effect, which confines the majority of the discharge to the surface layers of the plasma, or at least to obtain an emitting source of radiation which is largely thermally uniform. The electrodeless discharge has been called a cold plasma due to its non-isothermal nature (100), which means that the kinetic temperature of atoms and molecules, both ionic and neutral, is much less than the temperature of the electrons. The electronic temperature in a radio frequency electrodeless discharge may be of the order of 10,000 degrees Kelvin, while the atoms and molecules will have gas temperatures of the order of 400 degrees Kelvin.

Sealed EDLs have been successfully operated over a wide

range of radio and microwave frequencies, usually between 10 and 3,000 MHz, using a variety of power supplies and energy coupling arrangements. Because there are many interdependent parameters involved in lamp fabrication and operation, this is a very difficult topic to assess.

Several radio frequency oscillator circuits for electrodeless lamp operation have been described in the literature (2-6). These are all similar in that they have been operated between 10 and 100 MHz, and have all been inductively coupled to the EDL by directly mounting the EDL in the tank coil of the oscillator. Some of these circuits (3, 4, 6) have used heaters to boost the metal vapour pressures. However, Brewer (5) obtained excellent stability and high intensity from a rubidium lamp without using any extra heaters or thermostating precautions. He relied on the large thermal mass of the lamp, good thermal transport between the bulb and the tank coil, and the heat generated by the gas discharge to obtain optimum conditions. Gerard (3) recommends using d.c. current in accessory heaters to avoid partial a.c. modulation of the radiation output. However, the author has found that when low heater voltages are used, no modulation of the radiation output occurs when a.c. current is used, which suggests that the modulation is produced by an excitation and not by a thermal effect.

Brewer (5) and Bell et al. (4) contend that the radio frequency power supply should approximate to a constant power supply unit in order to achieve maximum lamp output stability.

If a voltage stabilised power supply is used, the power dissipated in the lamp will steadily climb as the lamp absorbs power, increasing its temperature and thus the metal vapour pressure and thereby lowering its impedance in the circuit (5), which produces a further increase in absorbed power. Current stabilisation is roughly equivalent to power regulation in an oscillator circuit, because any decrease in load impedance resulting from an increase in power would cause the power level to drop again.

There is a definite relationship between optimum frequency and lamp bulb dimensions (2, 4, 5); in fact, for a given bulb size there is a minimum frequency below which the lamp will not sustain a discharge (4). This frequency dimension relationship, as well as the fill gas pressure, is also involved in determining the effective lifetime of the lamp (2, 69, 75), because the momenta of neutral and charged species at the quartz surface determine the rate of clean-up of the metal.

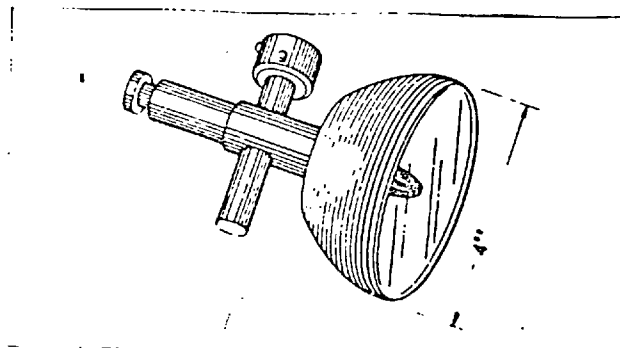
Most of the applications of radio frequency operated EDLs have been for alkali metals, mercury and cadmium (2-6, 69), although lamps containing iodides of other metals are marketed by one company (Sharpline Spectro-Source, Illinois, U.S.A.) for operation at 80 MHz.

The use of microwave frequencies for producing gaseous electrodeless discharges has increased rapidly in recent years, primarily due to the availability of inexpensive medical type diathermy units, which serve as simple sources of continuous

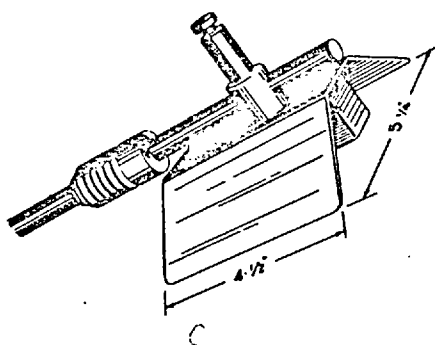
wave microwave power (78, 79). These units operate at 2450 MHz, are rated at a maximum power of 100, 200 or 240 watts, and are adaptable to a variety of antennas and cavities.

Forrester et al. (73) and Jacobsen and Harrison (75) have found that microwave frequencies are more efficient than radio frequencies, by at least an order of magnitude, for the conversion of electrical to luminous power. In addition, Meggers and Westfall (69) and Jacobsen and Harrison (75) have indicated that lifetimes of EDLs are extended with increased excitation frequency. Because greater luminosity efficiencies and longer lamp lifetimes were indicated with the use of microwaves, it was decided to devote this study exclusively to EDLs operated at a microwave frequency of 2450 MHz. Several types of microwave generators were used in this study (Microtron 200, E.M.S. Limited, England; Model 245, E.E.L. Limited, England; Model 100, Raytheon Company, U.S.A.; and a Microgen, Beckman Limited, England).

The microwave power from the magnetron may be coupled to the EDL by means of either a resonant cavity or a director antenna. The latter devices were developed for medical therapeutic use with the diathermy units and are nothing more than antennas with metal reflectors to direct the microwave beam. Both the "C" type and the "A" type (Raytheon Company, U.S.A.) antennas were used in this study (see Figure 3). After an initial investigation, the "C" type antenna was excluded from further work as it was found to be useless because of its inability to concentrate enough microwave power in the vicinity



'A' type antenna

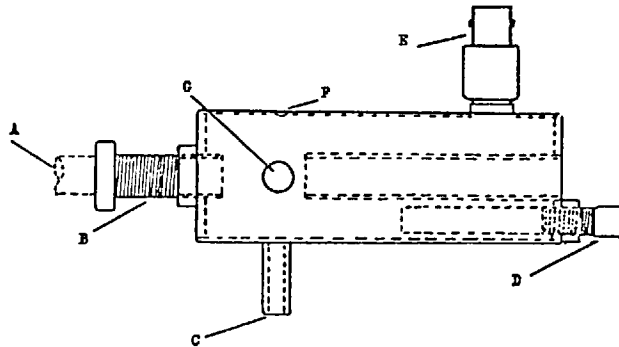


'C' type antenna

Figure 3

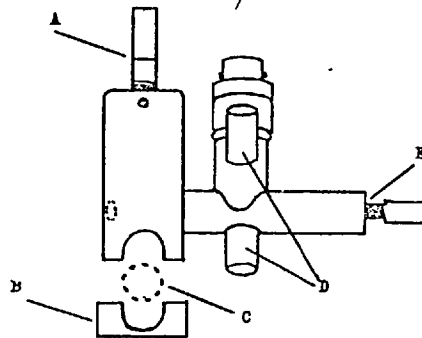
of the EDL. The microwave resonance cavities were developed to optimise the efficiency of coupling the microwave energy to the discharge (78, 79). Most of the basic types of cavities which have been used with electrodeless gaseous discharges have been described and catalogues by Fehsenfeld et al. (78, 79). Of these, the foreshortened $\frac{1}{4} \lambda$ coaxial (Evensen type) cavity and the foreshortened $\frac{3}{4} \lambda$ coaxial (Broida type) cavity, obtained from E.M.S., London, England, were used in this study (see Figure 4). The "A" type antenna has been found to be very successful for operating a variety of discharge lamps (16, 18, 61, 62, 72, 74, 77, 92, 98, 99, 101). Because the microwaves are not as concentrated as in the case of the resonance cavities, its major limitation in operating a wide variety of metal vapour discharge lamps seems to be its lack of available thermal support for the metal vapour. Not enough microwave power is available in the vicinity of the lamp to maintain an adequate vapour pressure of the metallic species required by the discharge. Tomkins and Fred (74) and Worden et al. (77) attacked this problem by enclosing the discharge tube in a furnace element mounted above the antenna. Zacha et al. (62) avoided the complications of a furnace by insulating the EDL from its environment, with either an open-ended quartz jacket packed with quartz wool (Figure 26) or with an evacuated quartz jacket (Figure 19).

Fehsenfeld et al. (78, 79) have presented an evaluation of the various microwave cavities with regard to coupling efficiency



Gas discharge cavity No. 210L: A—discharge tube, B—coaxial gap adjuster, C—air inlet, D—tuning stub, E—type C connector, F—air vent, G—discharge viewing aperture.

$\frac{3}{4} \lambda$ cavity



Gas discharge cavity No. 214L: A—tuning stub, B—removable cap, C—discharge tube, D—air inlets, E—coupling adjustments.

$\frac{1}{4} \lambda$ cavity

Figure 4

for helium and hydrogen. In general, this was a poor criterion with respect to operation of the sealed-off discharge lamps containing metals and metal halides, as it ignored the effects of the increased metallic vapour pressures which occurred with increased coupling efficiencies. In metal and metal halide lamps this increase in the amount of the metallic vapour is often accompanied by self-reversal of the emitted resonance lines. Since 1965 the Evenson and the Broida type cavities have been used fairly extensively (55, 60, 61, 93-97, 102) to operate sealed EDLs. Winefordner and co-workers have comparatively evaluated the "A" type antenna, the Evenson and the Broida type cavities (61, 94, 102), and with a few exceptions have found the antenna to be superior.

2.5 Evaluation of preparation and operating parameters of EDLs.

(a) Experimental System

The spectrometer system used for all lamp relative intensity and all atomic fluorescence relative intensity measurements consisted of a simple medium resolution monochromator, an ultra-violet sensitive photomultiplier, a d.c. amplifier coupled to a strip chart recorder (several different instrumental combinations have been used, but the basic system was as described). Relative intensities were read straight from the recorder (98, 99, 101). For intensity measurements of the EDLs, the lamp was mounted firmly and reproducibly on the entrance slit optical axis with the use of an optical bench. For atomic fluorescence measurements the EDL was mounted at approximately right angles to the

entrance slit optical axis so as to illuminate a fuel rich premixed air/propane flame, which was used as the atom reservoir. Microwave radiation was coupled to the EDL with either an antenna or a cavity via an in line voltage standing wave ratio meter, so that the amount of coupled and reflected powers could be measured.

(b) Evaluation of lamp blank preparation

The general method of preparation of EDL blanks has already been described (see Section 2.3(a)). For some lamps it was found that, during operation, they seemed to lose their fill gas, making reignition of the lamp difficult or, in some cases, impossible. This loss of fill gas was often accompanied by an increase in the presence of nitrogen, demonstrated by an increase in the intensity of its spectrum, and by a fairly rapid clean up of the filler material on the lamp walls. This clean up caused browning or blackening of the quartz and thus produced fairly large drift rates (approximately 5-6% of the lamp intensity per hour). These phenomena were probably due to minute cracks in the lamp walls, which allowed the fill gas to escape, and also due to the surface roughness of the quartz lamp walls which retained residual nitrogen and made many sites available for retention of the filler material (i.e. clean up). To overcome these problems the lamps were heated in a muffle furnace, to about 900^o C. for twelve hours (103), so that the surface roughness was decreased and the minute cracks sealed. The lamp blanks

were then connected to the vacuum rack and purged with a low pressure (5 torr) argon discharge for about 30 minutes to remove any air occluded by the lamp walls. This procedure greatly reduced the loss of fill gas and decreased the rate of nitrogen appearance and the rate of clean up of the filler material. This procedure also resulted in increased lifetimes of EDLs and a decrease in the rate of drift in the emitted resonance radiation intensity, as shown in Table 2-1.

Table 2-1

Effect of various methods of preparation of EDL blanks on the EDL lifetimes and their intensity drift rates.

Lamp type	Usual preparation technique ⁺		Furnace/argon discharge pre-treatment of EDL blank	
	Drift %/hr*	Lifetime hrs*	Drift %/hr*	Lifetime hrs*
Cd	5.5	340	1.9	1330
Zn	4.4	390	1.7	> 1500
As/I ₂	3.1	520	1.1	> 1500
MnCl ₂	6.2	210	2.0	980

⁺ see section 2-3(a)

* averaged for 5 lamps.

The rate of drift of EDLs could be further decreased, by about 30%, and their lifetimes increased, to greater than 1,500 hours by substituting a low pressure discharge of the filler material for the argon discharge.

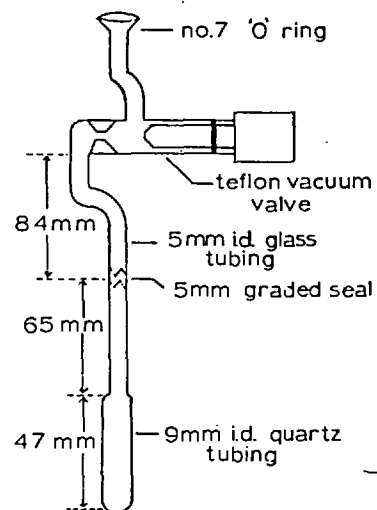
EDLs were prepared with four different quartz tubing diameters (16, 13, 8, and 5 millimeters internal diameter) to investigate the effect of lamp diameter on intensity, noise and lifetime of EDLs. The intensities of the 16 and 13 m.m. EDLs were significantly lower than those of the 8 and 5 m.m. lamps. Intensity tended to drop off rapidly when lamp inside diameters of more than 8 m.m. were used. The 5 m.m. lamps were the most intense used, but were characterised by excessive noise and short lifetimes; they were also much more liable to long term drift. Further studies were carried out exclusively on the 8 m.m. internal diameter lamps because of their high intensity, low noise and fairly long lifetimes.

(c) Evaluation of EDL preparation

Earlier studies on the effect of experimental variables on the intensity of EDL emission have made use of individually prepared lamps (55, 61), which made strict control of lamp dimensions very difficult. In order to

overcome this uncontrolled variable and to facilitate rapid evaluation of many other experimental variables, a refillable EDL blank (see Figure 5) was used (98, 99). This lamp blank was conveniently attached to the vacuum line by its "O" ring joint. Weighed amounts of filler material were easily introduced into the blank before connection to the vacuum line. The lamp was evacuated to about 10^{-5} torr, and the filler material sublimed about 1 cm. up the lamp walls, to degas the filler material and to facilitate rapid ignition of the lamp. The lamp blank and the vacuum line were then purged twice with the fill gas before final filling to the required pressure. The stopcock is then closed and the EDL removed from the vacuum line for experimental evaluation. Between successive runs with each EDL prepared in the above manner, the blank was cleaned with 50% nitric acid and 10% hydrofluoric acid, followed by a thorough washing with distilled-deionised water.

This refillable design is very useful for evaluating the effect of experimental parameters on the intensity of resonance radiation emitted from an EDL. Several sealed off lamps were prepared using various experimental conditions and in every instance the results obtained agreed, within experimental error, with the results obtained from the refillable EDL prepared under the same conditions. It is presumed, however that the



Refillable EDL Blank

Figure 5

standard EDL design, a permanently sealed EDL, will be the design of choice for long term operation, as slight leaks do occur with the refillable EDL. Evidence of such leaks are only observable after 30-40 hours of operation.

In order to study precisely the numerous experimental variables affecting the intensity of EDL resonance radiation, a full factorial design was prepared for several levels of several independent variables. The variables studied in this work include: weight and nature of the filler material introduced in the EDL blank, nature and pressure of the fill gas used in lamp preparation, and the amount of microwave power applied to the EDL via the "A" type antenna. Preliminary experiments with cadmium and mercury lamps with regard to the weight of the filler material allowed significant reduction in experimental effort. Lamps were prepared with 1, 3, 5, 10, 30 and 50 milligrams of filler material introduced into the lamp blank, for a wide range of fill gas pressures and applied microwave powers. Lamps with the larger amounts of the filler material (10, 30 and 50 milligrams) emitted less intensely and considerably less reproducibility (see Figure 6) than the lamps containing smaller amounts of filler material (1, 3, and 5 milligrams). The intensity and reproducibility of lamps containing these smaller amounts of filler material were the same, within experimental error. Lamps prepared with much smaller amounts (less than 0.1 milligrams) of material were liable to have considerably shorter lifetimes. These

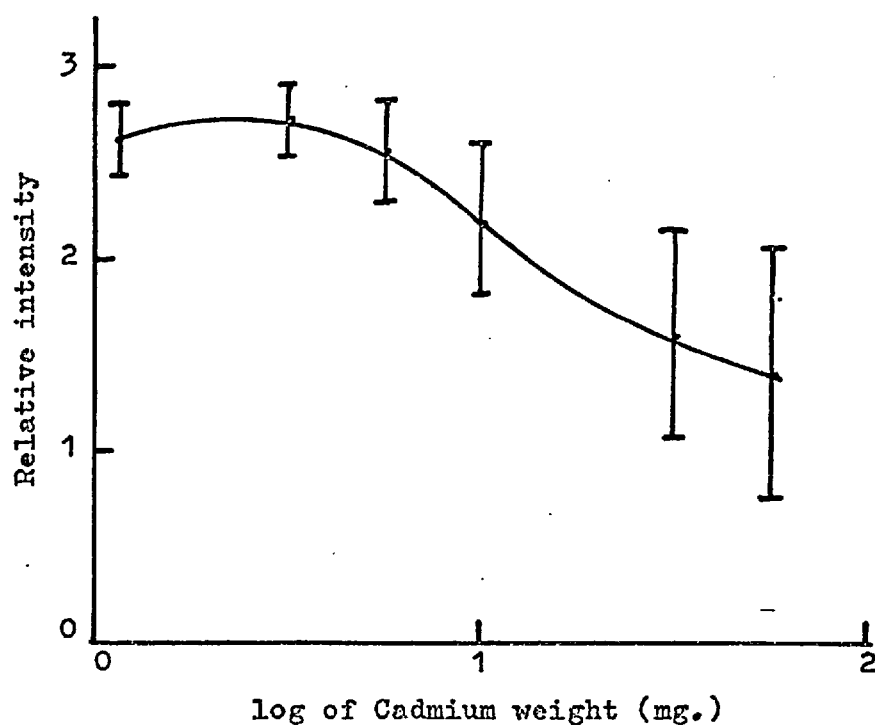


Figure 6

Effect of the weight of fill material (Cadmium metal) on the resonance line (228.8 nm.) intensity emitted from a Cadmium EDL.

I denotes the standard deviation at that point.

results were consistent with visual observation of the lamps in operation; lamps containing 10, 30 or 50 milligrams of material showed a metal film deposited on the interior walls of the lamp which irreproducibly reduced the transmission of the lamp walls.

As a consequence of this preliminary work, the weight variable was omitted from the experimental design; a fixed amount of 2 milligrams of filler material was used. The effect of the amount of material used on the resonance line intensity emitted by the EDL was found to apply equally well to other elements. Mansfield et al. (61, 92) found a similar dependence on the weight variable, although their investigation was solely for cadmium filler material. However, Cooke et al. (97) found that the optimum amount of fill material was of the order of 20 micrograms, for EDLs containing volatile materials operated in a foreshortened Broida type $\frac{3}{4}\lambda$ cavity. The probable explanation for this conflict is that in using a $\frac{3}{4}\lambda$ cavity, with its inherently greater coupling efficiency, instead of an "A" type antenna, Cooke et al. effectively increased the vapour pressure of their filler materials when larger amounts than 20 micrograms were used. This increased vapour pressure produced in the cavity operated EDL then produced self reversal and resonance line broadening of the resonance lines.

With the elimination of the weight variable, three mutually independent variables remained to be examined for

their effect upon EDL resonance line intensities. Preliminary data indicated that the full range of applied microwave powers could be described by measurements at 20, 40, 60, 80, and 100% of full scale meter deflection; these power levels were found to correspond to 40, 80, 120, 160, and 200 watts output. Therefore, five levels of the power level variable were investigated. Four different fill gases were used in this study: helium, argon, neon and air. Therefore, four discontinuous levels of the nature of the fill gas variable were investigated. For the pressure variable, an exponential design was chosen, fill gas pressures were adjusted to 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} , 1 and 10^1 torr. A final fill gas pressure condition was obtained by attempting to ignite a lamp with a pressure of 100 torr. Failing ignition, a pressure of 25 torr was used. For air fill gas, ignition failed at both 100 and 25 torr, and therefore the highest pressure of air fill gas used was 10^1 torr. Therefore 7 (or 6 for air fill gas) levels of fill gas pressure were investigated. The full factorial design, therefore, requires 135 ($5 \times 3 \times 7 + 1 \times 6$) individual measurements for the examination of each filler material. Initially, three replicates were obtained for each cell in the design; however, cell reproducibility was good and the intercell effects large, so that for the remainder of the design no replicates were used.

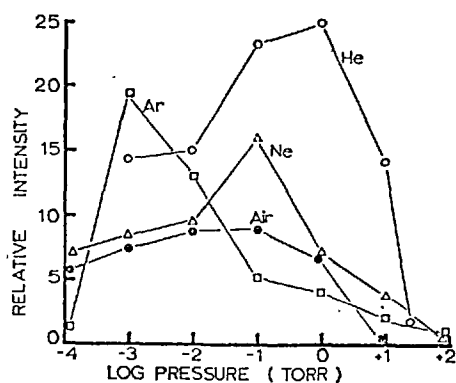
In an attempt to examine the effect of volatility of the filler material on the preparation of EDLs, three materials, with widely different boiling points were chosen for this study:

mercury (boiling point $357^{\circ}\text{C}.$), cadmium (boiling point $765^{\circ}\text{C}.$), and manganese bichloride (boiling point $1190^{\circ}\text{C}.$).

In order to simplify interpretation of the results they are dealt with by element.

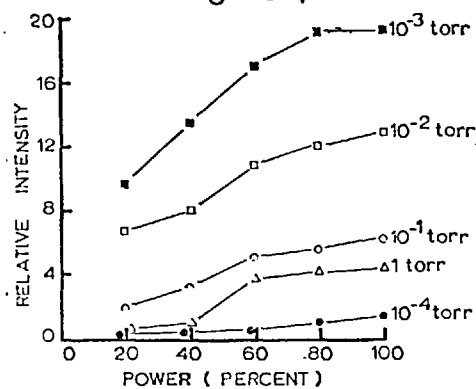
Cadmium EDLs : The nature of the fill gas effects the intensity of the cadmium 228.8 nanometre emission in a regular manner. A representative behaviour for the effect of fill gas nature on cadmium 228.8 n.m. emission is shown in Figure 7. These results were quite general, and can be extended to all power levels investigated. The most intense cadmium EDL was obtained when using helium fill gas at a pressure of 1 torr. It is evident from Figure 7 that cadmium 228.8 n.m. emission intensity is significantly enhanced at a considerably lower pressure, for argon fill gas (the most frequently used fill gas in past studies) than has been previously used (2 torr). As stated earlier, this behaviour is general and can be extended to all power levels, as shown in Figure 8.

Direct comparisons to previously prepared cadmium EDLs can be made if one considers that lamps have been previously optimised for argon fill gas at a pressure of 2 torr running at 100 watts of applied microwave power. Curves such as those presented in Figure 8 were obtained for helium, neon and air fill gases, with the obvious exception that the position of the maximum is shifted (see Figure 7). The effect of increasing microwave power on cadmium 228.8 n.m. emission is shown in Figure 9 for argon fill gas.



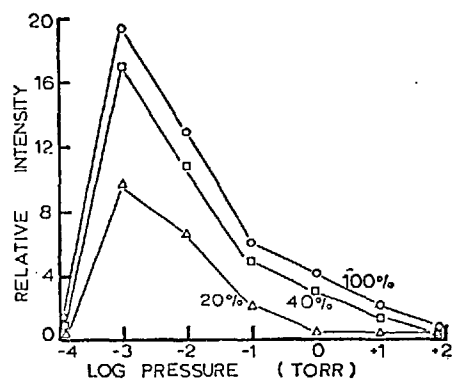
Effect of nature of fill gas on Cd EDL intensity: relative emission intensity of Cd (2288 Å) as a function of fill gas pressure at 200 W of applied microwave power.

Figure 7



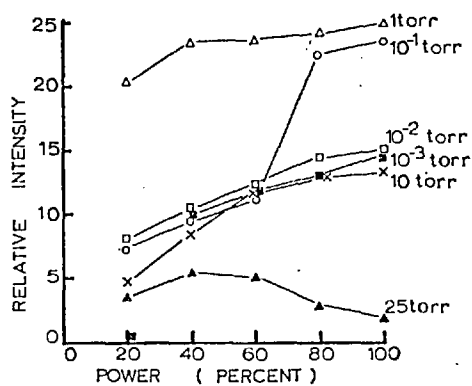
Effect of applied microwave power on Cd EDL intensity at various Ar fill gas pressures.

Figure 9



Effect of pressure of Argon fill gas on Cd EDL intensity at various power levels.

Figure 8



Effect of applied microwave power on Cd EDL intensity at various He fill gas pressures.

Figure 10

While the data in Figure 9 is for argon fill gas, these results are typical for the behaviour of neon fill gas. A peculiarity is observed for helium fill gas; curves of similar shapes to the argon and neon fill gas curves are observed for fill pressures of 10^{-3} , 10^{-2} , 1 and 10 torr, see Figure 10, while a marked difference is observed for the 10^{-1} torr helium fill pressure. At low powers (20 - 60%) the behaviour and intensity are similar to those for fill pressures of 10^{-3} , 10^{-2} and 10 torr. Between 60 and 80% power, there is an approximately two-fold increase in the cadmium emission intensity, and at higher powers (80-100%) the 10^{-1} torr curve approaches the 1 torr curve. The 1 torr lamp yielded the highest intensities for cadmium emission at all powers. At 25 torr a third kind of behaviour is observed; at about 50% power there is a change from the normal diffuse glow throughout the lamp to a pinched vertical arc which has a very bright appearance (61). However, this brightness is quite misleading; as power is increased about 50% a rapid decrease in net cadmium 228.8 n.m. emission occurs. This effect is most probably due to severe self reversal of the cadmium 228.8 n.m. resonance line brought about by preferential absorption of the central part of resonance line by the cool cadmium atomic vapour surrounding the not emitting central arc. This pinching of the discharge probably stems from the difference in the gas density between the wall and the axial areas. Because of the high heat transfer rate from the walls to the external air, the gas layer adjacent to

the EDL walls has a lower temperature, and therefore a higher density, than the gas in the axial region. The lower gas density along the axis, in turn, produces a longer mean free path for the electrons, which facilitates the operation of the discharge in this region. After its initial establishment, the discharge then narrows further, because the gas core along the axis heats up progressively and thus the gas density drops off further. Compression of the discharge also promotes excitation of the ion lines, which further decreases the intensity of the atomic lines already decreased by self reversal.

The intensity versus power results for air fill gas are similar to those reported for argon and neon (see Figure 9), except that at 10^{-1} torr there appears to be a maximum at about 40% power, and then the cadmium 228.8 n.m. intensity decreases with increasing power (similar to Figure 10, 25 torr case).

The optimal experimental conditions for achieving maximum cadmium 228.8 n.m. EDL emission intensity are therefore as follows: helium fill gas at a pressure of about 1 torr operated at 200 watts of applied microwave power. It would appear that a further increase in intensity could be obtained if larger microwave powers were applied, but a maximum of 200 watts was actually available for this work. These recommended operating conditions completely ignore any lamp lifetime considerations.

In general, the higher the fill gas pressure, the longer the lamp lifetime will be. This phenomenon is related to the rate of clean up of the fill gas in the lamp. At very low fill gas pressures the clean up process rapidly decreases the

initial fill gas pressure resulting in short lamp lifetimes. The clean up process occurs at higher pressures, but the total fraction of the fill gas effectively removed from the lamp atmosphere is considerably less. The actual clean-up rate of EDL fill gas is often faster for EDLs with low fill gas pressures because of their tendency to operate at higher temperatures. These high temperatures are attained by most of the microwave power coupling to the quartz lamp walls because of the difficulty of full coupling to very low pressure gases. It has been found, however, that when a lamp with a low fill gas pressure has failed, the process of fill gas clean up can usually be reversed by heating the lamp to red heat in a bunsen burner for two minutes. The lamp can then be reignited in the usual manner and it will operate at its former intensity. It may be observed that this procedure presents no real experimental difficulty because the lamp will nearly always fail by resisting reignition, once the lamp has been turned off, and not during its discharge period.

A comparison of the relative intensity of atomic fluorescence, of a 10 p.p.m. solution of cadmium chloride solution sprayed into a fuel rich air/propane flame, produced by cadmium EDLs, prepared under various conditions, with the relative intensities of the cadmium lamps is given in Table 2-2. While EDL emission intensities increase regularly with applied power, atomic fluorescence intensities are sometimes found to decrease at very large values of applied power. This

Table 2-2

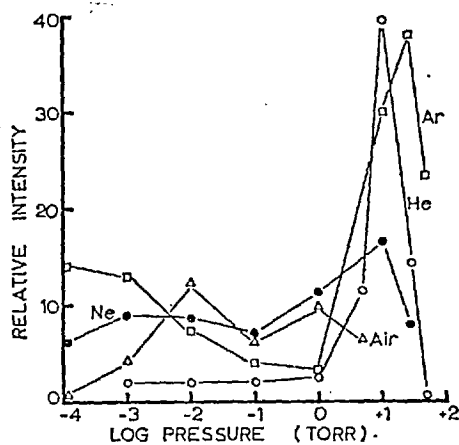
Effect of Cd EDL variables on fluorescence and EDL intensities

Pressure of fill gas (torr)	Percentage power	Relative fluores- cence intensity from a 10 ppm. CdCl ₂ solution	Relative EDL Intensity
Helium	100	105	1410
	67	88	1250
	33	69	780
	100	165	2500
	67	171	2370
	33	144	2300
	100	135	1440
	67	138	1210
	33	126	1000
Neon	100	24	380
	67	5.4	74
	33	2.4	22
	100	114	1590
	67	102	1290
	33	90	1100
Argon	100	13.5	360
	67	7.5	168
	33	3.6	78
	100	138	1950
	67	147	1770
	33	90	1230

decrease in fluorescence intensity suggests that at very large applied microwave powers there may be slight self reversal or considerable line broadening of the cadmium resonance line, leading to less available intensity, at the line centre, to excite the cadmium atomic vapour in the flame. However, the total or integrated line intensity of the cadmium resonance line has continued to increase with applied microwave power. This self reversal or line broadening only occurs when low fill gas pressures (< 2 torr) are used, and is probably caused by the larger temperature gradients and higher cadmium vapour concentrations that are found in low pressure lamps due to their higher operating temperatures. No data was gathered for air fill gas because of the low intensities produced.

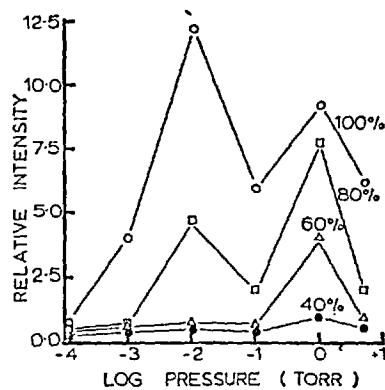
The fluorescence results for cadmium suggest that while integrated intensity measurements (i.e. EDL emission measured with a medium resolution spectrometric system) give a rough guide to the intensity at the line centre, they do not adequately describe the precise behaviour of this intensity. As a matter of convenience, gross intensity changes at the line centre are adequately described by the changes in the integrated intensity for cadmium EDLs. Thus, evaluation of EDL conditions may be performed by simply measuring the lamp intensity; gross changes at the line centre can be detected through this simple measurement procedure. More precise details of the line centre behaviour may be obtained through actual atomic fluorescence measurements.

Manganese EDLs : The nature of the fill gas affects the intensity of the manganese 403.0 n.m. emission, emitted by an EDL as shown in Figure 11. As with cadmium EDL emission, the general shapes of the curves apply at all power levels. However, some slight peculiarities are worth noting. In the case of air fill gas, the ratio of the relative intensities of the maxima at 10^{-2} and 10^0 torr change drastically with applied power, see Figure 12. The intensity of the 10^{-2} torr maximum decreases much more rapidly than the intensity of the 10^0 torr maximum, with decreasing power. A similar effect is seen in the case of argon fill gas, see Figure 13; the maximum at about 10^{-3} torr decreases much more rapidly than the maximum at about 10^0 torr, as the applied microwave power decreases. Similar behaviour is also observed for neon fill gas. This phenomenon, of two maxima in the intensity versus fill gas pressure curve, may be due to two modes of lamp operation. At low pressures, EDLs operate at much higher temperatures, as previously explained, evidenced by a dull red glow of the quartz lamp walls; much cooler operation occurs at higher fill gas pressures. The rate of sputtering at 1 torr will be considerably higher than at 10^{-2} or 10^{-3} torr. Consequently, it is suggested that the maximum occurring at higher fill gas pressures is mainly due to larger atomic vapour concentrations produced by the more efficient sputtering process. The maximum at lower fill gas pressures may be due to the increased volatility of the sample material at the higher operating



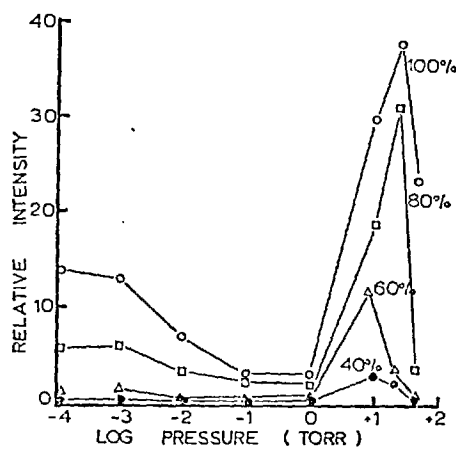
Effect of nature of fill gas on Mn EDL intensity: relative emission intensity of Mn (4030 Å) as a function of fill gas pressure at 200 W of applied microwave power.

Figure 11



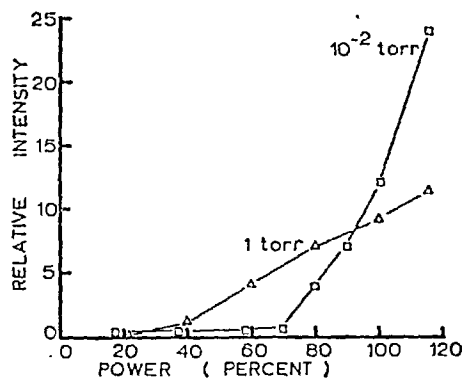
Effect of pressure of air fill gas on Mn EDL intensity at various power levels.

Figure 12



Effect of pressure of argon fill gas on Mn EDL intensity at various power levels.

Figure 13



Effect of applied microwave power on Mn EDL intensity at various air fill gas pressures.

Figure 14

temperatures of low pressure EDLs. Support for these two proposed lamp operation mechanisms is found when one examines the variation of EDL intensity with power at the maxima. Because the rate of sputtering is proportional to the applied microwave power, the atomic vapour concentration, which in turn is proportional to the lamp intensity, simply increases in proportion to the applied power. If it may be assumed that the lamp temperature (translational) is proportional to the applied power, then because the vapour pressure has a logarithmic relationship with temperature, thus the vapour concentration and the lamp intensity will increase approximately exponentially with applied power. As pointed out previously, there is less coupling of the radiant power to the lamp walls at 10^0 torr than at 10^{-2} torr and the rate of sputtering is much larger at 10^0 torr than at 10^{-2} torr. Therefore, the primary process at 10^0 torr may be assumed to be sputtering.

Experimentally, a linear increase of intensity with power at 10^0 torr is observed, see Figure 14, which supports the sputtering process theory. The primary process at 10^{-2} torr may be assumed to be a "heating effect" because of the low rate of sputtering and the high lamp operating temperature. Experimentally, a nearly exponential increase of intensity with power at 10^{-2} torr is observed, see Figure 14, which supports the heating effect theory.

To further substantiate these conclusions, both EDLs, i.e. the manganese 10^{-2} and 10^0 torr air filled EDLs, were

cooled during operation by blowing liquid nitrogen cooled nitrogen over the EDL bulb. As expected, the intensity for the heating effect controlled 10^{-2} torr EDL decreased by a considerable amount (90%), while the intensity for the sputtering controlled 10^0 torr EDL only decreased slightly (30%), see Figure 15. This cooling decreased the operating temperatures of both lamps, thus removing the major part of the heating effect without affecting the sputtering rate. The intensity versus power curves for the cooled EDLs are now essentially sputtering controlled, and it can be seen from Figure 15 that the sputtering rate is much higher for the 10^0 torr EDL than for the 10^{-2} torr EDL.

The decrease in intensity, brought about by this cooling of the EDLs, is related to the amount of atomic vapour produced by the heating effect. If this decrease is plotted against the applied microwave power, see Figure 16, an estimate of the heating effects for the two EDLs can be made. From Figure 16 it can be seen that the "heating effect" is about five times as large for the 10^{-2} torr EDL as for the 1 torr EDL, whereas, from Figure 15, it can be seen that the sputtering effect is about six times as large for the 1 torr EDL as for the 10^{-2} torr EDL. Similar explanations can be applied to the two maxima that occur in the neon and argon filled EDLs. However, this phenomenon only applies to EDLs containing high boiling filler materials. For low boiling materials, the heating effect is so much larger than the sputtering effect that sputter ceases to be observed. This effect was not observed for helium fill

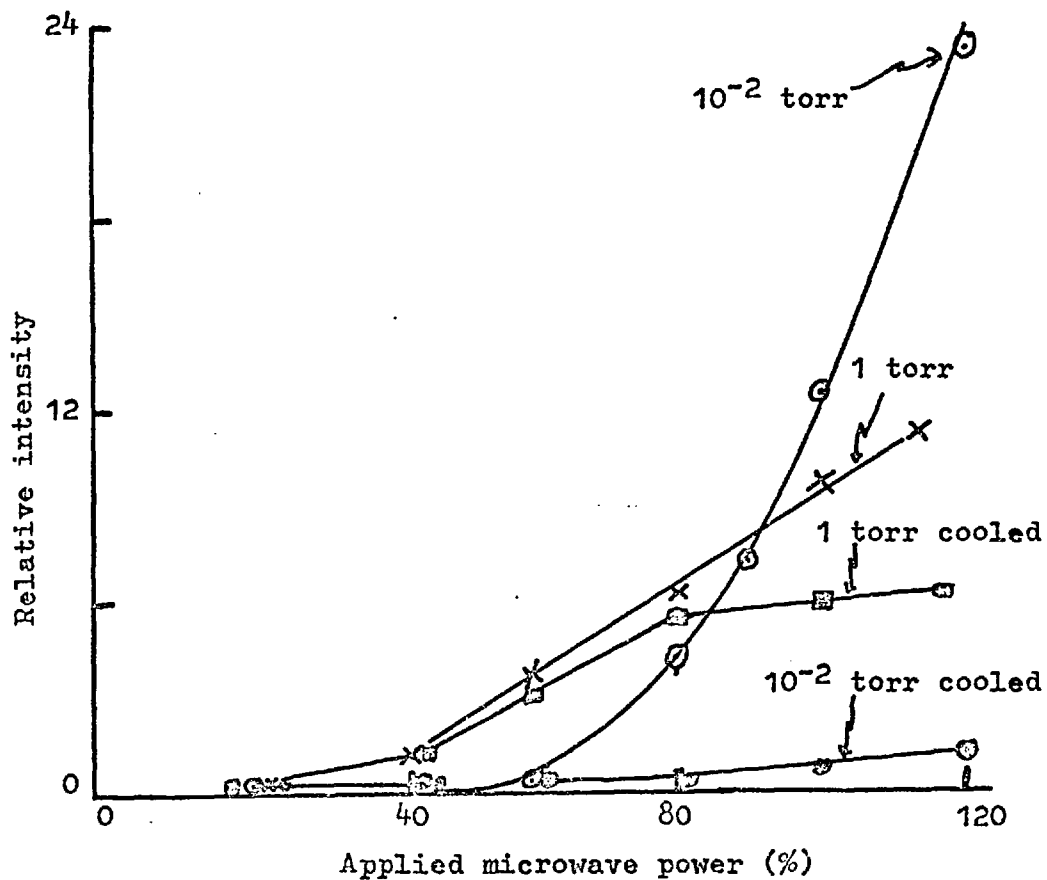


Figure 15

Effect of applied microwave power on manganese EDL resonance line intensity at two different air fill gas pressures, with and without cooling.

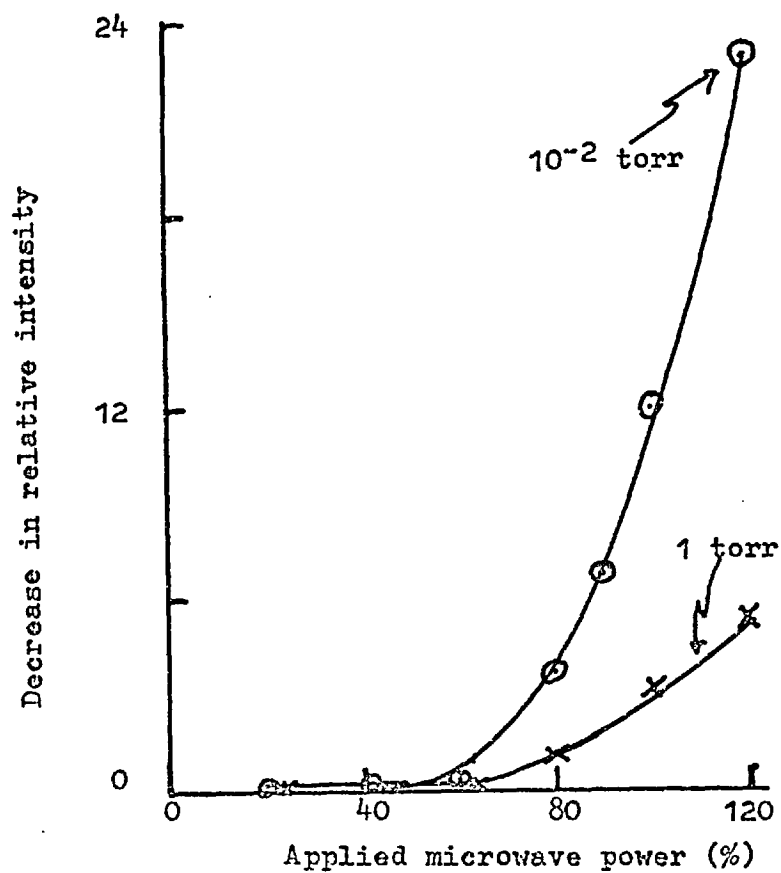
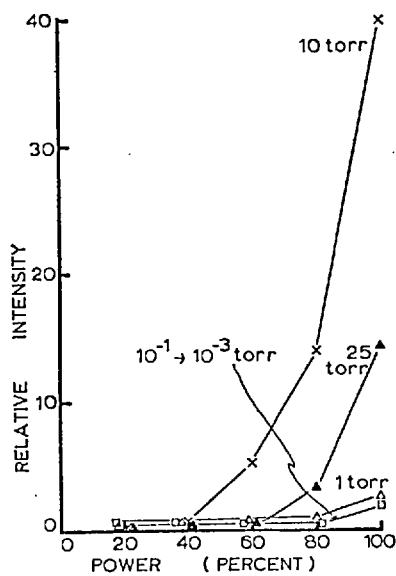


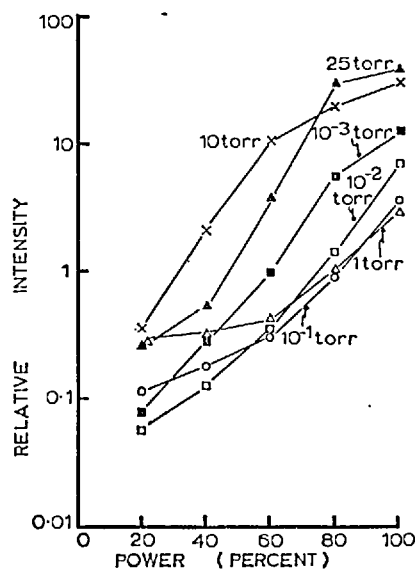
Figure 16

Effect of applied microwave power on the decrease in manganese EDL resonance line intensity caused by cooling, at two different air fill gas pressures.



Effect of applied microwave power on Mn EDL intensity at various He fill gas pressures.

Figure 17



Effect of applied microwave power on Mn EDL intensity at various argon fill pressures.

Figure 18

gas, even for high boiling filler materials. The increase in intensity of manganese resonance emission for helium with increasing applied microwave power is approximately exponential over the whole pressure range, see Figure 17, which suggests that the helium EDLs are "heating effect" controlled at all pressures. Helium filled EDLs probably behave in this manner because of their inherently higher operating temperature than those of argon, air or neon filled EDLs. It should be noted that the quartz walls were liable to glow red hot at the higher power settings for all helium fill gas pressures.

This nearly exponential increase in intensity of the EDL resonance line with increasing power also applies to the other fill gases, except for the cases already stated. Perhaps a clearer presentation of this behaviour is shown in Figure 18, for argon fill gas, where the logarithm of the relative manganese emission intensity is plotted against the applied microwave power.

For the case of cadmium EDLs, large changes in applied microwave power resulted in relatively small changes in the EDL intensity. For manganese, however, the increase in EDL intensity is approximately exponential with increasing power, which suggests that much more intense EDLs could be produced by using considerably higher powers than 200 watts. As the "heating effect" for the manganese EDLs seemed to be, in most cases, the controlling factor, another way of increasing the effective available power to the EDLs was to surround

them with a vacuum jacket of the type used by Winefordner and co-workers (62), as shown in Figure 19. The vacuum jacket proved to be very successful in increasing the intensity of manganese EDLs, see Figure 20, although further power would still have been advantageous as the intensity still increased exponentially with increases in applied microwave power.

During the atomic fluorescence measurements of manganese reported below, the microwave power supply was adjusted to yield radiant powers greater than 200 watts in order to determine whether this exponential behaviour continued at higher power levels. This power increase was accomplished by adjusting the power output to just below the overload "cut-out" limit of 250 watts.

A comparison of the relative intensity of atomic fluorescence produced by manganese EDLs, prepared under various conditions, to the lamp intensities is given in Table 2-3.

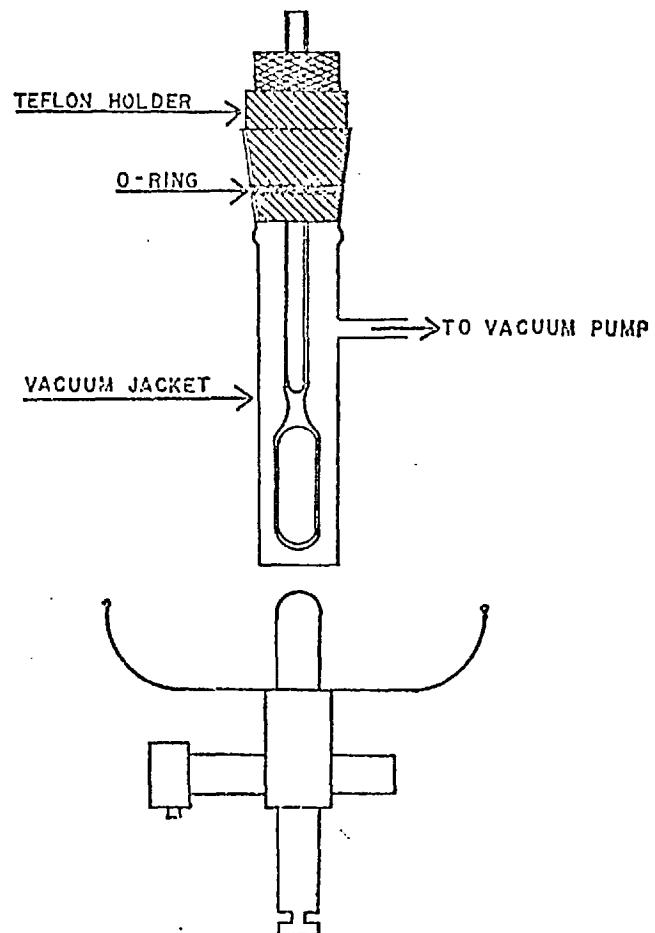
Table 2-3

Effect of Mn EDL variables on Mn fluorescence intensity and EDL intensity

Pressure of fill gas (torr)	Percentage power	Relative fluorescence intensity*	Relative EDL intensity
Helium	120	620	B
	100	400	4000
	67	120	830
	33	A	42
10	120	590	B
	100	470	1140
	67	12	100
	33	A	34
5	120	590	B
	100	470	1140
	67	12	100
	33	A	34

A no detectable atomic fluorescence

B no measurement was taken for this condition



Quartz vacuum jacket device for operating electrodeless discharge tubes

Figure 19

Table 2-3 (continued)

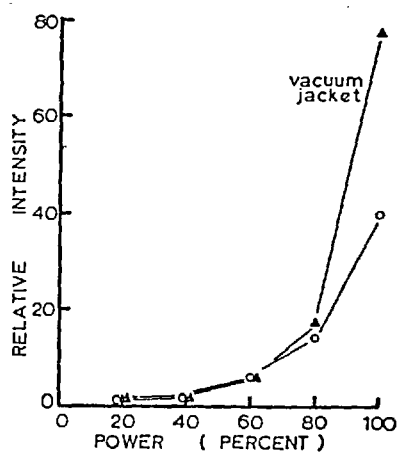
Pressure of fill gas (torr)	Percentage power	Relative fluorescence intensity*	Relative EDL intensity
Argon	120	300	B
	100	150	3800
	25	67	1260
	33	A	42
	120	360	B
	100	320	300
	10	67	1200
	33	A	120
	120	240	B
	100	160	1290
	10 ⁻³	67	260
	33	A	15
Neon	120	250	A
	100	160	1650
	10	67	700
	33	A	18
	120	200	B
	100	100	830
	10 ⁻²	67	34
	33	A	32
Air	120	99	1115
	100	75	930
	1	67	500
	33	12	65
	120	165	2430
	100	78	1230
	10 ⁻²	67	41
	33	A	36

* Atomic fluorescence measurements taken for a 1000 ppm. Mn solution aspirated into a fuel rich premixed air propane flame

By contrast to the cadmium EDL situation (see Table 2-2), approximately exponential increases in both the atomic fluorescence and the lamp intensities is observed. There is only slight evidence of self reversal or line broadening effects in the manganese resonance line, although at high powers (200-240 watts), a slight decrease in the rate of increase of the atomic fluorescence intensity with increase in applied power is noticed.

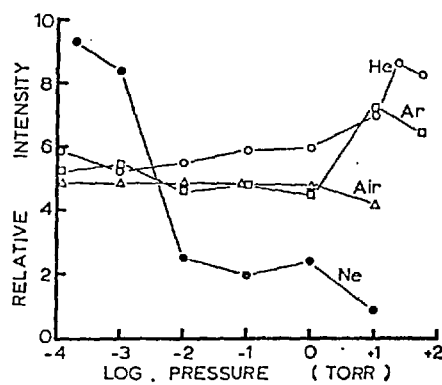
For manganese EDLs, therefore, simple measurements of the EDL intensity give very reliable indications of the efficiency of a particular lamp for atomic fluorescence, within the power range used in this study. The optimum conditions for construction and operation of manganese EDLs can be outlined as follows: helium fill gas at 10 torr fill pressure operated at a minimum of 240 watts in a vacuum jacket. Argon fill gas at 25 torr also produces high manganese EDL intensities, but the atomic fluorescence produced under these conditions is considerably less than for the 10 torr helium condition. This drop in efficiency is probably due to the higher fill gas pressure producing a more collisionally broadened manganese resonance line, resulting in less intensity at the line centre relative to the integrated intensity.

Mercury EDLs : The nature of the fill gas affects the intensity of the mercury 253.7 n.m. resonance line emission in the manner shown in Figure 21. These results are general with regard to the shapes of the curves; however, sharp reversals in intensity occur at between 60 and 80% power, see Figure 22. These reversals can usually be correlated to the



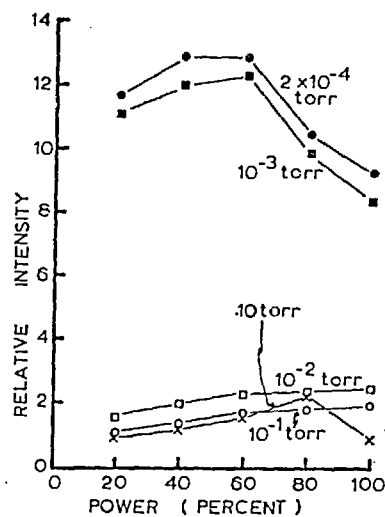
Comparison of vacuum jacketed EDL and normally operated EDL for the effect of applied microwave power on Mn EDL intensity at 10 torr He fill gas pressure.

Figure 20



Effect of nature of fill gas on Hg EDL intensity: relative emission intensity of Hg (2537 Å) as a function of fill gas pressure at 200 W of applied microwave power.

Figure 21



Effect of applied microwave power on Hg EDL intensity at various neon fill gas pressures.

Figure 22

appearance of a narrowing of the gaseous discharge inside the lamp. As power levels are further increased, the discharge forms a pinched arc in the centre of the EDL surrounded by a non-emitting sheaf; this effect has been previously observed by Winefordner and co-workers (61). This reversal in resonance line intensity occurs for all fill gases, and is probably caused by severe self reversal of the resonance line, which is associated with the pinched arc type discharge.

Atomic fluorescence of mercury could only be observed when the mercury EDLs were run at 10% power (20 watts) with cooling air blown across the EDL bulb. At all other power settings, no atomic fluorescence was observed; a wide variety of flame heights, sample concentrations and illumination conditions all proved to be unsuccessful at power settings above 10%. This failure to observe fluorescence suggests that self reversal of the resonance line starts at very low powers.

A particularly interesting phenomenon has been observed for cadmium EDLs containing a trace of mercury. Intense mercury 253.7 n.m. emission, which is capable of producing atomic fluorescence of mercury at all power levels, is produced. The introduction of a trace of mercury into a cadmium EDL is easily accomplished by adding 1 microlitre of mercury to a lamp blank and discharging this for thirty minutes while continuously pumping. The mercury is then emptied out of the lamp blank and a cadmium EDL is prepared, using this blank and the usual procedure. Mercury 253.7 n.m. resonance line

emission, for a cadmium EDL made in this manner with a fill gas of 1 torr of helium, is four times as intense as the most intense "pure" mercury EDL. The lamp is then capable of producing atomic fluorescence at all power levels, see Table 2-4.

Table 2-4

Effect of Hg-Cd EDL variables on Hg fluorescence and EDL intensity,
for a Cd-Hg containing 1 torr of helium fill gas —

Percentage power	Relative fluorescence intensity for 1000 ppm Hg solution	Relative EDL intensity
120	4.5	5800
100	4.0	4900
67	3.5	4200
33	0.8	650

Cadmium-mercury EDLs probably produce atomic fluorescence for mercury because they are less self reversed than pure mercury EDLs. Less self reversal is produced because the mercury vapour concentration in the lamp is much less, and there is also less likelihood of a pinched arc being formed.

(d) General observations on preparation of EDLs

In an attempt to inject some precision into the preparation of EDLs, three metals with a wide range of boiling points have been chosen for establishing guidelines. Boiling points for the pure metals or metal chloride are: mercury - 357°C.,

cadmium - 765°C. , and manganese chloride - 1190°C. (at one atmosphere). Resonance lines have been used in all cases to characterise the particular EDL. This extensive investigation of the effects of the nature and pressure of the fill gas, the amount of filler material, and the amount of microwave power, on the intensity of the resonance line emitted by an EDL has enabled us to limit the number of variables that need to be investigated for a further range of fill materials. In further studies only the nature and pressure of the fill gas used and the amount of microwave power applied to an EDL were investigated. It was also decided to limit the fill gases to helium and argon because of the low efficiency of air and the high cost of neon. To extend and complement the boiling point range of filler materials, a further ten filler materials were investigated. The ten filler materials chosen were:- tellurium iodide, stannous chloride, cupric chloride, selenium, cadmium iodide, zinc, amorphous tellurium, ferric chloride, thallium, and silver chloride.

The optimum fill gas pressure, for both helium and argon, and the intensity versus power response were found for each of the filler materials, as previously described. It was found that the optimum fill gas pressure, i.e. that pressure that yields the most intense atomic fluorescence consistent with stability, was dependent on the boiling point of the material used in the EDL. Figures 23 and 24 show this dependency for helium and argon fill gases respectively. For both fill gases, the optimum fill pressure increases with increasing boiling

Figure 23

Effect of boiling point of EDL fill material
on the optimum Helium fill gas pressure.

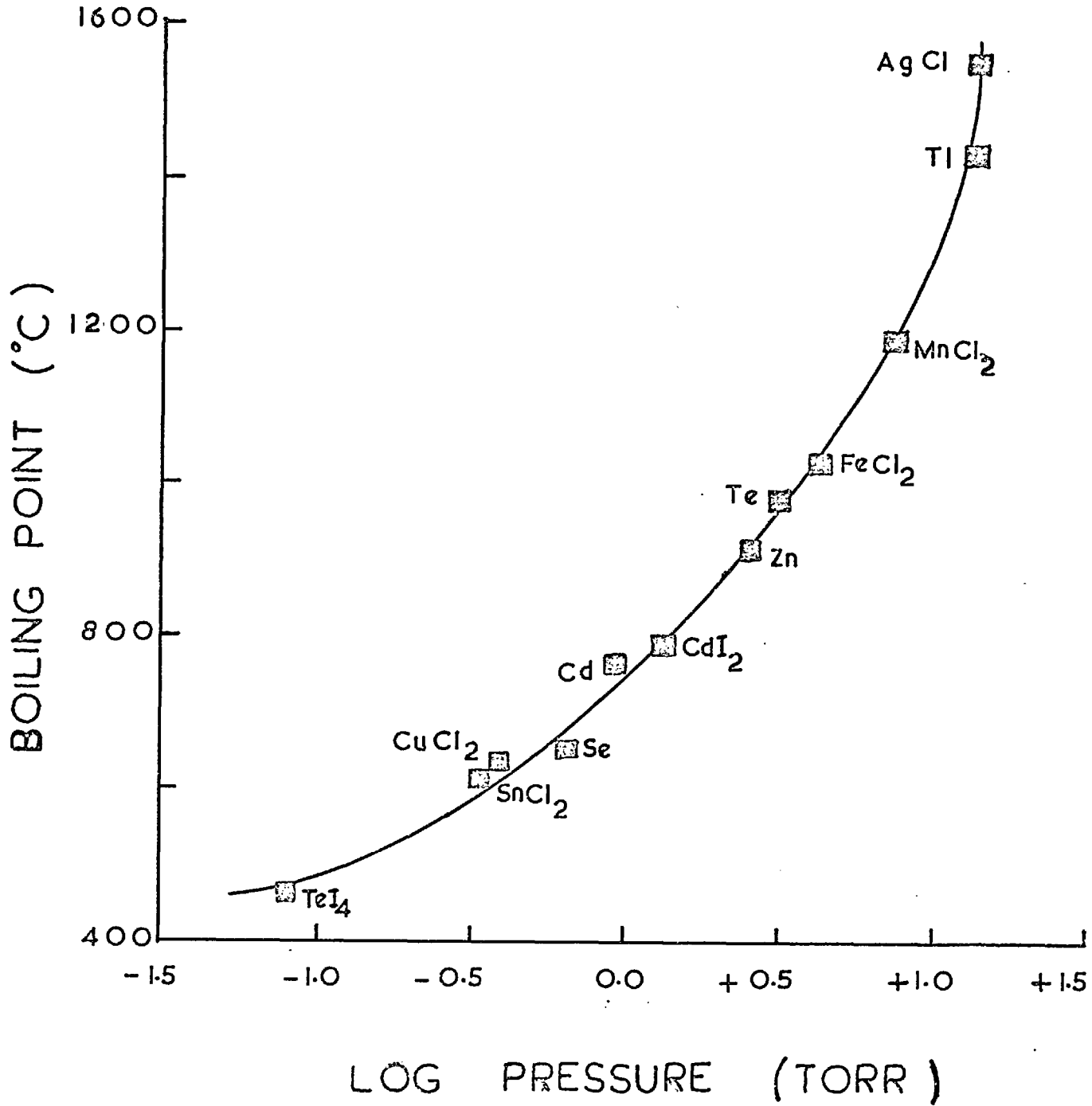
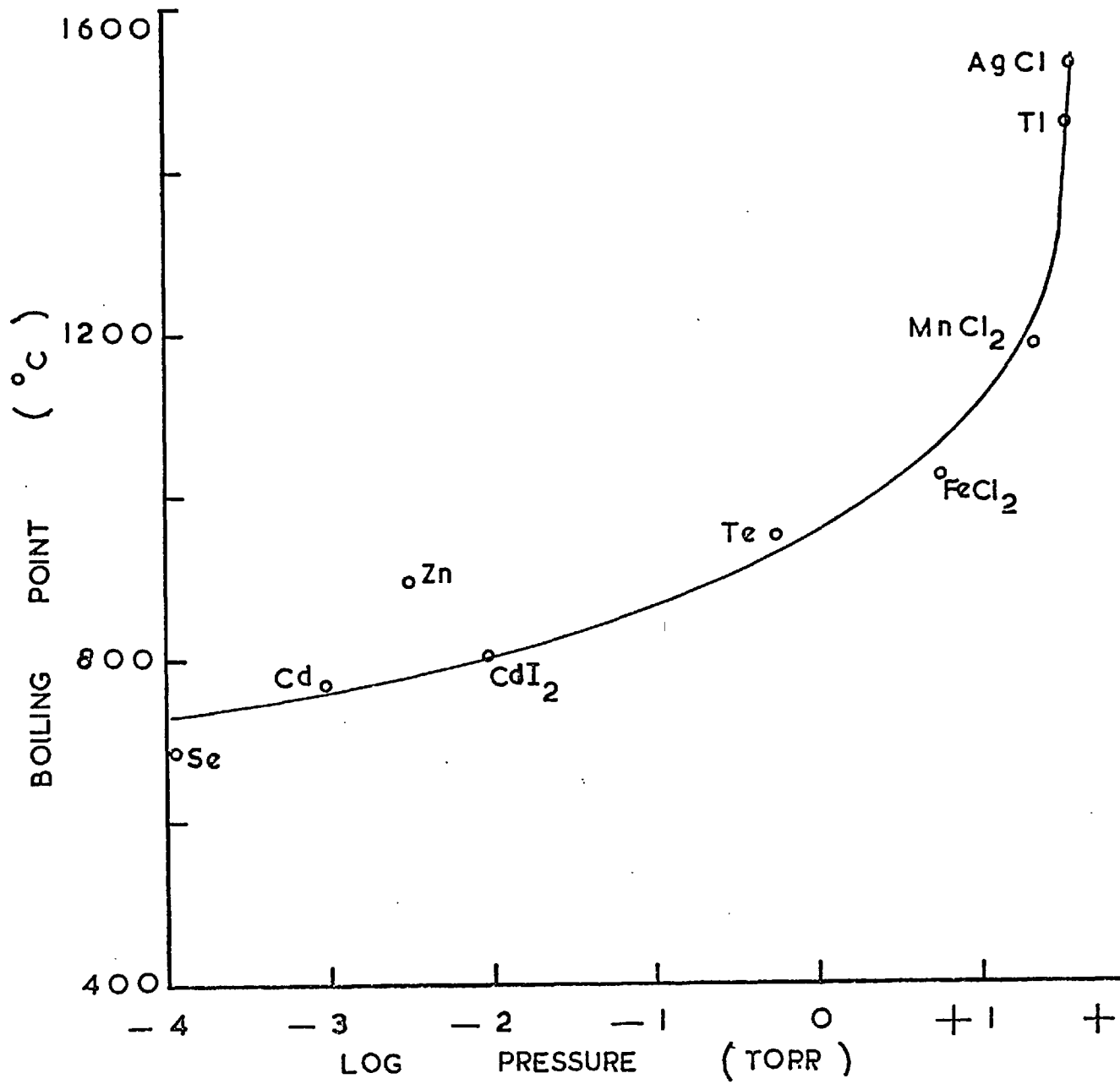


Figure 24

Effect of boiling point of EDL fill material
on the optimum Argon fill gas pressure.



point of the fill material; except that, at high boiling point (above $1400^{\circ}\text{C}.$) the optimum fill gas pressure is 20 torr for helium and 25 torr for argon, whereas at low boiling points (below $450^{\circ}\text{C}.$) the optimum fill pressure tends to zero. For high boiling point materials, the pressure of the fill gas is very critical, while for low boiling point materials the fill gas pressure is not nearly as important. The probable explanation for this behaviour at the two boiling point extremes is quite simple. Fill materials with low boiling points have sufficient vapour pressure to carry the discharge, even at the low temperatures of EDLs operated at very low powers, and the presence of the fill gas diminishes the amount of power carried by the vapour of the fill material. On the other hand, fill materials with high boiling points do not rely solely on this thermal process for the production of a sufficient vapour pressure, but on a combination of this thermal process and a sputtering of the fill material by the mobile excited fill gas atoms. The limitation of maximum optimum pressures of 20 torr for helium and 25 torr for argon for the high boiling materials are due to the formation of pinched arcs at higher pressures, which produce very severe self reversal.

When investigating the effect of applied microwave power on the intensity of atomic fluorescence produced by various EDLs, the EDLs were mounted above the "A" type antenna in three different configurations: the EDL alone, (Figure 25); the EDL in a quartz wool packed quartz tube (Figure 26); and the

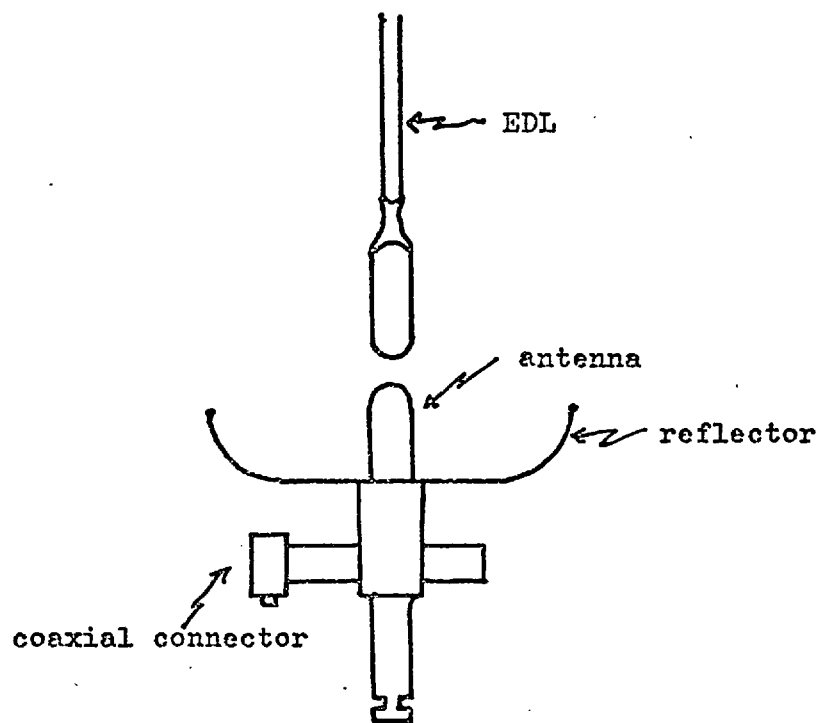
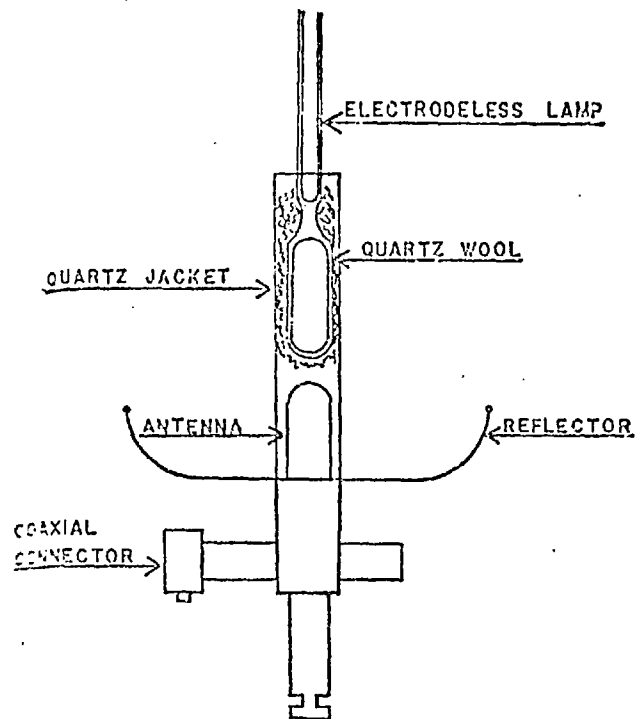


Figure 25

Mounting Configuration
of an EDL on an 'A' type
antenna.



Open quartz device for operating electrodeless discharge tubes

Figure 26

EDL in an evacuated quartz jacket (Figure 19) (61, 62). Both the quartz jacket and the quartz vacuum jacket were made out of quartz tubing 10 cm. long with an internal diameter of 2.2 cm. and a wall thickness of 0.2 cm. A simple rotary pump was used to pump the vacuum jacket down to about 0.5 torr. The amount of applied microwave power required to give the optimum operating conditions for an EDL, i.e. that power that yields the most intense atomic fluorescence consistent with stability, was found to be dependent on the boiling point of the fill material, see Figure 27. The amount of power required for a material with a given boiling point depends on which of the three mounting configurations is used. As expected, the vacuum jacketed EDL required the least power, and the EDL mounted alone needed the most. As the degree of thermal insulation of an EDL from its environment is increased, so does its operating temperature at a given power setting. This increase in operating temperature increases the vapour pressure, and thus the vapour concentration of the filler material. Thus the optimum operating vapour pressure of the filler material is reached at a lower power setting. As the amount of thermal insulation increases, so the optimum power decreases.

In order to simplify the behaviour patterns of the effect of power on the atomic fluorescence produced by an EDL, the EDLs are split into two groups. The groups are characterised by the boiling points of their filler materials:- group I boiling points below 900°C , and group II boiling points above 900°C .

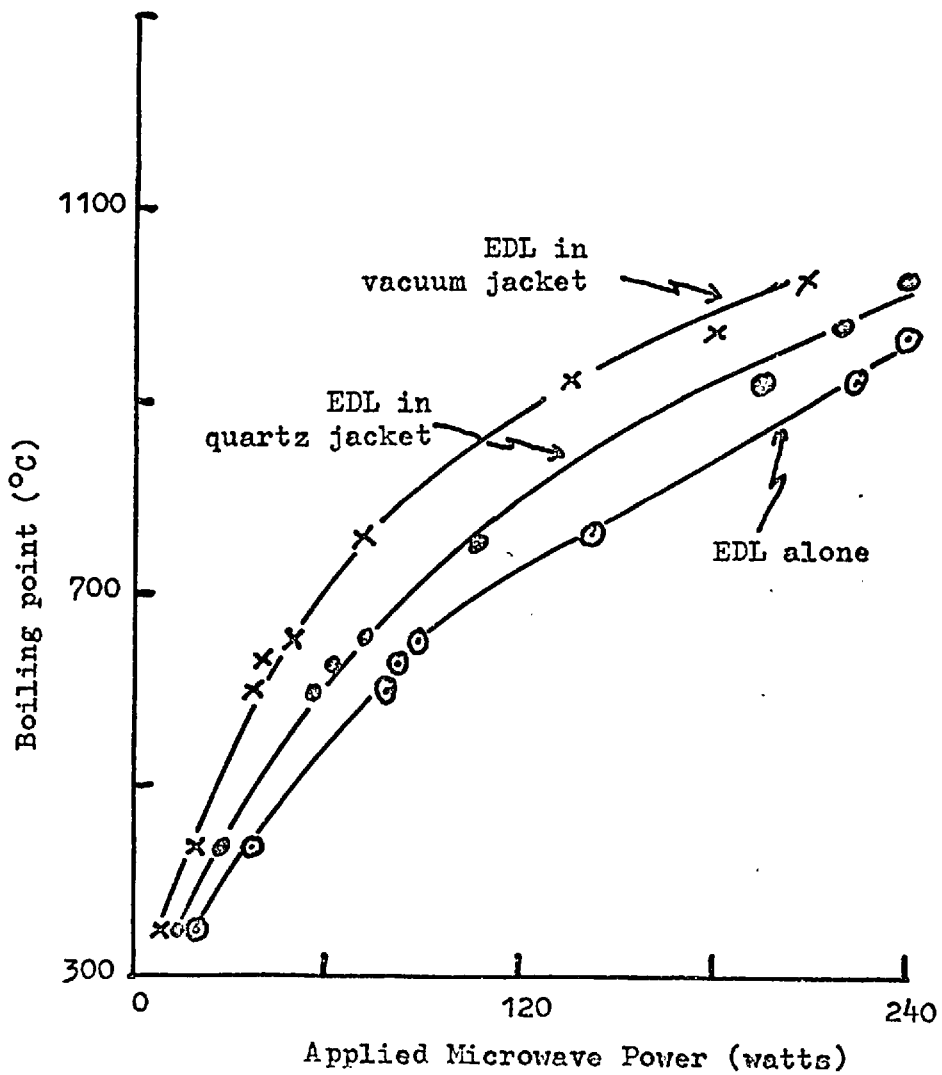


Figure 27

Effect of Boiling Point of the EDL fill material on the optimum applied microwave power of the EDL, for three different EDL mounting configurations.

The effect of applied microwave power on the intensity of the atomic fluorescence produced by group I EDLs is shown in Figure 28 for all three mounting configurations. All three configurations exhibit a decrease in atomic fluorescence intensity at high microwave powers; the microwave power level at which this decrease in intensity starts decreases with increased thermal insulation of the EDL. The effect of thermal isolation is to increase the effectiveness of the microwave power, and as the thermal insulation increases, smaller microwave powers are required to produce approximately the same discharge conditions. Group II EDLs, however, do not exhibit this atomic fluorescence intensity reversal, even for vacuum jacketed EDLs, see Figure 29.

The near exponential behaviour of the intensity of the atomic fluorescence, produced by the EDL when used by itself or in a quartz jacket, is probably due to the very low vapour pressure of the filler material which increases nearly exponentially with increases in temperature of the EDL. The intensity also increases exponentially probably because little or no line broadening and self reversal occur. The vacuum jacketed EDL only increases exponentially at low powers; at higher powers the operating temperature is high enough to produce an appreciable atomic vapour pressure and concentration, so that line broadening and self absorption processes start to compete with increases in intensity brought about by increased vapour concentrations.

These groupings of EDLs by boiling points are not quite as

Figure 28

Effect of Applied Microwave Power
on Atomic Fluorescence Intensity
produced by group I EDLs for three
different EDL mounting configurations.

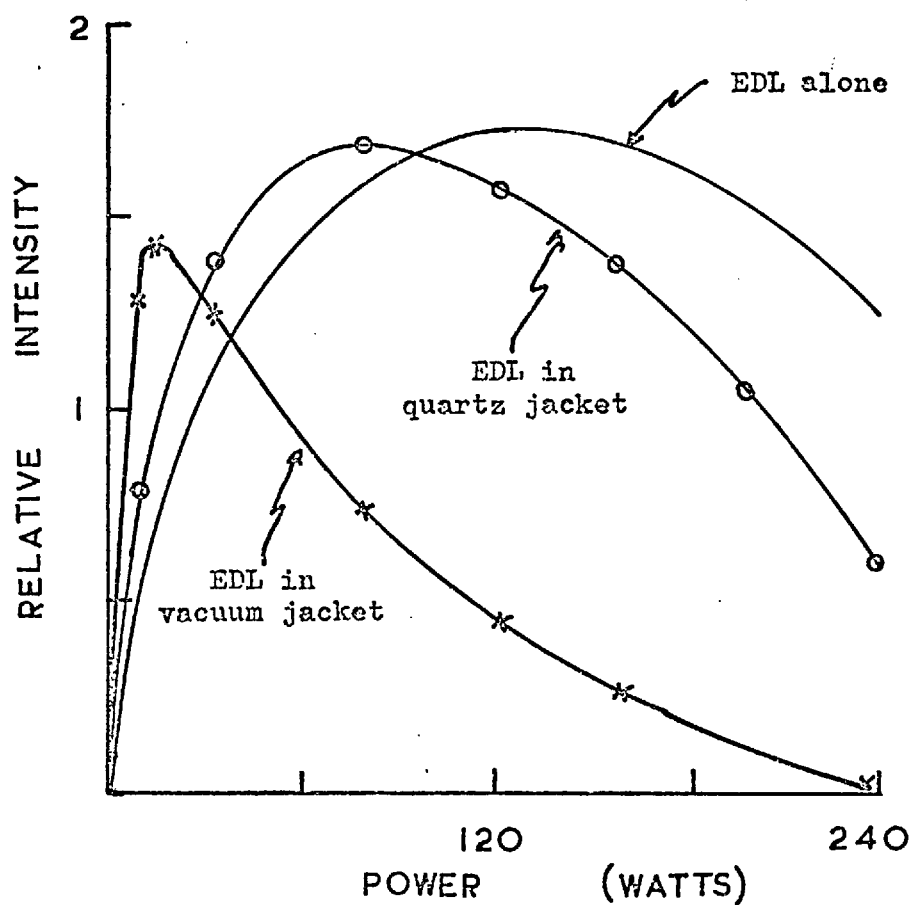
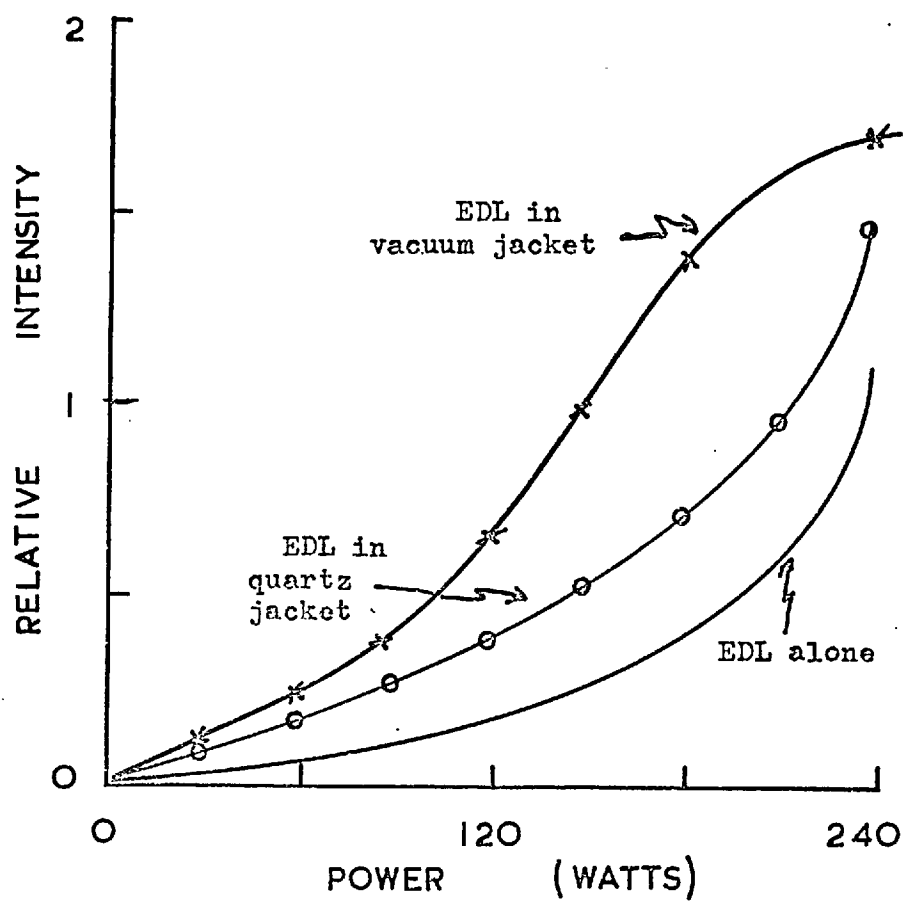


Figure 29

Effect of Applied Microwave Power
on Atomic Fluorescence Intensity
produced by group II EDLs for
three different EDL mounting
configurations.



rigid as explained above, but are only presented as a general guidance to their behaviour patterns. A gradual transition from one group to the other actually occurs.

With the results of this last series of experiments, see Figures 23, 24, 27, 28, and 29, it is now possible to predict the best fill gas pressure, filler material, amount of microwave power required, and configuration of the EDL.

2-6 General Procedure for making any EDL

The procedure for making an EDL for any element is outlined below:

(1) Make the EDL blank out of 7-9 mm. internal diameter quartz tubing, see section 2-3(a), with a bulb length of about 35 mm.

(2) Choose the compound that is to be used as the filler material; the compound should be the element or one of its halides. When making this choice, one should aim at finding a filler material that has a boiling point of between 600° and 1000°C . This allows the material to be sufficiently volatilised to produce an intense, non severely reversed discharge. If an element or a halide of this element is not available with its boiling point in this range, it is preferable to use a material with a boiling point below 600°C . rather than above 1000°C .

(3) The EDL blank should be placed in a muffle furnace, at 900°C ., for 12 hours; purged with a low pressure discharge of the filler material for 20 minutes, see section 2-5(b).

(4) The EDL blank is connected to the vacuum system and

any filler material left in the blank is sublimed out under vacuum. About 2 milligrams of the filler material are then introduced into the lamp blank and slowly vacuum sublimed about 9 mm. up the lamp walls. The lamp is then purged with the fill gas and pumped down to about 10^{-5} torr. The EDL is then filled with the fill gas to the appropriate pressure and sealed as quickly as possible. The fill gas pressure required is found by reference of the boiling point of the filler material to Figure 23 for helium fill gas, and to Figure 24 for argon fill gas.

(5) The optimum applied microwave power setting is found, in a similar way, by reference to Figure 27.

EDLs are most successfully operated in the least thermally isolated environment which is consistent with being able to attain the optimum power.

For example, it can be seen from Figure 27 that:

(a) An EDL containing a filler material with a boiling point of 900°C . could be optimally operated at 200 watts without a jacket; at 160 watts in a quartz jacket; or at 130 watts in a vacuum jacket. Thus, if 240 watts of microwave power are available, the EDL should be operated at 200 watts without a jacket (i.e. the least thermally isolated condition). But if only 180 watts are available, it should be operated at 160 watts in a quartz jacket, or if only 140 watts are available, it should be operated at 130 watts in a vacuum jacket.

(b) An EDL containing a filler material with a boiling point of 1300°C . requires more than 240 watts for all three configurations;

the best conditions for operation would be 240 watts in a vacuum jacket, as this is the nearest to the optimum conditions.

EDLs, to be used other than for atomic absorption, should always be filled with helium gas as these lamps are more intense than those filled with argon. This higher intensity is due to the higher operating temperature of helium EDLs; unfortunately, this higher temperature increases the line widths of the atomic resonance lines by increasing the Doppler, collisional and resonance line widths. Thus, if an EDL is ever used for atomic absorption, i.e. for arsenic or selenium, argon fill gas should be used because of the inherently narrower resonance produced, which is very important in atomic absorption spectrometry.

Many EDLs, of uninvestigated elements, have been successfully made using the above procedure.

2-7 Microwave Coupling Devices.

All of the optimisation of the preparation and operating procedures carried out as described above were exclusively for the "A" type antenna; however, many other types of coupling devices are also available. For microwaves, the coupling devices can be split into three groups:-

- (1) Antennas: initially designed for medical therapeutic work.
- (2) Cavities: designed specifically for gaseous discharges.
- (3) Waveguides: designed mainly for coupling microwave power of frequencies above 3000 MHz.

Two microwave antennas were investigated : the "A" and "C"

types available from Raytheon Company, U.S.A. The "C" type antenna was found to be useless, except for mercury EDLs, as it was unable to concentrate enough power in the area of the EDL to produce a metal vapour discharge. The "A" type antenna was found to operate very successfully as demonstrated in the optimisation of EDL preparation and operating conditions experiments described above.

Three different types of cavities were investigated: the foreshortened $\frac{3}{4} \lambda$ Broida type, the foreshortened $\frac{1}{4} \lambda$ Evenson type (both obtained from Electro Medical Supplies Limited, Wantage, U.K.), and a foreshortened $\frac{3}{4} \lambda$ Broida type fitted with two capacitative tuning stubs (obtained from Evans Electro Selenium Limited, Halstead, Essex, U.K.). All three of the cavities coupled the microwaves to the EDLs more efficiently than either of the antennas. Unfortunately, unlike the antennas, they reflected fairly large quantities (10-50%) of the applied microwave power back to the magnetron, in the microwave generator, making reproducible intensities difficult to obtain.

Ideally, all the filler material in an EDL should be in the vapour phase during operation. However, this is rarely true, and frequently small amounts of solid material are present. The amount and the position of this solid material changes during operation of an EDL, and these changes produce variations in the coupling efficiency of the microwave coupling device. When a cavity is used, changes in coupling efficiency greatly affect the amount of power reflected back to the magnetron,

which in certain circumstances can actually affect the amount of power produced. This change in power output causes a further change in the discharge conditions of the EDL, which can affect the position and the amount of any solid material present in it. This process usually results in a cyclic variation in the intensity of the radiation output of the EDL. A resistive attenuator, with a power attenuation of 3db., obtained from Electro Medical Supplies Limited, Wantage, U.K., connected between the magnetron and the microwave cavity was found to diminish this effect by attenuating both the forward and the reflected microwave power. In consequence, an increase in stability of operation of the EDL was achieved, see Table 2-5. Because of the very small amounts (2-5%) of power reflected back to the magnetron by the "A" type antenna, the attenuator has very little effect on the stability of operation of an EDL when used with the antenna.

The drift and the short term noise of the intensity of resonance radiation emitted from several EDLs were measured for both the "A" type antenna, and the Broida $\frac{3}{4}\lambda$ cavity, with and without the attenuator in circuit (see Table 2-5).

The attenuator, when used with the cavity, decreased the short term noise by 14%, except for those EDLs that operate at applied powers of less than 20 watts (mercury and selenium) for which a decrease in noise of about 50% was observed. This latter observation is probably a result of excessive instability of the magnetron at low microwave power outputs. When the

Table 2-5

Effect of attenuator on noise and drift of resonance radiation intensity emitted by EDLs, for the "A" type antenna and the $\frac{3}{4}\lambda$ cavity

Lamp type	Wavelength of measurement n.m.	No attenuator				Attenuator *			
		A type antenna +		$\frac{3}{4}\lambda$ cavity		A type antenna +		$\frac{3}{4}\lambda$ cavity	
		Noise %	Drift %/hr.	Noise %	Drift %/hr.	Noise %	Drift %/hr.	Noise %	Drift %/hr.
Cd	228.8	1.1	-0.5	3.1	-2.0	1.0	-0.5	2.7	-2.1
Zn	213.9	1.2	-0.6	3.3	-2.2	1.2	-0.5	2.8	-2.1
PbI ₂	283.3	1.4	-0.5	4.2	-1.8	1.4	-0.6	3.6	-1.7
TlCl	276.7	1.0	-1.1	2.8	-2.0	1.0	-1.0	2.4	-2.1
Hg	253.7	0.9	-0.2	5.0	-3.2	0.8	-0.3	2.5	-2.3
Se	196.1	1.1	-0.4	6.4	-3.6	1.1	-0.5	3.8	-2.9

* Twice as much power is required when the attenuator is in circuit.

+ EDLs operated in a vacuum jacket.

cavity is used in conjunction with the attenuator, or when the "A" type antenna is used, both mercury and selenium EDLs require applied powers of greater than 20 watts, thus this instability is avoided. Little or no decrease of the noise was observed when the "A" type antenna was used in conjunction with the attenuator, because of the low reflected power characteristic of antennas. The drift of resonance line intensity was not significantly affected by the use of the attenuator. For all of the EDLs investigated, the short term noise and the drift were considerably less for the "A" type antenna than for the $\frac{3}{4}\lambda$ cavity, even when the cavity was used in conjunction with the attenuator. Also, the time taken to reach a stable EDL intensity (the warm up time) was shorter for the "A" type antenna (3-4 minutes) than for the cavity (9-15 minutes). The attenuator lengthened the warm up times considerably, probably because it had to come to thermal equilibrium before a stable microwave output was obtained.

Consequently the "A" type antenna was found to be more effective than the $\frac{3}{4}\lambda$ cavity for use with EDLs for atomic spectrometry. The "A" type antenna does have the disadvantage of requiring higher microwave powers; it is also a health hazard because of its property of emitting microwave power over a fairly large area. Care should be taken to place the "A" type antenna well away from the operator as his eyes may be damaged by continual close exposure.

The Evenson $\frac{1}{4}\lambda$ cavity has a better coupling efficiency

than either the "A" type antenna or the Broida $\frac{3}{4}\lambda$ cavity, but it reflects large amounts of microwave power. However, it is possible at any instant to tune the cavity, with the use of its two tuning stubs, so that virtually no power is reflected back to the magnetron. Unfortunately, the cavity soon drifts out of tune producing much more short term noise and drift of the EDL intensity than that produced by the $\frac{3}{4}\lambda$ cavity. No further investigation of the $\frac{1}{4}\lambda$ cavity was carried out; its only use in atomic spectroscopy would be in applications where large concentrations in power are required and where stability is of little importance.

Due to the greater coupling efficiencies of the cavities, over the "A" type antenna, they can be used advantageously for EDLs containing high boiling point filler materials, for which the "A" type antenna is unable to supply the optimum power.

EDLs prepared and operated under the optimum conditions for the "A" type antenna, as previously described, can always be made to operate successfully in either of the cavities, although much lower applied microwave powers are required. However, no claim is made to these being the optimum values. Previous studies (63, 104, 105) suggest that the choice of fill gas pressure is much less critical and applied microwave powers are much lower than for those found to be optimum for the "A" type antenna. Methods other than attenuation have been tried by several workers to overcome the problems associated with high reflected powers. Broida and co-workers (78) have reported

that the percentage of reflected power can be reduced by a factor of six by the addition of a matching stub located on the coaxial connector. Aldous et al. (63, 129) have found this type of matching stub to give an improvement in noise and warm up times, for EDLs of many elements, over the standard $\frac{3}{4}\lambda$ cavity. Aldous (63) has found that even better matching can be realised by using capacitative tuning stubs, resulting in shorter warm up times and an increase in "the quality of the spectral output" from a wide range of EDLs.

The warm up times, short term noise and drift of an EDL in a $\frac{3}{4}\lambda$ cavity fitted with two capacitative tuning stubs (obtained from Evans Electro Selenium Limited, Halstead, Essex, U.K.) were measured for several EDLs and compared to the values obtained from a standard $\frac{3}{4}\lambda$ cavity, see Table 2-6. The warm up times and the short term noise were found to be about 50% smaller for the tuned cavity, but the drift rate was increased by about 100%.

Table 2-6

Comparison of short term noise, drift and warm up times between a standard $\frac{3}{4}\lambda$ cavity and an EEL tuned $\frac{3}{4}\lambda$ cavity.

Lamp type	Standard $\frac{3}{4}\lambda$ cavity			EEL tuned $\frac{3}{4}\lambda$ cavity		
	Warm up time mins.	Noise %	Drift %/hr.	Warm up time mins.	Noise %	Drift %/hr.
Gd	10	3.1	-2.0	5	2.0	-5.3
Zn	12	3.3	-2.2	5	2.2	-5.2
PbI ₂	14	4.2	-1.8	6	2.3	-4.7
TlCl	14	2.8	-2.0	7	2.0	-5.6
Hg	10	5.0	-3.2	6	2.1	-4.8
Se	9	6.4	-3.6	4	3.2	-6.1

The decrease in short term noise for the tuned $\frac{\lambda}{4}$ cavity was probably due to the much lower amount of reflected power. The increase in drift rate was due to the cavity gradually drifting out of tune; this drift could be decreased by constant attention to the tuning stubs to keep the reflected power at a minimum.

CHAPTER III

ATOMIC SPECTRAL SOURCES FOR ALKALI AND ALKALINE EARTH ELEMENTS

3.1 Introduction

The previously described method for the production of microwave excited electrodeless discharge lamps was found to be unsatisfactory for the alkali and alkaline earth elements, with the exception of beryllium (108), because of the rapid irreversible attack of the vapour of these elements on the quartz walls of the lamps. This attack is accompanied by a rapid decrease in the spectral output (6, 83, 133) which makes them unsuitable for atomic spectrometry. The attack produces a frosting, and sometimes a blackening, of the quartz walls, which both decreases their transmission and effectively removes the fill material. Aldous et al. (133) reduced this problem for potassium sources by preboration of the EDL blanks, and for potassium, sodium, and magnesium sources by using a sodium vapour resistant two-ply glass for blank fabrication. Although both of these techniques increased the lamp lifetime to about 100 hours, because of difficulties in lamp blank fabrication fairly high failure rates were encountered. Ham and Walsh (83) reported that pyrex can be used for about 10 hours for sodium hollow cathode discharge lamps before darkening of the surface became serious. However, the author has found that EDLs made out of pyrex are attacked rapidly and often deform because of the high running temperature of the lamps. Mansfield (92) and Mansfield et al. (61) have reported the successful fabrication of magnesium, strontium and calcium EDLs using their iodides. This is contrary to the observations of the author and Cooke (105).

Human et al. (64) have recently tried an altogether different approach for copper and calcium sources; they directly coupled microwave power to the anode of a hollow cathode discharge lamp while it was operated in the conventional manner. These sources were both stable and long-lived, but their intensity was only seven times as intense as a normal HCL, thus making them unsuitable for atomic fluorescence spectrometry.

In an effort to overcome the short lifetimes and high drift rates associated with the attack of alkali and alkaline earth vapours on the quartz walls of EDLs, five different arrangements were investigated. Two of these arrangements were solely for sodium spectral sources.

3.2 Soda-glass EDLs

The attack of sodium vapour on EDL walls when using sodium metal or a sodium halide produces sodium silicate (6), which steadily diminishes the transmission of the quartz resulting in high drift rates. In an attempt to stop this silicate formation, soda-glass was used as a fill material for an EDL prepared in the normal manner (see Chapter II). Although a slight frosting of the quartz occurred, the lamp radiation at the 303.2 n.m. and the 589 n.m. doublets was intense, stable and long-lived. Because of the low vapour pressure of sodium in soda-glass, the optimisation of the operating and preparation conditions was carried out using a $\frac{3}{4}$ λ Broda type cavity. Table 3-1 gives the optimum fill gas pressure and microwave power for both helium and argon filled EDLs, and compares their short term

noise, drift rates and lifetimes. The helium filled lamp is more intense, noisier and has a larger drift rate and a shorter lifetime than the argon filled lamp.

Table 3-1

Comparison of argon and helium filled soda-glass EDLs. Intensities were measured at the 589 n.m. doublet.

EDL optimum operating conditions	Relative Intensity	Short term noise (%)	Drift (%/hr.)	Average lifetime (hours)
12 torr of He 170 watts	120	2	-3.0	160
7 torr of argon 190 watts	82	1.5	-1.9	250

Both the argon and the helium filled soda-glass EDLs have been used successfully for atomic absorption and fluorescence spectrometry. Recently Woodward (106) has extended this approach by using commercially available borates and laboratory prepared silicates for lithium, potassium and sodium, and commercially available magnesium phosphate as fill materials. His lamps were intense, but their lifetimes were fairly short, about 30 hours. He did not optimise his preparation and operating conditions and he did not report any noise and drift rates.

3.3 Flowing atmospheric argon discharge (FAAD) in a purex tube.

A low pressure discharge of a rare gas was found capable of vapourising and exciting the sodium atoms in soda-glass when it was used as a fill material in an EDL, see Section 3.2.

Unfortunately, the walls of these EDLs became slightly frosted

resulting in a lifetimes of 150-250 hours which necessitated fairly frequent manufacture of replacement lamps. An investigation of a flowing rare gas system was carried out in an effort to eliminate this problem.

Pratt (107) found that argon at atmospheric pressure flowing through a tube, contained in a $\frac{3}{4}$ λ Broida type cavity, is capable of producing a gaseous discharge when excited with 100 watts of microwave power. The author has found that this type of atmospheric discharge is capable, under certain conditions, of heating the inside of the tube walls to between 650 and 800°C. Initially, a 7 m.m. internal diameter pyrex glass tube with a wall thickness of 1 m.m., through which argon passed at atmospheric pressure, was placed inside a $\frac{3}{4}$ λ cavity, see Figure 30. When microwave powers of above 70 watts were applied to the cavity, this arrangement was capable of producing a discharge which vapourised sodium atoms from the pyrex walls of the discharge tube. These atoms were then excited in the argon discharge region where they emitted intense sodium resonance radiation. The maximum resonance radiation was produced by an argon flow rate of 100 mls./minute with 170 watts of applied microwave power. Under these conditions the discharge tube walls became extremely hot, and after approximately an hour of continuous operation the discharge would melt a hole in the wall through which it shorted to the cavity. This atmospheric argon discharge in the flowing system took the form of several pinched arcs which frequently changed position in the tube. The change of position of the

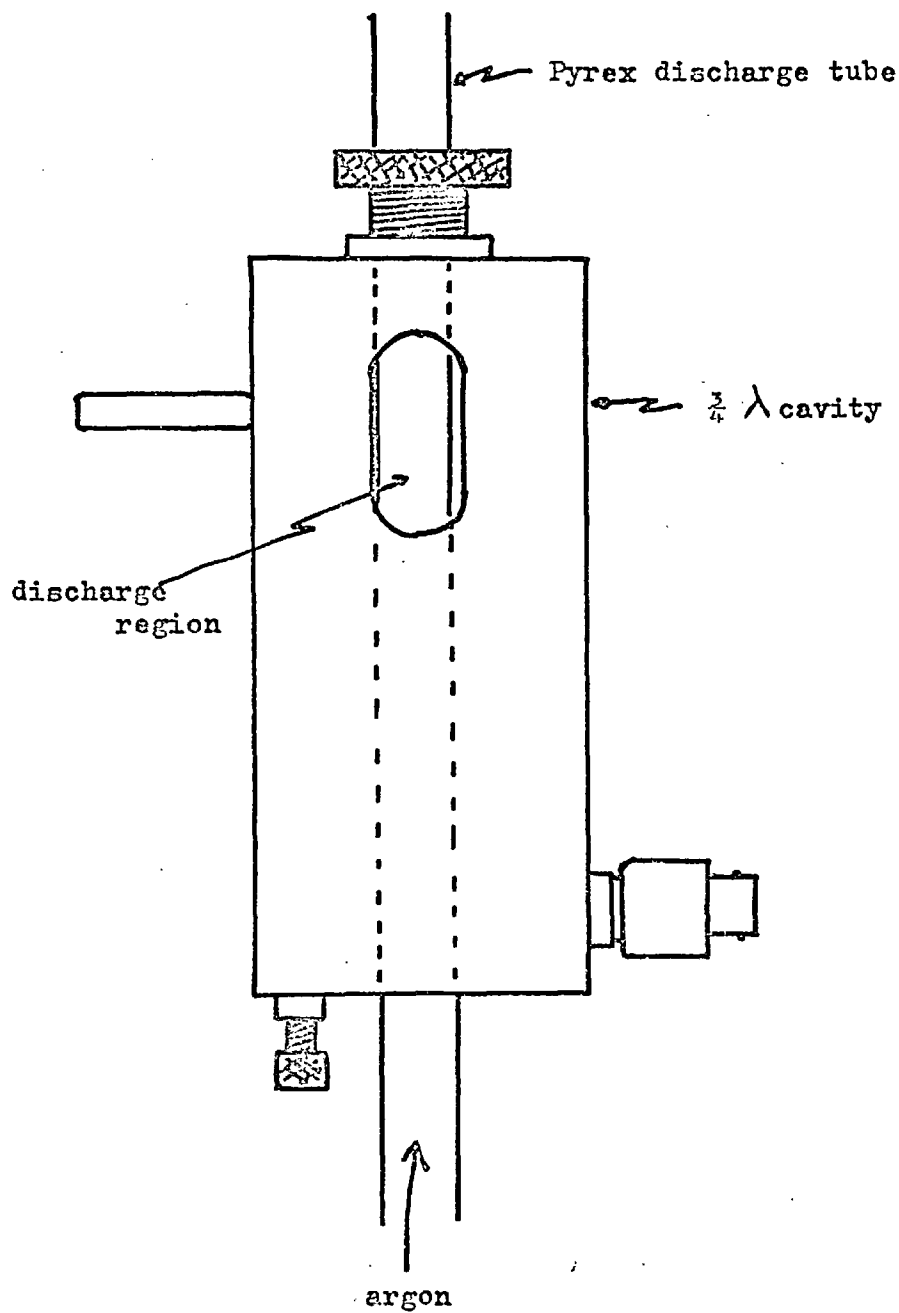


Figure 30

FAAD Lamp

discharge and its tendency to burn holes in the pyrex walls produced large changes in the sodium emission intensity and very high noise levels. To diminish this instability the pyrex discharge tube was modified, as shown in Figure 31. The modified discharge tube was made by drawing out a piece of pyrex tubing (9 m.m. external diameter, 3 m.m. wall thickness) so that the discharge region of the tube had an internal diameter of about 1.5 m.m. and a wall thickness of about 2 m.m. The argon discharge was confined to the drawn out section by adjusting the position of the discharge tube in the cavity. The narrow bore of this section reduced the emission flicker noise by confining the discharge to one position. The increased heat capacity of the thicker walls stopped the discharge from melting or holing the discharge tube.

The effect of applied microwave power and argon flow rate on the intensity of sodium atomic fluorescence produced by the sodium resonance radiation emitted by the discharge was investigated for both the $\frac{1}{4} \lambda$ and $\frac{3}{4} \lambda$ cavities. The spectrometric system used was the same as that used in Chapter II except that an argon hydrogen diffusion flame was used. The conditions which gave the best atomic fluorescence signal are given in Table 3-2.

Table 3-2

Optimum conditions for a FAAD pyrex discharge tube.

Cavity	Applied microwave power (watts)	Argon flow rate mls/min	Relative fluorescence intensity
$\frac{1}{4} \lambda$	100	200	104
$\frac{3}{4} \lambda$	150	220	151

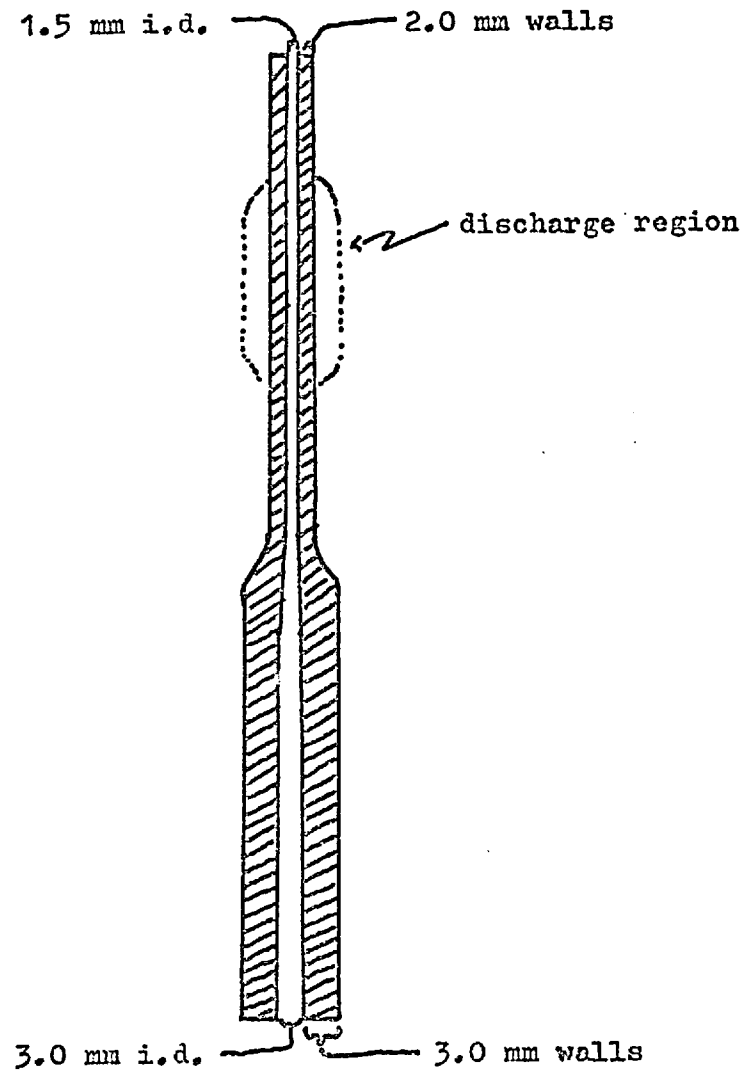


Figure 31

Modified Discharge Tube
for a FAAD lamp.

The short term noise of the emitted resonance radiation was slightly less for the $\frac{3}{4}\lambda$ cavity (1.5%) than for the $\frac{1}{4}\lambda$ cavity (1.9%). Both cavities gave low drift rates of about 1% of the resonance radiation intensity per hour, and very long lifetimes; no failure has yet been observed. The only apparent deterioration was a slight searing of the inside of the discharge tube walls. Although the $\frac{3}{4}\lambda$ cavity requires more power and a higher argon flow rate, for the maximum intensity, than the $\frac{1}{4}\lambda$ cavity, it gave a superior performance with respect to intensity and short term noise. The line to background ratio for the 589 n.m. line pair was better than 100:1, and for the 303 n.m. line pair better than 80:1, for both cavities. The limits of detection of the sodium atomic fluorescence at 589.0 n.m. produced by irradiating an argon hydrogen diffusion flame, into which sodium solutions were sprayed, with the soda-glass EDL, the FAAD in a pyrex tube and a Wotan vapour discharge lamp were compared. The FAAD was found to give the lowest limit of detection, see Table 3-3, followed by the soda-glass EDL; the vapour discharge lamp was much worse than the other two sources, probably because it was very self reversed.

Table 3-3

Limits of detection of sodium atomic fluorescence
for three different primary sources

Source used	Limits of detection of sodium (ppm)
Wotan vapour discharge lamp	0.05
Soda-glass EDL	0.004
FAAD in a pyrex tube	0.002

3.4 Flowing atmospheric argon discharge (general application)

The flowing argon discharge described in 3.3 has been found to emit stable, intense resonance radiation for a considerable time. The vapourisation of the metal vapour (i.e. sodium) depended on its presence in the walls of the discharge tube. Thus, the applicability of this method is limited to those elements that could be incorporated into the wall material from which the discharge tube is made without affecting its transmission of the resonance radiation.

Another method of introducing the vapour of various metals into the argon discharge was investigated to circumvent this problem. The tube through which the argon flowed, and in which the discharge was contained, consisted of a 10 in. length of quartz tubing with an internal diameter of 13 m.m. and a wall thickness of 1 m.m. A quartz cup with an external diameter of 10 m.m. was joined onto a 7 in. length of 4 m.m. diameter quartz rod. About 1 gram. of the element (or a halide of the element), whose spectrum it was desired to excite, was placed into the cup. The cup was then inserted into the quartz tube and adjusted so that it just appeared at the bottom of the discharge viewing aperture, see Figure 32. The argon flow was then started and the discharge initiated by turning on the microwave power and sparking a "tesla" vacuum tester against the discharge tube in the viewing aperture region. The quartz cup and the material in it are heated by the argon discharge, and under the appropriate conditions this temperature becomes

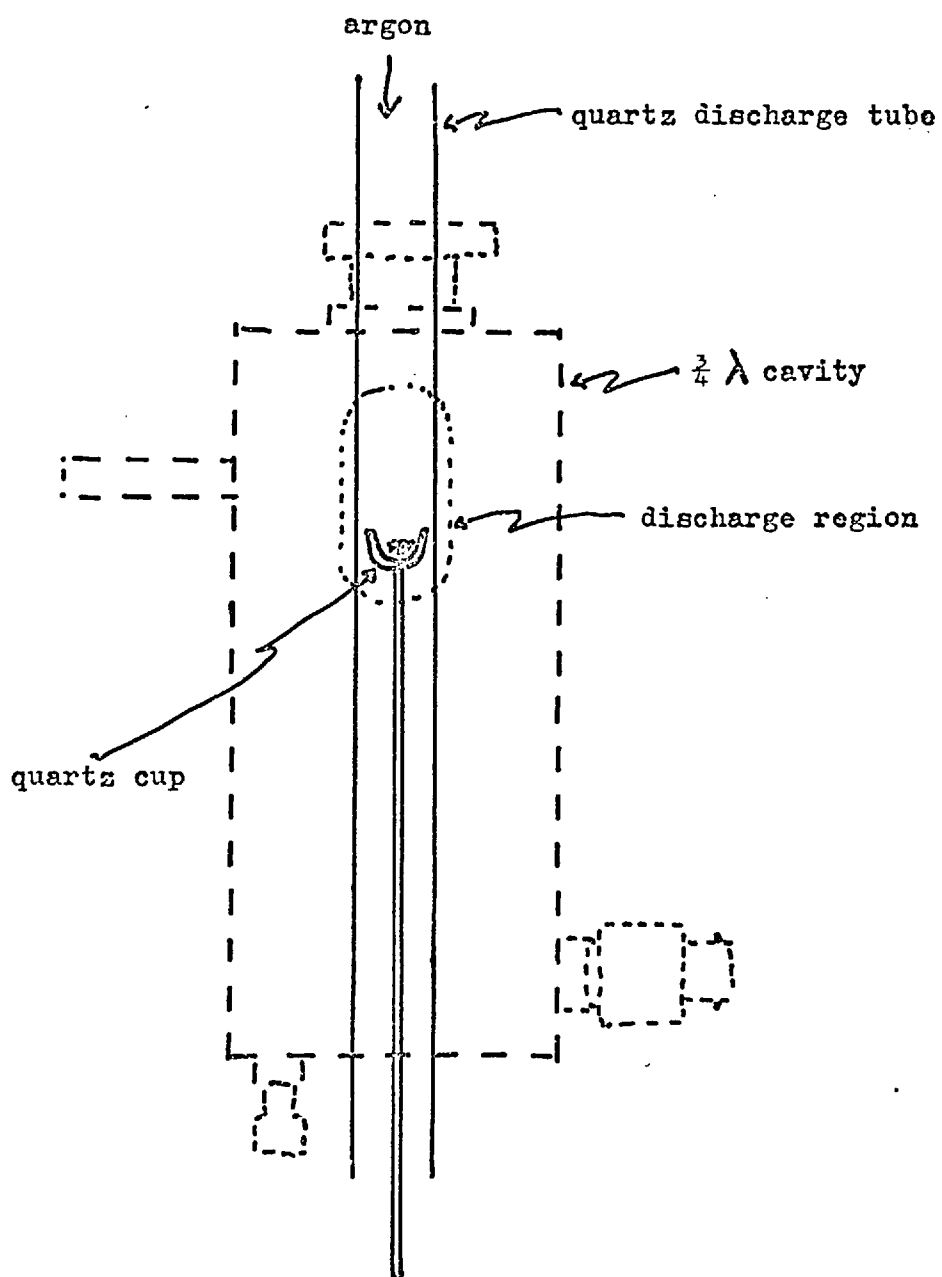


Figure 32

FAAD lamp modified for
quartz cup operation.

sufficiently high to vapourise enough fill material to produce an atomic vapour discharge, which will strongly emit the resonance radiation of the fill material. The vapourised fill material is swept through the discharge by the argon flow, where it cools down and is deposited on a part of the discharge tube not in the discharge region. This net transference of material from the cup to another part of the discharge tube gradually empties the cup, which will eventually result in no more atomic vapour reaching the argon discharge; at this point the discharge will emit solely argon radiation, and the lamp may be said to have failed. The cup can then be refilled with fill material and the lamp reignited and the process repeated.

The effect of applied microwave power and the argon flow rate on the intensity of resonance radiation emitted from FAAD lamps containing the alkali and alkaline earth elements (Li, Na, K, Rb, Cs, Be, Ca, Mg, Sr, and Ba) was investigated. Both the elements and their halides were used as cup fill materials; the halides were found to be more useful as they produced more intense resonance radiation and longer lamp lifetimes. The elements were more easily vapourised, and in some instances caught fire as little pieces dropped from the bottom of the discharge tube. Of the halides, the chlorides were found to give higher intensities and better stabilities, with the exception of potassium, where the bromide was used. Potassium bromide gave a similar intensity to the chloride, but the stability and lifetime were much better for the bromide.

The emission of radiation from the discharge was found to be very unstable at argon flow rates below 20 mls./min. and above 360 mls./min. At very high powers (above 190 watts), the quartz cup often fused to the quartz discharge tube making further filling of the cup impossible. Table 3-4 gives the conditions that produce the most intense radiation emission and the amount of short term noise, drift and lifetime of the radiation output for various alkali and alkaline earth elements. The lifetimes are for 1 gram, of fill material in the cup, and all the results are an average of five runs.

Generally, the fill materials with the higher boiling points (CaCl_2 , BaCl_2 , KBr , MgCl_2 and NaCl) gave the most satisfactory results. They give low noise levels and drift rates and long lifetimes. Beryllium chloride has a low boiling point and when used as a fill material results in excessive noise and drift rates and a very short lifetime. These results from Table 3-4 suggest that the less volatile the fill material, the longer was the lamp's lifetime and the lower the noise and drift rates. Materials with high volatilities were quickly removed from the cup and the discharge region to a cooler part of the discharge tube, resulting in an early failure of the lamp and high drift rates. Slight changes in the operating temperature of a FAAD lamp caused large differences in the rate of vapourisation of volatile materials, which resulted in a noisy radiation output. Several other materials (elemental aluminium, manganese chloride, elemental zinc, cuprous chloride,

Table 3-4

Optimum operating conditions, noise, drift rates and lifetimes for several FAAD lamps.

Cup fill material	Resonance line wavelength (nm)	Boiling point of fill material (°C.)	Optimum power (watts)	Optimum argon flow rate (mls/min)	Noise (%)	Drift (%/hr)	Lifetime (hours)
LiCl	670.7	1390	150	180	2.2	-1.9	2.2
NaCl	589.0	1413	160	150	2.0	-1.9	2.4
KBr	766.5	1435	165	150	1.8	-2.0	2.4
RbCl	780.0	1390	150	145	1.9	-1.9	2.1
CsCl	852.1	1290	130	140	2.6	-2.3	1.8
BeCl ₂	234.9	520	85	136	10.1	-8.0	0.33
MgCl ₂	285.2	1412	160	170	1.7	-1.3	2.5
CaCl ₂	422.7	> 1600	175	200	1.3	-1.2	3.2
SrCl ₂	460.7	1250	130	150	2.0	-1.9	1.8
BaCl ₂	553.6	1560	170	180	2.1	-1.3	2.3

silver chloride and elemental copper and mercury) covering a wide range of boiling points ($357-2595^{\circ}\text{C.}$) were used to further investigate these effects of volatility of the fill material on the lamp's performance. The results from this investigation, see Table 3-5, confirm that materials with low volatilities gave the lowest noise and drift rates and longest lifetimes. Successful FAAD lamps cannot be made for volatile fill materials. When mercury, the most extreme case, was used as a fill material, very high noise (35%) and drift rates ($-42\%/ \text{min.}$) were encountered, together with a very short lifetime (1.2 minutes). Elemental copper (boiling point 2595°C.), when used as a fill material, gave very low noise and drift rates and long copper discharge lifetimes. However, the copper resonance lines were only weakly emitted, thus making elemental copper unsuitable as a fill material for FAAD lamps.

If the maximum acceptable limit on noise is 3.0% and on drift is $-3.0\%/ \text{hr.}$ and the minimum lifetime is 1.5 hours, then the limitations on fill materials for use in FAAD lamps, where high intensity is desired, can be summarised as follows:-

- (1) The fill material should have a minimum boiling point of 1240°C. , so as to keep the noise, drift rate and lifetime within acceptable limits;
- (2) The fill material should have a maximum boiling point of about 2200°C. to ensure that enough atomic vapour is produced so that an intense atomic radiation is emitted.

Table 3-5

Optimum operating conditions, noise, drift and lifetimes
of FAAD lamps for materials with various volatilities.

Cup fill material	Resonance line wavelength (nm)	Boiling point of fill material (°C.)	Optimum power (watts)	Optimum argon flow rate (mls/min)	Noise (%)	Drift (%/hr)	Lifetime (hours)
Cu	324.7	2595	200	210	1.2	-1.0	8.0
Al	396.2	2056	200	200	2.3	-1.2	4.1
AgCl	328.1	1550	170	175	2.4	-1.4	2.5
CuCl	324.7	1490	160	170	2.5	-1.5	2.4
MuCl ₂	279.5	1190	120	130	2.8	-3.1	1.3
Zn	213.9	969	100	105	3.9	-5.1	0.85
Hg	253.7	357	60	35	34	-42%/min	0.02

The best boiling point for the fill material is between 1400 and 1650°C. where high intensity, good stability and a long lifetime are obtained.

In comparison with other atomic spectral sources, the lifetimes of the FAAD lamps (1.6-5 hours) are very short, but because of the simplicity of remaking the lamp, this does not present a major problem. When the lamp fails, that is it no longer emits the intense atomic resonance radiation of the fill material, the cup is removed from the discharge tube, refilled with the appropriate fill material, replaced in the discharge tube, and the discharge is reignited. After several refillings, it is often necessary to wash the discharge tube with distilled water to remove any excess fill material which has built up in the bottom section of the tube.

These sources were evaluated for atomic fluorescence studies of the alkali earth elements, copper and silver. FAAD lamps containing cuprous chloride and silver chloride were included in this investigation because their EDLs have relatively short lifetimes as a result of the metal plating out on the quartz walls following the thermal breakdown of the chloride into chlorine and the metallic element. A premixed air/hydrogen flame was used for all the atomic fluorescence studies, except for beryllium when a premixed nitrous oxide/acetylene flame was used. During operation of the FAAD lamps, some vapour of the fill material was swept out of the bottom of the discharge tube, by the argon flow. Because of the nearness of this tube to the analytical flame, some of this vapour becomes entrained by the flame when it produced a very large background signal.

To overcome this problem a one metre length of polythene tubing was attached to the end of the discharge tube, and the open end of the polythene tubing was placed as far away from the flame as possible. This procedure completely removed this interference without affecting the performance of the lamp. The limits of detection, i.e. that concentration of the analyte which produced an atomic fluorescence signal twice as large as the noise signal, were determined experimentally for all the alkaline earth elements using their FAAD lamps. Table 3-6 gives the fill material of the FAAD lamp, the wavelength of measurement of the fluorescence signal, the experimentally obtained limit of detection, and the best limit of detection obtained by other workers with the source that they used. All fluorescence measurements were made on a Perkin-Elmer model 290 atomic absorption spectrophotometer modified as described by Browner et al. (110) using a capillary burner of the type described by Aldous et al. (156), and an argon separated flame was burnt.

Table 3-6

Comparison of limit of detections for FAAD lamps to the best previously obtained for alkaline earth elements.

Fill material	Wavelength (n.m.)	Limit of detection for FAAD lamp (ppm)	Best limit of detection previously obtained (ppm)	Source used to obtain this limit of detection
BeCl ₂	234.9	0.9	0.01	Be/I ₂ EDL (108)
MgCl ₂	285.2	0.0008	0.001*	Mg HCL (109)
CaCl ₂	422.7	0.002	0.02	Ca/I ₂ EDL (62)
SrCl ₂	460.7	0.005	0.03	Sr/I ₂ EDL (62)
BaCl ₂	553.7	0.025	7 ⁺	150W xenon arc(111)
CuCl	324.7	0.001	0.001	Cu HCL (65)
AgCl	328.1	0.0001	0.0001	Ag/I ₂ EDL (62)

- * A different method of calculating the limit of detection was used in this study; the probable corrected value would be about 0.003 ppm.
- + In this study, barium was determined by scatter off the barium salt particles; no studies on the atomic fluorescence of barium have been previously reported.

The FAAD lamps were found to be very useful for atomic fluorescence spectrometry. They gave superior limits of detection for magnesium, calcium, strontium and barium; the same limits of detection for copper and silver; and worse limits of detection for beryllium, than those given by the best previously used sources.

From these atomic fluorescence studies, it was concluded that FAAD lamps were excellent sources of intense, stable, not too severely self reversed atomic resonance line radiation for the alkaline earth elements, with the exception of beryllium. Fortunately beryllium is the only alkaline earth element for which a stable, intense, long lived EDL has been made (108). The atomic fluorescence produced by alkali element FAAD lamps was not investigated, with the exception of sodium, because no valid comparison studies were available, but their intensities and stabilities were of the same order as the alkaline earth lamps. A limit of detection of 0.001 ppm. was obtained for sodium atomic fluorescence, when an argon/hydrogen diffusion flame was used, which compares very favorably with the values obtained for the soda-glass EDL and the FAAD in a pyrex tube lamp, see Table 3-3.

FAAD lamps were found to be 500-1000 times as intense, have shorter warm up times (approximately 3-5 minutes), but were slightly noisier than hollow cathode lamps.

3.5 Microwave excitation of atomic vapours produced by hollow cathode discharges.

Simple hollow cathode lamps (23, 116), whilst being excellent sources of atomic radiation for atomic absorption spectrometry, lack sufficient intensity to give low limits of detection for atomic fluorescence spectrometry. Improvements in lamp design by the use of ceramic or quartz shielding around the cathode have greatly increased the intensity of the resonance radiation, which has made atomic fluorescence measurements with these sources feasible (112, 117). The intensity of these shielded cathode lamps is comparable to the high intensity HCL developed earlier by Sullivan and Walsh (32). These lamps, which rely on subsidiary electrodes to further excite the atom cloud produced at the cathode mouth, have given worthwhile improvements in output for a few elements (32). Sources of this kind have been used successfully for atomic fluorescence spectrometry by West and co-workers for the determination of magnesium (109), silver (113) and cobalt (94), and by Matousek and Sychra (66, 114, 115) for iron, cobalt, nickel and gold. However, neither of these HCL modifications is capable of producing atomic resonance radiation as intense as that emitted by microwave excited EDLs. The radiation emitted from EDLs is usually 10-100 times as intense as that emitted by the best modified HCL. As microwaves have been found to be extremely efficient at converting electrical to luminous power, it was decided to investigate the possibility of exciting with microwaves the atoms produced by a hollow cathode discharge. A hollow cathode discharge was used to produce the

atomic cloud at its mouth because it can be applied to almost any element no matter that its vapour pressure. Two arrangements for this microwave excitation of the atom cloud were investigated.

The first involved using an "A" type antenna to direct microwaves into a conventional hollow cathode lamp in such a way that the microwaves traversed the mouth of the cathode, where they could excite the atoms produced, in a similar way to the secondary electrodes of a high intensity hollow cathode, see Figure 33.

The second arrangement involved the construction of a demountable HCL which was small enough to be fitted into a $\frac{1}{4} \lambda$ Broida type microwave cavity, see Figure 34.

(1) Microwave excitation of a conventional HCL

Microwave power was directed into a conventional hollow cathode, which was operating in its normal manner at its recommended d.c. current, via an "A" type antenna. The position of the "A" type antenna relative to the HCL was investigated, and the optimum position of the "A" type antenna stub was found to be at right angles to the cathode viewing axis and in a plane 1.5 cm. in front of the cathode mouth, see Figure 35. If the antenna stub was moved further towards the cathode than this optimum position, most of the microwave power coupled to the cathode causing it to become red hot. In some cases the cathode would become so hot that the material inside it, or sometimes even the whole cathode, would melt. Under these

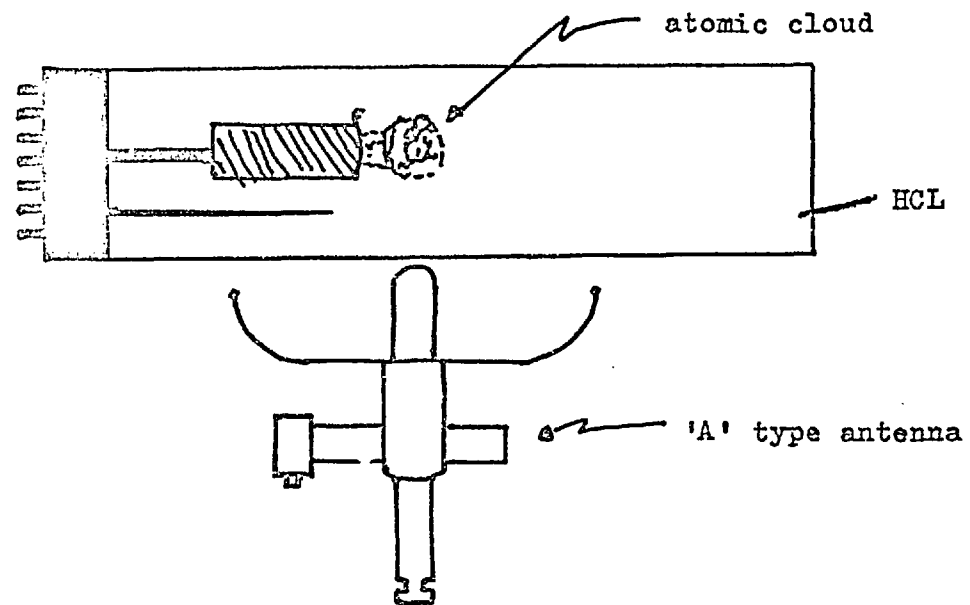


Figure 33

Arrangement for Microwave
Excitation of the Atomic
Vapour produced in a
Conventional HCL.

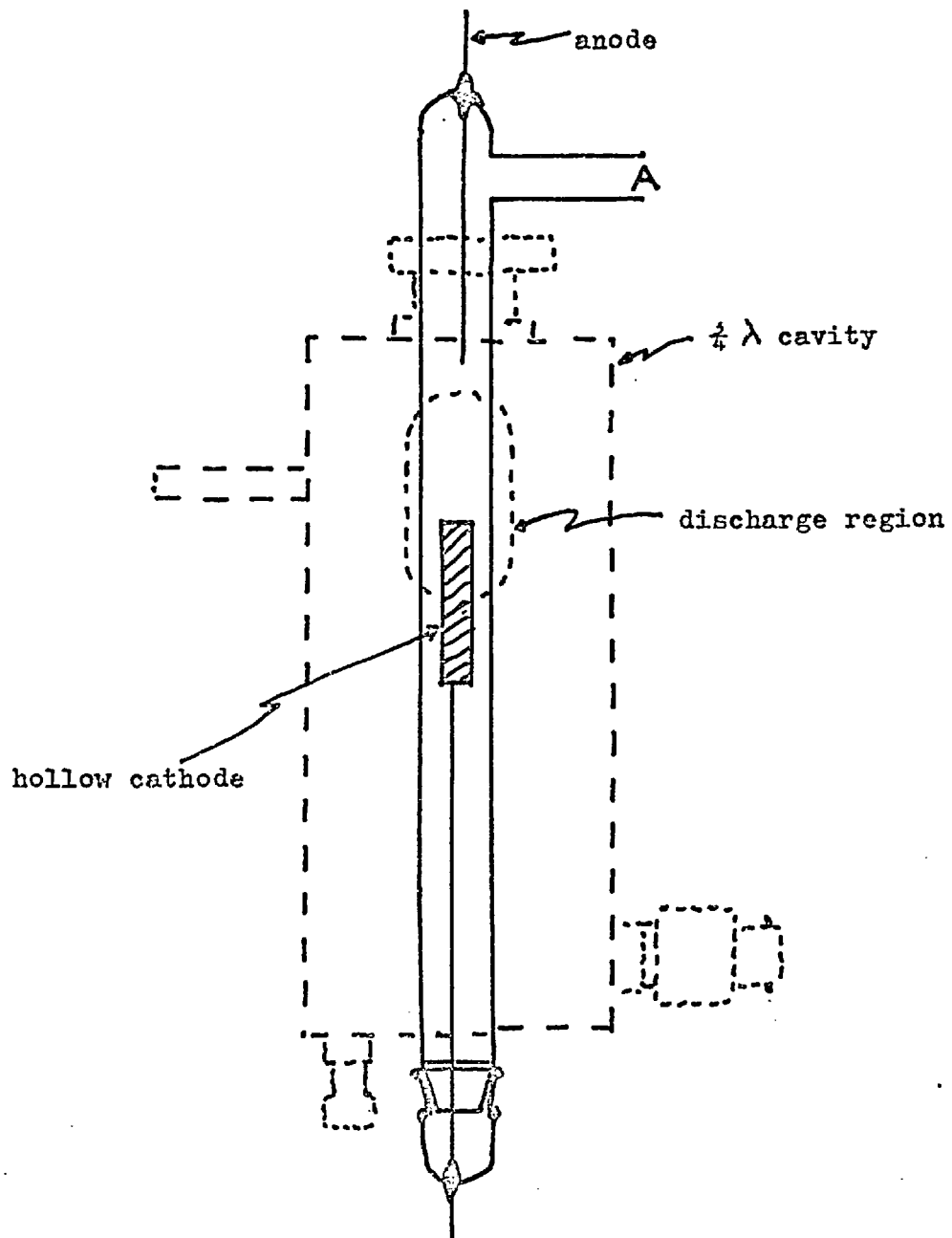


Figure 34

Arrangement for Mounting the
Demountable HCL in a $\frac{1}{4} \lambda$ cavity.

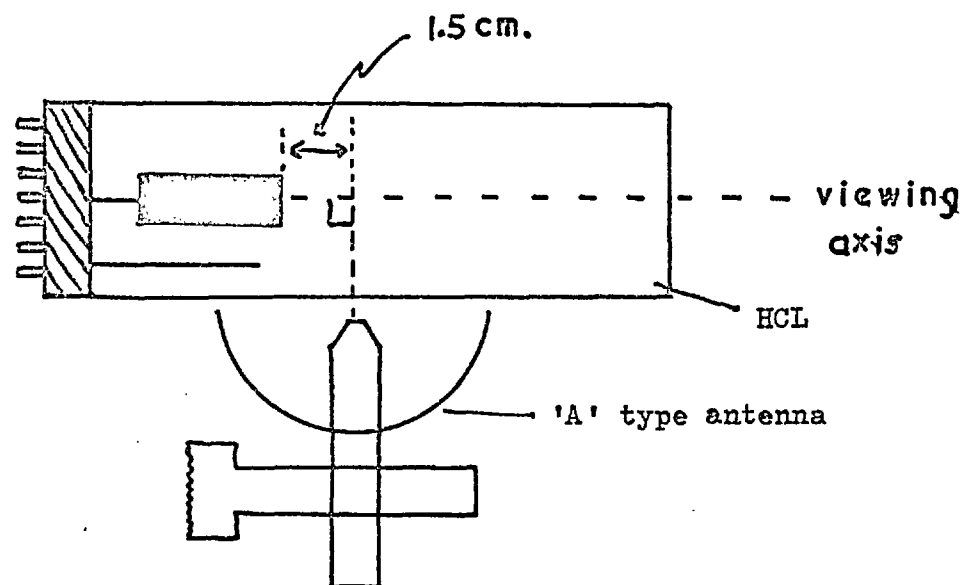


Figure 35

Optimum Mounting Position of
the 'A' type antenna for
Microwave Excitation of the
Atomic Vapour Produced in a
Conventional HCL.

conditions the resonance lines emitted from the cathode were always self reversed and often their intensity was very unstable. When the antenna was progressively moved further away from the cathode than the optimum position, the microwaves coupled progressively more with the HCL fill gas and less with the sputtered atomic vapour cloud.

There was an approximately linear relationship between resonance line intensity and the amount of microwave power applied to the antenna. Table 3-7 shows this increase in resonance line intensity with increasing microwave power for magnesium, calcium and copper HCLs.

Table 3-7

Effect of microwave power on the output intensity of three different hollow cathode lamps

Applied micro-wave power (watts)	Cu resonance line intensity at 324.7 n.m.	Mg resonance line intensity at 285.2 n.m.	Ca resonance line intensity at 422.7 n.m.
0	5.2	8.9	3.1
40	1210	1660	1010
80	2900	4010	2100
120	3800	5800	2910
160	4400	6910	3520
200	5010	7700	3910

An applied power of 200 watts increased the resonance line intensity by about three orders of magnitude. Unfortunately, the noise and drift rates were also increased and the lamp lifetimes

were considerably shortened. When maximum applied microwave power was used, the lamp lifetimes decreased to 40-60 minutes, which makes this technique very expensive and generally unsuitable for use in analytical chemistry. However, for certain applications where high intensity is required for a short time and expense is not a major limitation, this technique may prove useful.

When microwave power was coupled to the atomic cloud, an increase of about 75% occurs in the d.c. current flowing in the HCL circuit. The microwave discharge, which was considerably larger than the secondary discharges of high intensity HCLs, deposited some of the metal from the hollow cathode on the HCL walls. This effective removal of the metal from the hollow cathode to the walls was probably responsible for the shorter lifetime.

(2) A demountable HCL which can be fitted into a $\frac{3}{4}\lambda$ microwave cavity.

A demountable hollow cathode was designed and constructed so that it could be placed inside a $\frac{3}{4}\lambda$ Broida type cavity, see Figure 34. The initial design was constructed out of 12 m.m. outside diameter pyrex tubing with 1.5 m.m. wall thickness; however, during operation the tube walls became very hot and often collapsed. Additionally, the discharge preferentially emitted the sodium spectrum. These two problems necessitated the use of quartz tubing of the same size as the pyrex tubing. Unfortunately, when using quartz tubing the seals round the electrodes were very fragile; however, breakage could be avoided

by very careful handling. The anode consisted of a 8 c.m. length of 2 m.m. diameter tungsten rod, both steel and graphite cathodes were used. The graphite cathode was found to be superior as it gave less background radiation, was easier to clean and construct. A hollow cathode was made by drilling a 1 c.m. deep 5 m.m. diameter hole into a 8 c.m. length of 7 m.m. diameter graphite; this cathode was then pressure fitted onto a length of 2 m.m. tungsten rod. The cathode assembly could be removed from the lamp by disconnecting the B14 quick fit joint.

After removing the cathode from the lamp, it was filled with 0.5 grams of the element, or one of its halides, whose spectrum it was desired to produce. The demountable lamp was then placed into the $\frac{3}{4}\lambda$ cavity and the cathode assembly reinserted into the lamp. The outlet A was connected to a vacuum system capable of evacuating the lamp to a pressure of 10^{-2} torr. The lamp was then pumped down to 10^{-2} torr, twice flushed with argon, and re-evacuated to $2-4$ torr. A stabilised power supply capable of being adjusted from 200-500 volts was connected to the cathode and the anode, and its voltage gradually increased from 200 volts until a strong discharge was produced. After 30 minutes of this discharge, the lamp was pumped down to 10^{-2} torr for a period of 5 minutes to remove any moisture or occluded gases that were released during the discharge. This procedure was repeated until the background emission from the discharge had been minimised. The lamp was then filled with argon to a pressure of 3 torr and the

voltage across the anode and cathode adjusted until a current of 80-100 milliamps was flowing in the anode/cathode circuit; resonance line radiation of the material in the cathode was then emitted from the hollow cathode. The microwave power was then turned on and it was noticed that the intensity of the discharge became much more intense. When the discharge became more intense the rate of vapourisation of the cathode fill material increased, which expanded the discharge to completely fill the anode/cathode gap. Whereupon, the d.c. current increased at an exponential rate until the power supply fuse blew. To overcome this "runaway" situation, the distance from the anode to the cathode was increased from 3.5 c.m. to 7.0 c.m., and a 2500 ohm load resistor was connected in series with the anode/cathode circuit. Under these conditions, the d.c. current was limited to a maximum value of 200 milliamps, when the maximum voltage was used, and the discharge never expanded enough to completely fill the cathode/anode space. The effect of d.c. current, microwave power, and the pressure of the argon fill gas on the resonance line intensity was investigated for several elements (aluminium, barium, strontium, calcium, copper, and magnesium) and several metal halides (sodium chloride, potassium chloride, magnesium chloride and calcium chloride). The optimum values (i.e. those values which gave the most intense resonance radiation consistent with stability) of the d.c. current and microwave power were found and are given, together with the short term noise and drift rates, in Table 3-8. The optimum fill gas pressure was found to be 2.5 torr for all the lamps investigated; lower pressures often produced weak unstable discharges and higher pressure caused pinched arcs to form.

Table 3-8

Optimum values of d.c. current and microwave power, noise and drift rates for various microwave excited demountable HCLs.

Cathode fill material	Boiling point of fill material (°C.)	Resonance line (nm)	Optimum d.c. current (mA)	Optimum microwave power (watts)	Short term noise (%)	Drift rate (%/hr)
Al	2056	396.2	170	140	20	-9
Ba	1638	553.6	150	120	26	-14
Sr	1384	460.7	110	95	30	-15
Ca	1440	422.7	115	100	23	-13
Cu	2595	324.7	190	160	18	-7
Mg	1107	285.2	85	70	30	-14
NaCl	1413	589.0	110	100	25	-14
KCl	> 1500	766.5	150	110	24	-12
MgCl ₂	1412	285.2	120	95	25	-14
CaCl ₂	> 1600	422.7	160	120	22	-12

The optimum microwave power and d.c. current increases with the boiling point of the fill material, whereas the noise and drift rates decrease with increasing boiling point. The very high levels of noise and the very fast drift rates of the resonance line intensity make this type of source unsuitable for use in analytical atomic spectrometry.

The metal vapour of the alkali and alkaline earth elements only slightly attacked the quartz walls of the lamp and because of its demountable design, they were easily cleaned with dilute hydrofluoric acid. The 0.5 gram charge of cathode fill material lasted approximately five hours; after which time the cathode had to be recharged; unfortunately, because of the degassing procedure

this process took much longer than that for the FAAD lamps.

3-6 Conclusion

Five methods of producing intense resonance radiation of elements, for which satisfactory conventional EDLs cannot be made, have been investigated. Both the methods of microwave excitation of hollow cathode produced atomic vapours have been found to be unsatisfactory for analytical atomic spectrometry, either because of high cost and short lifetimes or because of high noise levels and drift rates. The other three methods of producing stable intense atomic spectral sources have been found to be satisfactory. The two methods specifically for sodium resonance radiation are very cheap, simple to construct and easily operated. They emit intense and stable sodium resonance radiation, and have very long lifetimes; they are considerably more efficient at producing atomic fluorescence of sodium atoms than is the Wotan vapour discharge lamp. However, the general FAAD lamp (i.e. the cup discharge lamp) was found to be superior to both of these specific methods for sodium with the exception of lifetime considerations. It is also applicable to any element which has a compound with a boiling point between 1240 and 2200°C. The FAAD lamps produce very intense and stable atomic resonance lines, they have fairly short lifetimes, but because of the ease with which they can be recharged, they are ideally suited to analytical atomic spectrometry and especially atomic fluorescence measurements.

CHAPTER IV

SOURCE MODULATION

4.1 Introduction

The analytical chemist, in his pursuit of greater accuracy and in the study of smaller effect phenomena, frequently finds it necessary to develop new methods and more sophisticated instruments to help him. For example, when a scientist is faced with a severe noise problem, he may often be unaware of simple techniques that will allow better results to be obtained. Further, he may even be less aware of recent advances that in some instances allow vastly improved signal to noise ratios (S/N) to be attained.

Often simple, though sometimes complicated, earthing or isolation procedures will remedy the problem. At other times, a mere change of components, rather than the system is all that is required. For many measurements, "traditional" d.c. and a.c. techniques are sufficient. However, it may be necessary or beneficial to use one of the relatively recent developments in signal processing (synchronous or phase sensitive detection, pulse counting, signal averaging, or correlation techniques). All these methods are especially concerned with the measurement of weak electrical signals buried in noise.

(a) D.C., A.C. and Synchronous Measurement Systems

A common method of noise attenuation is to limit the bandwidth of the monitoring instruments by filtering. Assuming the majority of the noise occurs at frequencies different from the signal, then the smaller the bandwidth

(that still includes the signal) the better the signal to noise ratio. If the instrument bandwidth is wider than the desired signal's bandwidth, the extra bandwidth only admits extra noise and can be discarded without losing any of the signal.

D.C. systems limit the bandwidth about d.c. and may also include a differential common mode rejection. Inherent problems in d.c. measurements often include zero drift, zero offset and the predominance of low frequency flicker (or $1/f$) noise over white noise near d.c. (118).

To avoid the region of $1/f$ noise and to minimise the background and drift, a.c. methods are usually employed. This involves selective modulation of the analytical information at some point before the amplifier, and detection of the resulting a.c. signal. Subsequent rectification reconverts the signal to d.c. for output purposes. The problem with a.c. methods is to make the bandwidth very small so as to reduce the noise, and at the same time to ensure that (i) the signal centred at a frequency of f_0 remains within that bandwidth, and (ii) the amplifier does not drift from this frequency f_0 . This means that while the a.c. amplifier can be tuned, it may only be tuned for a relatively wide bandpass.

To use a smaller bandpass, one must resort to a phase locked or synchronous system (119). The bandwidth can then be made as narrow as desired (consistent with the rapidity of measurement required) by increasing the resistance/capacitance

time constant of the system.

(b) Pulse counting techniques

Pulse counting techniques assume that average signal pulses are greater in intensity than average noise pulses, even if the signal pulses are less frequent. Provision can be made to eliminate extraordinarily large pulses (if they are assumed to be noise). Pulse counting techniques employ a discriminating system which results in the counting of pulses with heights within a range $h_0 \pm \Delta h$ only, where h_0 is the average signal pulse height. The main problem with this method (one of practice rather than theory) involves the choice of the range $h_0 \pm \Delta h$. Further, the method is not useful when the noise pulses become as large as the signal.

Morton (120) and Malmstadt and co-workers (121) have recently investigated this pulse technique as applied to photon counting and Alger et al. (122) have used a similar system for atomic fluorescence and emission spectrometry.

(c) Signal Averaging

The above considerations involving filtering to reduce the bandwidth and hence the noise, are of little value if the signal and the noise occupy the same part of the frequency or height spectrum. If a waveform is repetitive, the S/N can sometimes be improved by making use of the redundant information inherent in repetition. So-called "signal averagers" operate on the principle of sampling each signal pulse, dividing it into segments to obtain resolution, and then storing a voltage or count

proportional to the level of each segment. By observing many repetitions of the input waveform, it is possible (operating in real time) to see experimental results while the experiment is in progress, even though the signal may be so obscured by noise that the raw data seems to contain little or no information. Averagers demand only that some means be available for synchronising them to a repetitive signal that is to be extracted from the noise.

(d) Correlation Techniques

Time correlation can be used in two broad application areas, autocorrelation and crosscorrelation. Autocorrelation involves the comparing of a waveform against a time-delayed version of itself, and can be used to detect an unknown periodic signal in the presence of noise or to measure some particular band of signal or noise frequencies. It is useful for the detection of signals buried in noise when no reference or synchronising signal is available. (If such a signal is available, the above methods are simpler and less expensive). Crosscorrelation involves a comparison of two waveforms (both of which may be obscured by noise or other signals not common to both waveforms) to determine the degree of conformity between them.

In both instances, the following operations are required:

- (i) one of the amplitude-time functions (signal) must be delayed with respect to the other (or to itself in autocorrelation);
- (ii) the displaced or delayed function (signal)

must be multiplied by the other to produce an instantaneous product; (iii) the instantaneous product must be averaged by integration over a period. If these steps (delay, multiplication and averaging) are repeated for each value of delay available in the interval of interest, a correlation function (correlogram) is generated. Unfortunately, the interpretation of the correlogram is very difficult.

4.2 Modulation

In a.c. flame fluorescence spectrometry, d.c. to a.c. signal conversion can be carried out by modulating the flame signal, the wavelength of observation or the primary light source.

(a) Flame Signal Modulation

In the past fifteen years, several methods of selectively modulating the flame signal have been reported. In 1956 Dickey et al. (123) modulated the flow of gaseous samples into a flame with a mechanical needle valve. Dickey and Hoffman (124) used a similar device to vary the acetylene flow rate into an oxyacetylene flame to study the OH emission. In continuing the study of OH emission, Rogge et al. (125) used a two flame signal modulation technique based on the periodic comparison of the analytical flame with a reference flame. Lang (126) modulated his signal by periodically deflecting the flame out of the optical path. A direct approach to the selective modulation of

atomic emission and atomic absorption signals was obtained by varying the analytical solution flow rate into the flame, either by compressing the tube leading to the aspirator capillary (127, 128) or by periodically switching the liquid input to the flame between a blank solution and the analytical solution (130).

In an effort to overcome the amplitude instability of the a.c. component associated with tube compression techniques (131), Neu et al. (132) periodically dipped a flexible tube connected to the aspirator capillary into the analytical solution. The solution flowing to the nebuliser was broken into short columns separated by air bubbles. A problem was that the air bubbles permitted the individual liquid columns to oscillate about their mean positions which produced frequency, phase and amplitude instability. Rudiger et al. (131) and Trampisch and Herrmann (134) modified the dipping tube technique by driving the completely submerged tip of the capillary tube up and down in the analytical solution with a sewing machine.

In 1966, Lang (135) achieved flame and solvent modulation by periodically throttling the air supplied to the flame. Recently, Antić-Jovanović et al. (136, 137) reported a modulation method for a dual spray-chamber burner; analyte and solute aerosols were alternately switched at the junction of the two feed lines to the burner head. Marinkovic and Vickers (138, 139) have recently tested a modification of

the Antić-Jovanović modulator for flame emission and atomic absorption spectrometry.

(b) Wavelength Modulation

Many systems have been proposed for wavelength modulation; they all basically consist of repetitively sweeping the atomic spectral line of interest across the detection system. Bullock and Silverman (140) and Brehm and Fassel (141) mechanically scanned the spectrum produced in a direct-reading spectrometer by moving the exit slit. Harber and Sonnek (142) and Fassel and co-workers (143) both used image-dissector phototubes (IDPs) for wavelength modulation. The electrons ejected from the photocathode of the IDP are magnetically swept across a metal plate, in which an aperture has been cut. The plate is situated in front of a dynode chain, thus photo electrons only enter the dynode chain when the electron image of entrance slit of the monochromator is coincident with the aperture. Snelleman (158) used an oscillating galvanometer mirror to rapidly and repeatedly scan an absorption line, and he listed the advantages of using a wavelength modulated a.c. system in conjunction with a continuous primary source. Snelleman et al. (159) used a similar system except that the oscillating mirror was replaced by a vibrating quartz microscope slide.

Wavelength modulation corrects for background radiation and by eliminating a fixed exit slit minimises the effects

of monochromator drift, which can be serious when narrow slit widths are used.

(c) Source Modulation

In atomic fluorescence spectrometry the limiting noise at the limit of detection is mainly due to the shot noise produced by the flame background and to the flicker noise of the flame background. Modulation of the excitation source can drastically reduce the flame flicker noise by judicious choice of the modulation frequency. Many workers have modulated the source radiation by simply placing a mechanical chopper between the source and the flame. This technique is very widespread and many commercial instruments incorporate this facility. Unfortunately, mechanical chopping presents several problems: (i) the whole of the source flicker noise is transformed to the chopping frequency and there is thus no reduction in this noise; (ii) light from the primary source is often scattered off the chopper blade edges to bypass the flame and produce a high background, and its associated shot noise; (iii) the source and the chopper have to be kept some way away from the flame to stop chopper induced drafts producing further flame flicker noise.

To overcome these difficulties associated with mechanical modulation of the primary source, two approaches have been developed: optical and electrical modulation.

Optical modulation is only used for resonance emission and consists of periodically interposing an atomic vapour into the light path. The atomic vapour absorbs the resonance radiation emitted by the primary source. Thus, not only can the source emission or the source induced emission be isolated from foreign emission, but the resonance lines can be distinguished in the spectrum of the source. However, it should be borne in mind that optical modulation can only be used effectively when emission from the atomic vapour is considerably weaker than the emission from the light source. Theoretically, the optical method of modulation makes it possible to dispense with the monochromator system; in practice, however, the presence of more than one resonance line in the spectra of most elements must be taken into consideration, as well as the increase in shot noise resulting from the exposure of the photo-detector to the unmodulated emission from the lamp.

Optical modulation was first used by Alkemade and Milatz (144); light from the source (a metal-vapour lamp) was alternatively sent through a flame (into which the appropriate element was sprayed) or past the flame. Gatehouse and Walsh (145) used a hollow cathode discharge lamp with a hollow cylindrical cathode, through which the light from the source passed, as a method of producing the absorbing media. The power supplied to the cylindrical

hollow cathode was modulated electrically, which produced a modulated atomic vapour in the cylindrical cathode. This vapour was used to absorb the light output of the source (another hollow cathode lamp). Bowman et al. (146, 147) mounted the modulating hollow cathode electrodes into the same envelope as the source hollow cathode. Lowe (148) found that he could do away with the modulating electrodes; by pulsing a HCL, he found that the large atomic cloud produced at the mouth of the cathode would absorb the radiation emitted from the hollow cathode during the non-pulsed period. Sebestyen (149) made a comparison of both of these secondary hollow cathode modulation techniques and the pulsed HCL technique. He found the pulsed technique to be the best of the three when used in conjunction with a double gated amplifier.

Electrical modulation of the source has been approached differently, depending on the actual source used. Modulation of the output of HCLs has been achieved by supplying them with stabilised a.c. voltages (150) or an interrupted current (151) and is now widely used in commercially available equipment.

Recently West et al. (93, 110) and later Thompson and Wildy (152, 153) have described methods of electrically modulating microwave excited EDLs by transformer coupling a low voltage (ca. 12v peak to peak) a.c. signal into the anode circuit of the magnetron. Unfortunately, this

method of modulation has certain disadvantages as indicated by West et al. (154). Because the secondary of the transformer is in the anode circuit, the d.c. magnetron current may cause saturation of the transformer core resulting in distortion of the modulation waveform applied to the transformer primary. Also, because a transformer is generally designed for low frequency sinusoidal waveforms, the frequency and function of the modulation is hence somewhat limited. These problems can be overcome by directly injecting the modulation waveform at the error sensing or the inference point of the stabilising element of a stabilised magnetron power supply. It was decided to investigate this method of modulation, a range of modulation frequencies and functions have been used, with a view to the use of EDLs for atomic fluorescence spectroscopy. Modulated EDLs were not used for atomic absorption spectroscopy as adequate modulation procedures are available for HCLs.

4.3 Experimental

Apparatus

The experimental system used is shown diagrammatically in Figure 36. The modulator used was a function generator (Hewlett Packard, Model 3310A) capable of generating various waveforms (triangular, square, sine, ramp or pulse) at different frequencies (1×10^{-4} Hz - 5×10^6 Hz) and amplitude (0 - 35V peak to peak). The modulation amplifier

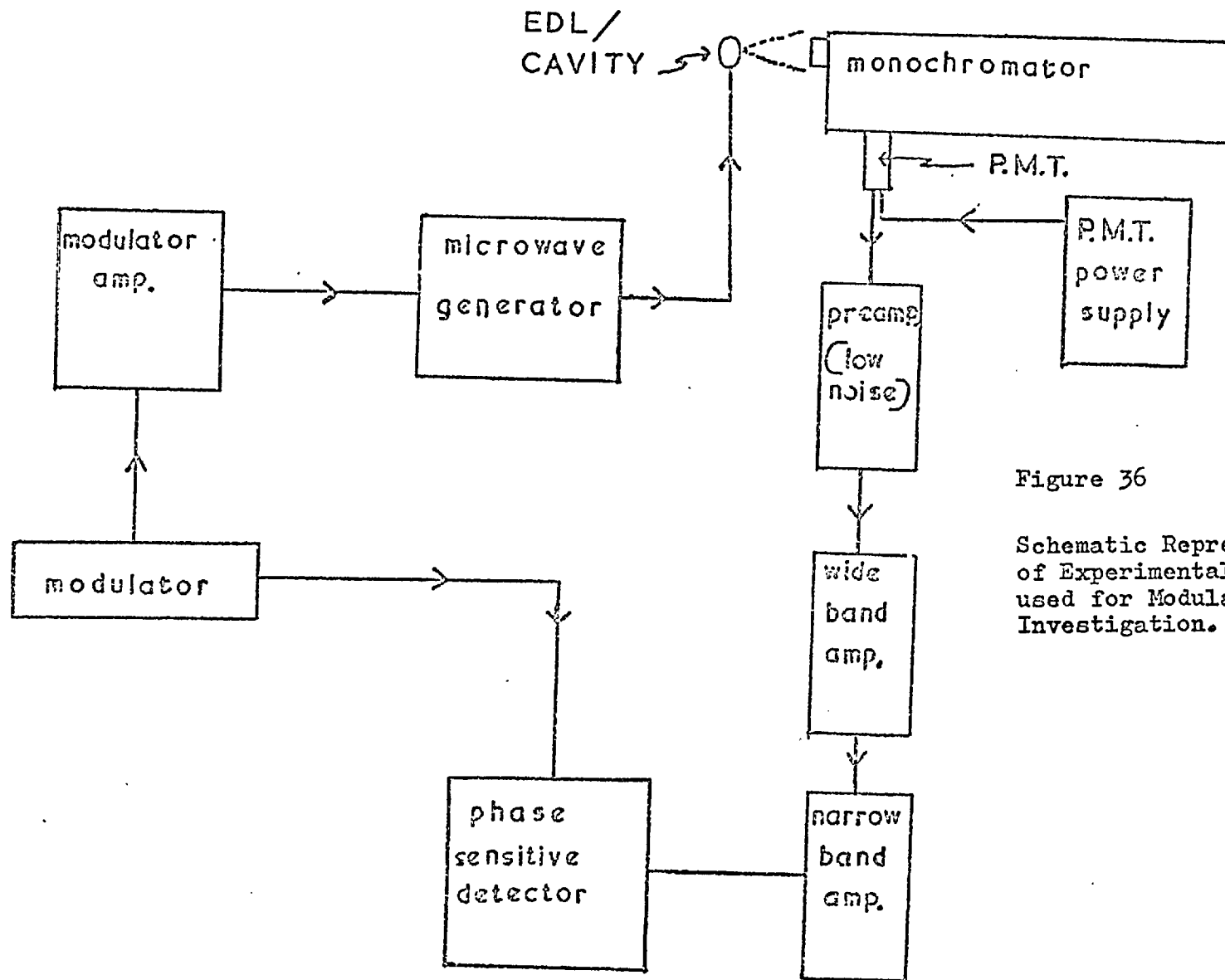


Figure 36

Schematic Representation
of Experimental System
used for Modulation
Investigation.

was a modified prototype modulation unit (Evans Electroselenium Ltd., Halstead, Essex, U.K.) used as a voltage amplifier. The microwave generator (Evans Electroselenium Ltd., Halstead, Essex, U.K. Model 245) was current stabilised and modulation of the magnetron output was effected by injecting the modulation waveform at the error sensing point of the stabilising element of the magnetron power supply. The EDLs were operated in a Broida-type three quarter wave cavity (Evans Electroselenium Ltd., Halstead, Essex, U.K.) fitted with two capacitative tuning stubs. The detector system consisted of a 1 m. grating spectrophotometer (Optika Ltd., Walthamstow, London, U.K. Model 331/3000) giving a reciprocal linear dispersion of $20\text{\AA}/\text{mm}$ coupled to a photomultiplier (E.M.I. Ltd., Hayes, Middlesex, U.K. Model 9592B) operated at 850V supplied by a stabilised power supply (Brandenburg Ltd., Thornton Heath, Surrey, U.K. Model 472R). A slit width of 0.005 mm ($0.1\text{\AA}$ spectral bandpass) was used for all direct source evaluations and a slit width of 3.6 mm for all atomic fluorescence measurements.

The signal from the photomultiplier was amplified by a low noise wide band preamplifier, a wide band amplifier and a variable frequency, variable 'Q', narrow band amplifier (AIM Electronics Ltd., Cambridge, U.K. Models LNA/133, ACA 123 and TFO 129 respectively). The variable frequency, narrow band amplifier was used with

a 'Q' setting of 100 which gave a bandpass (at the 6 db points) of $f_0/100$ Hz, where f_0 is the frequency of maximum amplification of the narrow band amplifier and also the frequency of modulation.

The amplified signal was detected by a phase sensitive detector (AIM Electronics Ltd., Cambridge, U.K. Model PSD122A) which was phase-locked to the modulator.

A fuel rich premixed air-acetylene flame was used for all atomic fluorescence studies.

The method of preparation of the EDLs was similar to that described in Chapter II, except that the lamp blanks were baked at ca. 1000°C for ca. 12 h and purged using an intense argon discharge for ca. 30 minutes prior to preparation of lamp. The purging procedure greatly increased the average lifetime of the lamps and decreased the long term drift by decreasing the rate of wall discolouration. All lamps were filled to a pressure of between 3-4 torr of argon before sealing.

4.4 Results and Discussion

(a) Degree of Modulation

The apparatus used in this investigation was capable of producing a maximum percentage modulation of the magnetron current of ca. 75%; unfortunately, at this level there was a considerable amount of short term noise (ca. $\pm 8\%$) superimposed on the emitted radiation from the modulated EDL. This noise level decreased to below $\pm 1\%$

when the current modulation was decreased to 63% or below and hence this level of modulation was used because it was capable of giving the greatest emitted intensity consistent with the low noise. However, the percentage modulation of the coupled microwave power was found to be ca. 50% when the current modulation was 63%. This was probably caused by a greater reflection of microwave power from the cavity at the modulation maximum than at the modulation minimum.

(b) The Frequency and Function of the Modulation Wavelength

The effect of the modulation frequency for several different EDLs, viz. Cd, Hg, Zn, Sb, Se, As, and Pb, on the intensity of emitted resonance lines was investigated. All of the sources gave a maximum modulated output at a frequency of ca. 20,000 Hz (Figure 37). This maximum would probably have occurred at a higher frequency, but for the drop off in modulation amplifier response which commences at about 18,000 Hz.

This investigation was repeated using various waveforms, viz. triangular, sine, square, ramp and pulse, and although for each function the optimal frequency occurred at ca. 20,000 Hz, each waveform gave a different relative intensity of emission, see Table 4-1. For all frequencies of operation the square waveform gave the greatest intensity of radiation and was used for all further studies unless otherwise stated.

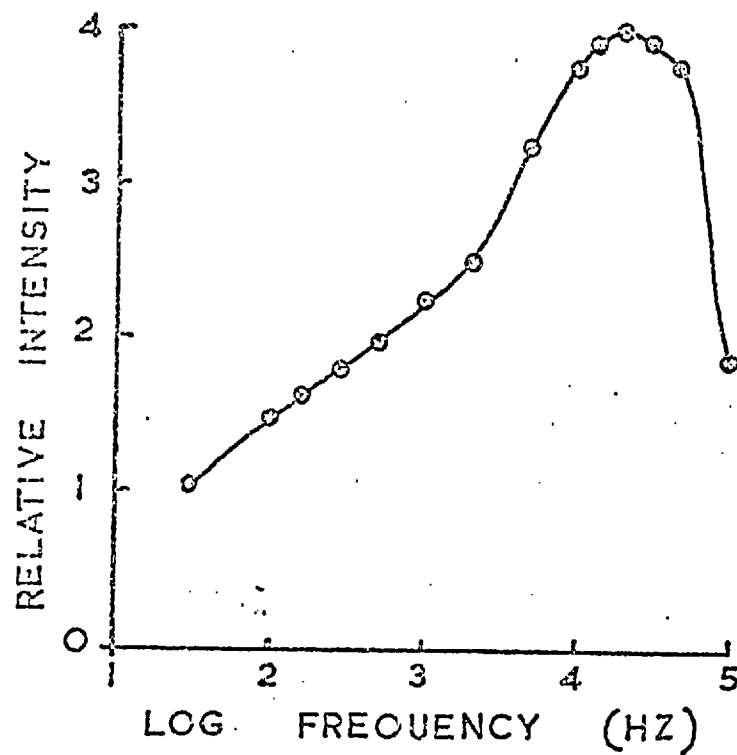


Figure 37

Plot of Frequency of Modulation
vs. Radiation Intensity for a
Mercury EDL (microwave power
40 watts, measurements made at
253.7 nm.).

TABLE 4-1

Effect of various modulation waveforms on the
relative intensity of the resonance radiation from
a modulated EDL measured by phase sensitive
detection system.

Waveform used	Relative Intensity		
	100 Hz	1000 Hz	10,000 Hz
pulse 	1.0	1.8	2.7
pulse 	0.7	1.3	2.0
square wave	3.6	7.0	10.0
sine wave	2.8	5.0	7.2
triangular wave	2.5	4.8	7.0
ramp 	2.4	4.8	6.9
ramp 	2.5	4.8	7.0

(c) Microwave Power

The amplitude of the a.c. component of the resonance atomic fluorescence intensity of a modulated EDL (for a given percentage of modulation) is governed by the gradient of the atomic fluorescence intensity vs. microwave power curve obtained from an EDL operating in the d.c. mode. A long (ca. 25 cm) mercury EDL (155) was chosen for the preliminary investigation of this effect because the atomic fluorescence intensity vs. microwave power curve for d.c. mode of operation showed a maximum, thus giving positive, negative and zero gradient portions (Figure 37). When this source was used in the a.c. mode, the atomic fluorescence intensity vs. microwave power curve obtained (Figure 39) was completely different from that obtained in its d.c. mode of operation (Figure 38). The atomic fluorescence intensity measured by the phase sensitive detector system (i.e. the amplitude of the a.c. radiation component) was approximately proportional to the gradient of the atomic fluorescence intensity vs. microwave power curve for d.c. operation (n.b. the negative output of the phase sensitive detector indicates a phase shift of 180°). Figure 40 shows how a triangular modulation waveform produces an a.c. component of the emitted radiation from a modulated EDL. If the EDL had been optimised for d.c. operation (i.e. a microwave power setting of ca. 70-80 watts) and then modulated, then no signal would be observed on the

Figure 38

Plot of Atomic Fluorescence
Intensity vs. Applied Microwave
Power for Mercury (microwave
power d.c., measurements made
at 253.7 nm.).

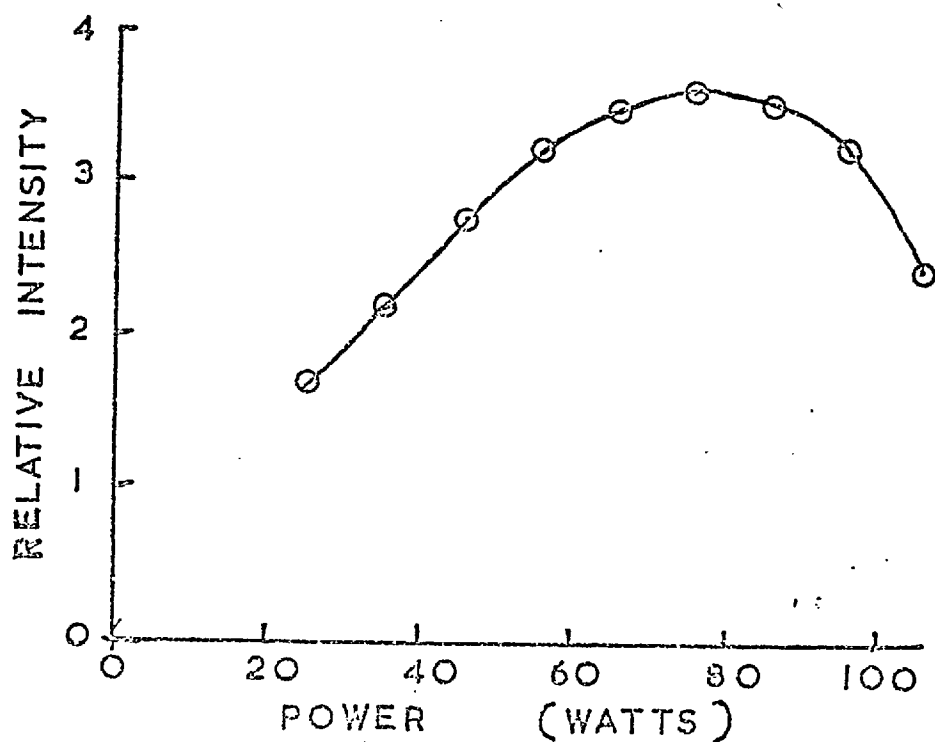
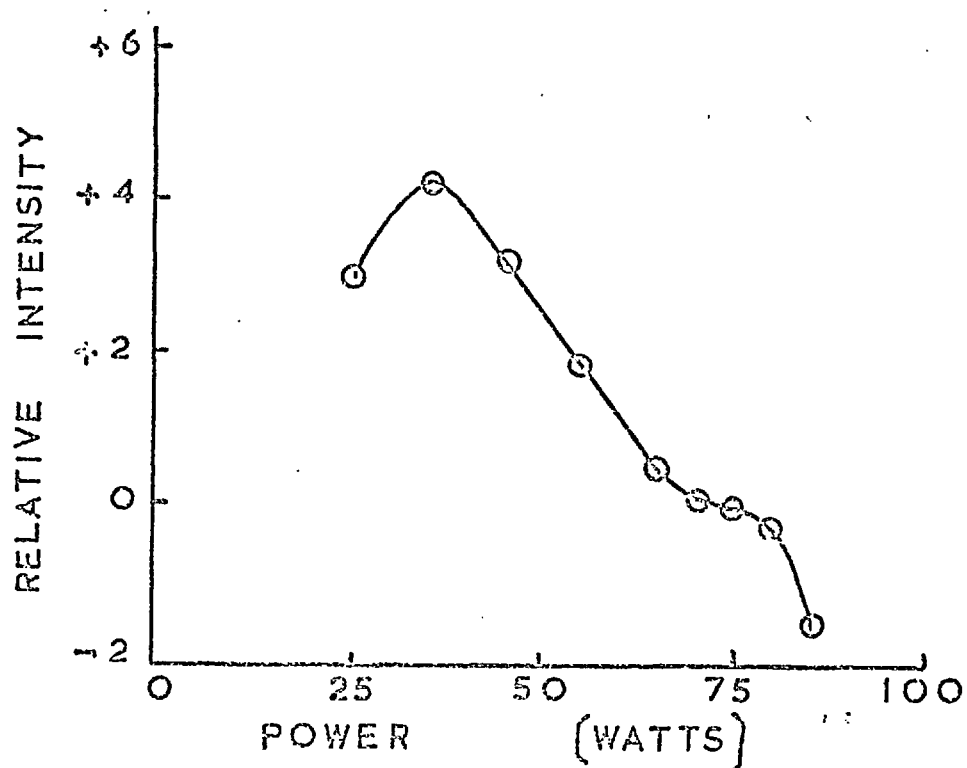


Figure 39

Plot of Atomic Fluorescence
Intensity for Mercury vs.
Applied Microwave Power
(modulation frequency 18 KHz,
50% modulation, measurements
made at 253.7 nm.).



phase sensitive detector for two reasons: the amplitude of the a.c. component of the radiation is very small as a result of the shallow gradient and the frequency of the a.c. component of the emitted radiation is twice that of the modulation frequency (Figure 40).

The amplitude and the phase relationship of the modulated radiation was compared with the modulated waveform by applying both the modulator and photomultiplier outputs to the two input channels of a double beam oscilloscope. This was carried out for a triangular, sine and square waveform with the mercury EDL at different microwave power settings (Figure 41). All three waveforms exhibited frequency doubling at the optimal d.c. operating power and a 180° phase shift at higher microwave powers (Figure 41).

Thus, in order to find the optimal microwave operating power for an EDL used in the a.c. mode, it is necessary to measure experimentally the atomic fluorescence intensity vs. microwave power behaviour in the d.c. mode of operation. The microwave power at which the maximum gradient occurs gives the optimal microwave power for the a.c. mode of operation. In some instances, when self reversal causes a drop in resonance line intensity, this maximum gradient may occur at higher microwave powers than the optimal d.c. operating power. However, as long as the detector system

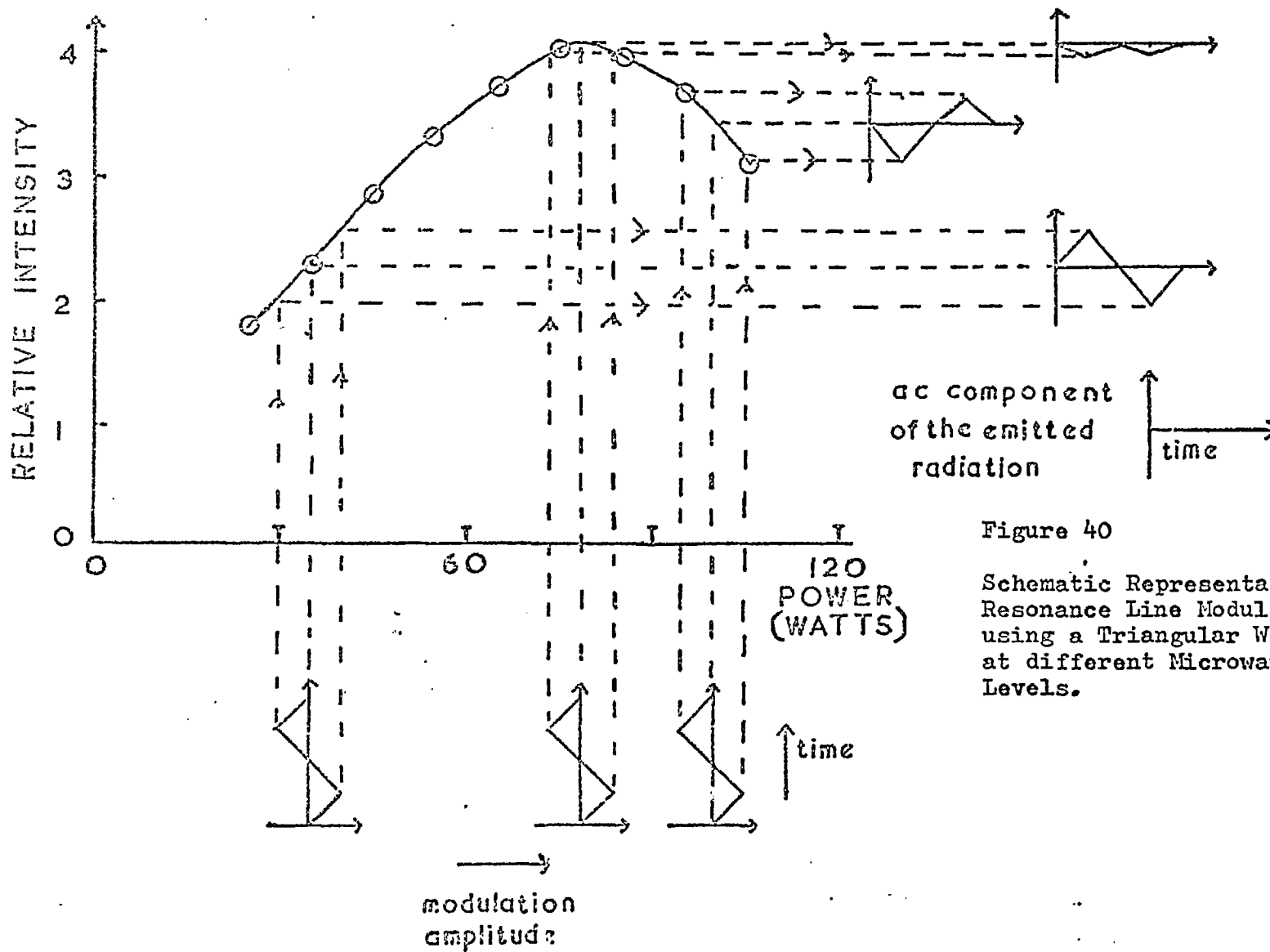


Figure 40

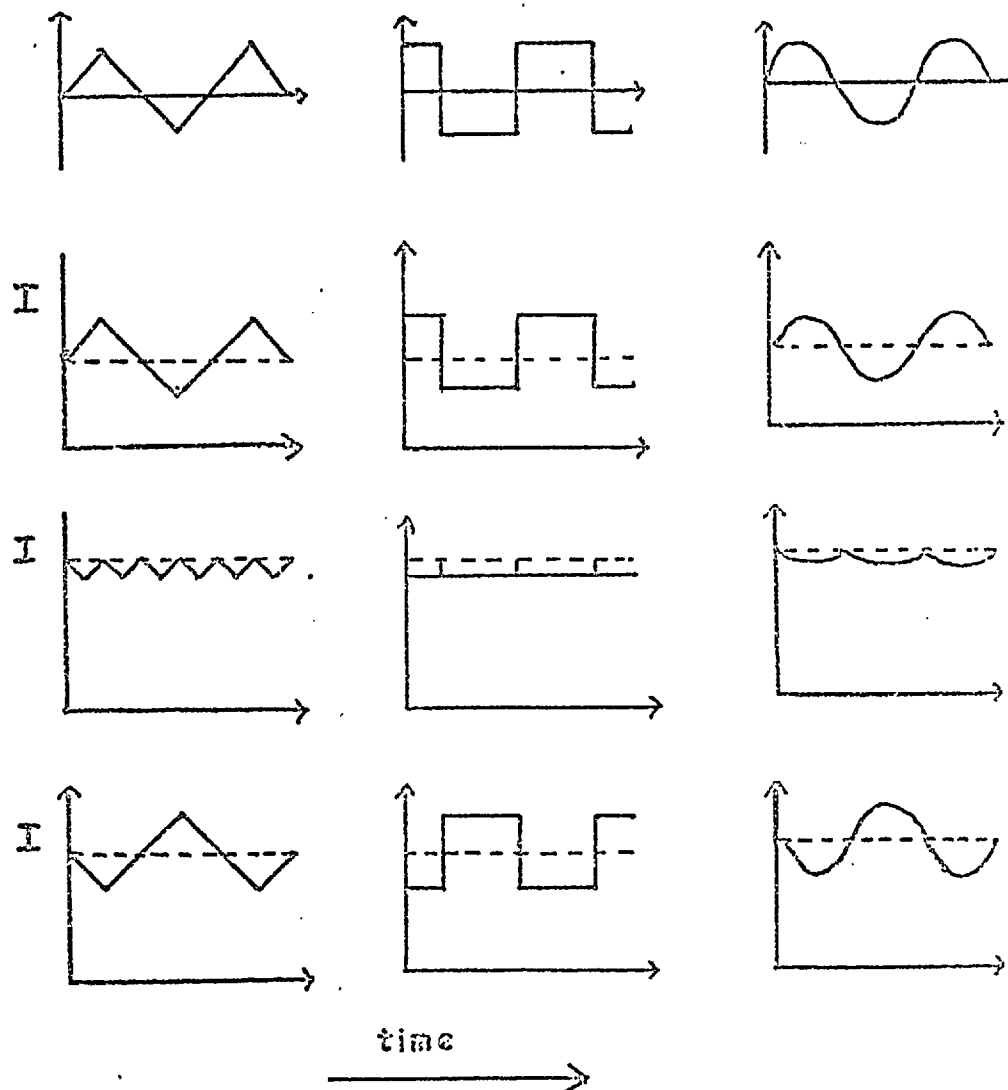
Schematic Representation of Resonance Line Modulation using a Triangular Waveform at different Microwave Power Levels.

modulation
waveform

Figure 41

Schematic Representation of
Radiation Intensity Produced
by various Modulation Wave-
forms at different Microwave
Power Levels.

(dotted line resonance
indicates d.c.
radiation level) radiation
intensity



is capable of measuring a signal which has a consistent phase shift of 180° , then this would be the optimal operational microwave power level for the a.c. mode of operation. This procedure was used for all EDLs investigated.

(d) Optimal Operating Conditions

These conditions, for use in the a.c. mode of operation, were experimentally determined for Cd, Hg, Zn, Sb, Se, As, and Pb EDLs, see Table 4-2. A comparison of the noise and drift of these sources was then made when operated in the d.c. mode, in the a.c. mode with transformer coupled modulation and in the a.c. mode with modulation injected at the error sensing point of the stabilising element, see Table 4-2. In every instance operation in the a.c. mode was found to be superior with respect to noise and drift characteristics. In addition, modulation of the stabilising circuit was found to produce less noise and drift than transformer coupled modulation. When operated in the a.c. mode, the mean microwave power of operation was always less than that used in the d.c. mode leading to an increased lifetimes of the EDL. This caused a decreased rate of attack of the EDL fill material on the quartz walls of the source envelope.

TABLE 4-2

Optimal Operating Conditions, Noise and Drift for EDLs used in ac and dc modes

Material	Wavelength (nm)	Optimum power (watts)		Average peak to peak noise measured over 30 min. period			Drift (percentage/hr)		
		dc mode	ac mode	dc mode	dc mode transformer modulation	ac mode stabilisation modulation	dc mode	ac mode transformer modulation	ac mode stabilisation modulation
Cd	228.8	60	35	2.2	1.3	0.3	-3.6	-1.2	-1.0
Hg	253.7	38	25	2.5	2.6	0.5	-4.6	-1.7	-1.2
Zn	213.9	65	38	1.0	0.4	0.4	-3.5	-1.7	-1.2
Sb/I ₂	231.1	40	25	2.7	1.3	0.5	-4.3	-1.5	-1.2
Se	196.1	38	25	3.1	1.6	0.7	-2.8	-1.3	-1.3
As/I ₂	193.7	40	28	1.8	0.7	0.4	-2.5	-0.9	+0.2
Pb/I ₂	283.3	50	30	3.0	1.7	0.9	-5.8	-2.3	-1.5

4.5 Resistor Switched Modulation

Although modulation of the stabilising circuit of the magnetron power supply has been found to be very satisfactory, it has two limitations: (i) a voltage amplifier capable of giving an a.c. output of about 200 volts (peak to peak) is required; and (ii) as this a.c. amplifier is by necessity a.c. coupled to the error sensing point of the stabilising element, the modulation can only be set about a mean power level, which limits the powers between which the magnetron can be modulated.

To overcome these two problems, a new type of modulator was built (Figure 42). This modulator contains a variable resistor, similar to the power control resistor in the magnetron anode circuit, which could be switched 'in' or 'out' of circuit by a transistor. When the modulator resistor is 'out of circuit' the anode resistor controls the modulation power minimum, and when it is switched 'in circuit' the modulation power maximum is controlled by the modulator resistor. The rate of switching of the resistor, i.e. the modulation frequency, is controlled by the Hewlett Packard Oscillator used in the previous modulation study. This system was capable of being modulated between any two levels within the power range of 15-100 watts, which gives a maximum percentage of modulation of 85%. The system was only capable of square wave modulation, but could be used at any mark

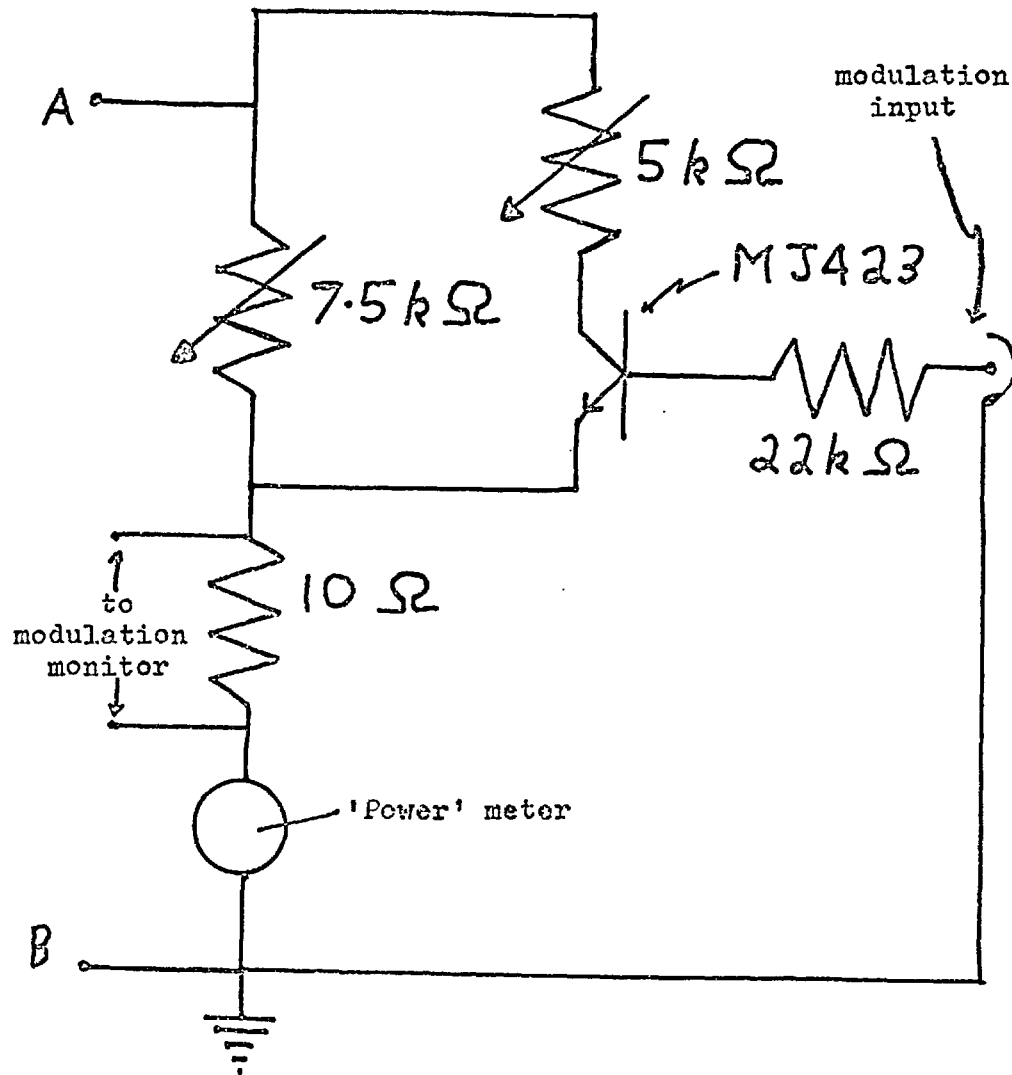


Figure 42

Circuit Diagram of the Switched Resistor Modulator (A - goes to positive side of the magnetron power supply. B - goes to the magnetron anode).

space ratios. The maximum frequency of modulation to which the transistor responded fully was 25,000 Hz; however, this could easily be extended, if desired, by using a different transistor.

The short term noise, drift and signal levels of various EDL intensities produced by this form of modulation were compared to those obtained from the stabilisation modulation, see Table 4-3. The short term noise was found to be about 25% less, the drift was about the same and the signal magnitude was about 30-80% higher than those obtained with stabilisation modulation.

4.6 Conclusion

Modulation of the primary source results in less noise and drift than that obtained in d.c. operation. Three methods of modulation have been investigated (transformer coupled, stabilisation and switched resistor). Switch resistor modulation was found to be superior to the two other methods; it gave the lowest noise and drift rates and the highest a.c. signal level. Additionally, the switched resistor modulator was both simple and cheap to construct and more versatile in operation than the other two methods.

Generally modulated EDLs require less mean power than those operating in the d.c. mode, which leads to longer lamp lifetimes. Modulation allows the use of

TABLE 4-3

A COMPARISON OF NOISE, DRIFT AND SIGNAL MAGNITUDES FOR SEVERAL EDLS USING BOTH STABILISATION AND SWITCHED RESISTOR MODULATION

EDL used	Stabilisation Modulation					Switched Resistor Modulation				
	Upper power (mod. peak) watts	Lower power (mod. trough) watts	Noise %	Drift %/hr	Signal magnitude	Upper power watts	Lower power watts	Noise %	Drift %/hr.	Signal Magnitude
Cd	50	20	0.4	-1.0	4.2	56	15	0.3	-1.1	8.2
Hg	35	16	0.6	-1.2	5.6	36	15	0.5	-1.3	6.1
Zn	54	22	0.4	-1.7	4.8	61	15	0.3	-1.5	8.1
Sb/I ₂	36	16	0.5	-1.3	4.6	38	15	0.5	-1.4	4.9
Se	35	16	0.7	-1.3	4.5	36	15	0.6	-1.4	5.2
As/I ₂	38	18	0.4	+0.2	5.7	41	15	0.5	-0.1	6.2
Pb/I ₂	43	17	0.9	-2.2	6.3	46	15	0.7	-1.6	8.3

N.B. all modulation was at 10KHz ~ square wave
1:1 mark space ratio (ie optimum conditions)

lock-in, phase sensitive detection systems which are capable of increasing the signal to noise ratio in analytical measurements. The optimum frequency of modulation was found to be ca. 20,000 Hz using a square waveform for both stabilisation and switched resistor modulation. Unfortunately, the transformer coupled modulation was only able to operate at 50 or 100 Hz with a sine waveform.

CHAPTER V

N O I S E

5.1 Introduction

The sensitivity of an instrument cannot be increased ad infinitum simply by increasing the amplification of the detection system, because superimposed on any signal is a component call noise. Noise may be defined as spurious signal components occuring within the capability of the measurment system (139). Thus the signal output recorded on an analogue system can be viewed as a d.c. voltage or current (the signal) on which an a.c. component (the noise) is superimposed.

The limiting sample concentration, C_m , for any instrumental technique, where the noise is random and free from readout drift, is usually defined for spectrochemical methods (158, 159, 160) as that sample concentration, C_m , which gives a signal to rms noise ratio, S/N , of

$$(S/N)_{C_m} = \frac{3\sqrt{2}}{\sqrt{n}} \quad (1)$$

for a confidence level of 99.7%

Where 3 corresponds to three standard deviations, $\sqrt{2}$ is needed because the noise is the quadratic sum of the noise on the background (or blank) signal and the noise on the sample signal, and n is the number of pairs of sample - background measurements.

The work in this thesis is mainly concerned with atomic fluorescence, which is a luminescence process. The measured photoanodic current from the photodetector, i , in amperes,

is given by:

$$i = N e B M \quad (2)$$

where N is the number of photons striking the photocathode of the photomultiplier per second, e is the charge of an electron, (1.6×10^{-19} coulombs) and BM is the overall gain of the phototube.

The measured readout voltage (or signal), E , is given by

$$E = G R_L i \quad (3)$$

where R_L is the load resistance, in ohms, connected to the photo anode of the photo multiplier and G is the overall voltage gain of the amplifier-readout system. Now the number of photons striking the photocathode per second is proportional to the intensity of the atomic fluorescence, I_F . The fluorescence intensity emitted in all directions, I_F , is evaluated from (161)

$$I_F = \frac{\bar{\Phi}_F}{I_F} I_0 (1 - e^{-kL}) \quad (4)$$

where $\frac{\bar{\Phi}_F}{I_F}$ is the power efficiency, i.e. the ratio of the radiant power emitted by the fluorescence to the radiant power absorbed. I_0 is the intensity of the radiation incident on the absorbing sample, L is the path length over which absorption occurs, and k is the average absorptivity coefficient which includes the concentration of the absorber.

Thus from equations (2), (3) and (4) it can be seen that the measured signal (or readout voltage) is directly proportional to the incident intensity of the primary source.

Thus, if the intensity of the primary source is increased, which has been the object of the work in Chapters II, III and IV, the signal will also increase. This increase in signal produces an increase in the signal to noise ratio for a given concentration of sample, and thus the limiting detectable sample concentration is decreased. Another way of increasing the signal to noise ratio for a given sample concentration is to decrease the noise level, which is the aim of the work in this chapter.

5.2 Types of noise found in spectrophotometric systems.

A spectrophotometric system usually consists of the following: a monochromator or filter to isolate the radiation of interest, a photodetector (usually a photomultiplier tube) to convert the optical signal to an electrical signal, and an amplifier-readout system to amplify and display this electrical signal. In atomic fluorescence flame spectrophotometry, which is the main consideration of this thesis, we have an excitation (primary) source and a flame in addition to the measurement system described above. Every component part of the total system is capable of producing noise, which may or may not be a limiting factor in the final signal to noise ratio. A brief description of the types of noises produced in various parts of the spectrophotometric system is given below:-

(a) Monochromator: if a monochromator has a tendency to drift from or about the wavelength at which it has been set, variations (i.e. noise) in the signal level may be produced. This drift may be due to thermal or mechanical oscillations, however, as in atomic fluorescence the monochromator slit widths and thus the spectral bandpass are large, which minimises the contribution of this effect.

(b) Photomultiplier tube (PMT): when using a PMT at very low light levels, two noises, namely shot and Johnson noises, will generally become significant. The shot noise, N_s , is the random fluctuation of the electron current from any emitting surface of a PMT. This results in a variational noise current superimposed on the PMT current. The rms shot noise photoanodic current, in amperes, is given by:

$$i_s = \sqrt{2e(i + id) \Delta f BM} \quad (5)$$

where i is the photoanodic current flowing through the PMT due to light striking the photocathode, id is the dark current due primarily to thermionic emission from the photocathode, BM is the overall gain of the PMT, e is the charge of an electron, and Δf is the frequency response bandwidth of the amplifier-readout system. The shot noise readout voltage, N_s , is given by:

$$N_s = \sqrt{2e(i + id) \Delta f BM G^2 R_L^2} \quad (6)$$

The rms Johnson noise voltage, N_j , is a randomly varying

potential difference arising between the terminals of a resistor caused by thermal agitation of electrons within the resistor, and is given by:

$$N_J = \sqrt{4kT R_L G^2 \Delta f} \quad (7)$$

where T is the temperature of the load resistor in degrees Kelvin, and k is the Boltzmann constant. Generally the Johnson noise is negligible at room temperature compared with shot noise, thus it will be neglected in any further discussion.

(c) Primary source and flame: both the flame and the primary excitation source produce noise, which is caused by a flickering of the light output. This type of noise has been variously called "flicker noise", "1/f noise", and "current noise". Unlike Johnson and shot noise, which are white (that is, of equal amplitude at all frequencies) 1/f noise shows an approximately 1/f distribution, where f is the frequency of measurement (162). The actual frequency distribution of 1/f noise is governed by $1/f^n$, where the index n varies between 0.7 and 2.0 (163); however, for most flames and light sources n approximates to unity and it will be taken to such in any further discussion. Winefordner et al. (4) have used a formula for calculating the 1/f noise, N_f , which does not allow for any variation of its magnitude with frequency. It can only be assumed, therefore, that they were considering the system to be operating under d.c. or fixed frequency

conditions. The formula they used was:

$$N_f = \frac{e}{\mathcal{E}} i_{S/F} \sqrt{\Delta f} R_L G \quad (8)$$

where $i_{S/F}$ is the photoanodic current, in amperes, due to radiation of intensity $I_{S/F}$ striking the photocathode of the PMT, and $\frac{e}{\mathcal{E}}$ (the flicker factor) is the rms fluctuation in intensity, $I_{S/F}$ per unit of intensity, $I_{S/F}$, per unit frequency response bandwidth, i.e.

$$\frac{e}{\mathcal{E}} = \Delta I_{S/F} / I_{S/F} \text{ for a } \Delta f = 1\text{Hz}$$

But when one allows for a variation of noise level with frequency the flicker factor $\frac{e}{\mathcal{E}}$ is replaced by F/f , where F is the flicker constant and f is the frequency of measurement. The flicker constant is a characteristic of a flame or a source, and is independent of frequency. The equation for $1/f$ noise now becomes:

$$N_f = F/f i_{S/F} \sqrt{\Delta f} R_L G \quad (9)$$

For the $1/f$ noise of a flame, $i_{S/F}$ is the photoanodic current produced by the flame background, whereas for the $1/f$ noise of a source $i_{S/F}$ is the photoanodic current produced by the atomic fluorescence of the analyte.

(d) Amplifier-readout system: the amplifier-readout total rms noise voltage, N_A , is made up of two independent noises, one of which is a $1/f$ type noise and the other which is just a constant, C_A , which is inherent in any electronic system. N_A is given by:

$$N_A = \sqrt{\left(\frac{F}{f} (i + id) \sqrt{\Delta f} R_L G\right)^2 + C_A^2} \quad (10)$$

5.3 Noise in atomic fluorescence spectrometry

The specific types of noise present in any given spectrochemical analysis depend on the apparatus used and which method of analysis is employed.

Noise is important both in determining the precision and the limit of detection of an analytical method. Our main concern with this work has been the limit of detection, where the S/N ratio has been defined as being equal to $3\sqrt{2}/\sqrt{n}$ (approximately equal to 2 for six blank/signal readings). Thus, the limit of detection of a given analytical method is governed by the signal to noise ratio measured at its limit of detection. The noises that are important at the limit of detection of an AFS method are usually the shot noise produced by the flame background radiation and the 1/f noise of that flame background; in comparison Johnson noise, monochromator noise and amplifier noise are usually negligible.

At the limit of detection in AFS the photoanodic current due to the flame background is of the order of 10^{-7} amperes. The flame flicker constant is about 10^{-1} , the effective gain of a PMT is about 10^6 , the dark current of a PMT is about 10^{-9} amperes. Under these conditions, the shot noise current i_s is given by:

$$\begin{aligned} i_s &= \sqrt{2e BM \Delta f (1 + id)} \\ &\approx \sqrt{2 \times 1.6 \times 10^{-19} \times 10^6 (10^{-7}) \Delta f} \end{aligned}$$

now assuming the measurement system to be a.c. with an operating frequency of 100 Hz and an electrical bandwidth of 10 Hz.

$$i_s \approx 5.5 \times 10^{-10} \text{ amperes.}$$

The flame $1/f$ noise current i_f is given by:

$$\begin{aligned} i_f &= \frac{F}{f} i \sqrt{\Delta f} \\ &= \frac{10^{-1}}{10^2} 10^{-7} \sqrt{10} \\ &\approx 3.2 \times 10^{-10} \text{ amperes.} \end{aligned}$$

Thus the $1/f$ and the shot noise are about the same magnitude; however, for flames with higher backgrounds the $1/f$ noise will be larger than the shot noise, while for flames with smaller backgrounds, the shot noise will be larger than the $1/f$ noise.

It was decided to investigate some noise parameters using the tuned amplifier/phase locked system described in Chapter IV.

The bandwidth of the tuned amplifier is controlled by a 'Q' control; now the bandwidth depends on both the operating frequency and the 'Q' setting of the tuned amplifier, i.e.

$$\Delta f = f/Q \quad (11)$$

Substituting this in the equations for shot and $1/f$ noise we get:

$$N_s = \sqrt{2e B M (i + i_d) G^2 R_L^2 f/Q} \quad (12)$$

and

$$\begin{aligned} N_f &= \frac{F}{f} i R_L G \sqrt{f/Q} \\ &= \frac{F i R_L G}{\sqrt{fQ}} \end{aligned} \quad (13)$$

As both these noises are independent of each other, the total noise N_T is found by:

$$N_T = \sqrt{(N_S)^2 + (N_F)^2} \quad (14)$$

which gives:

$$N_T = \frac{R_L G}{\sqrt{Q}} \sqrt{2e B M (i + id)f + \frac{F^2 i^2}{f}} \quad (15)$$

From this equation it can be seen that the total noise of the system should be proportional to $1/\sqrt{Q}$ or that the signal to noise ratio equals $K/\sqrt{Q}$, where K is a proportionality constant. To check this derivation a 0.005 ppm Cd solution was nebulised into an air/propane flame and irradiated with a cadmium EDL modulated at 10KHz (as described in Chapter IV). Signal to noise ratios of the atomic fluorescence produced were measured at different 'Q' settings; the results are given in Table 5-1

TABLE 5-1

Variation of S/N for different amplifier 'Q' settings - for the atomic fluorescence of Cd

'Q' value	S/N of Cd AF	$K = S/N/\sqrt{Q}$
5	3.85	1.73
10	5.23	1.66
32.8	9.5	1.66
330	28.5	1.65

The results of this experiment confirmed that the signal to noise ratio is directly proportional to $\sqrt{Q}$, within experimental error. Thus for this type of a.c. system we can obtain the best signal to noise ratios, and thereby the lowest limit of detection, by using the highest 'Q' value available to us. Unfortunately, with very high values of 'Q' it is difficult to keep the tunable amplifier at the same frequency as that of the modulation, which can result in signal amplitude variation (frequency drift noise).

As the equation for total noise has now frequency terms in it, it should be theoretically possible to obtain the frequency at which the noise is at a minimum by differentiating it with respect to the frequency and solving for the minima. If we differentiate equation 15 with respect to the frequency we get:

$$\frac{dN_T}{df} = \frac{R_L G}{\sqrt{Q}} \left(2e BM (i + id)f + Fi \right)^{-\frac{1}{2}} \cdot \frac{1}{2} \left(2e BM (i + id) \cdot \frac{-F^2 i^2}{f^2} \right) \quad (16)$$

now at a maxima or minima $dN_T/df = 0$; when we let $dN_T/df = 0$ and solve for f we get two solutions:

$$2e BM (i + id)f + Fi/f = 0 \quad (17)$$

$$\text{and } 2e BM (i + id) \frac{-F^2 i^2}{f^2} = 0 \quad (18)$$

The first solution gives us a maxima or minima at a negative frequency which has no meaning in this particular case.

The second solution gives us:

$$f = \frac{Fi}{\sqrt{2e BM (i + id)}} \quad (19)$$

From the original equation for N_T it can be seen by inspection that as $f \rightarrow 0$ the $1/f$ noise term increases rapidly, and as $f \rightarrow \infty$ the shot noise term increases rapidly, thus a solution for f that falls between $f = 0$ and $f = \infty$ is likely to be a minima.

Now when using flames that are normally used for AFS i (the photoanodic current produced by the flame background) is approximately one hundred times as large as id (10^{-7} amperes compared to 10^{-9} amperes); thus id can be neglected in this equation for f , which gives us:

$$f = \frac{F/i}{\sqrt{2e BM}} \quad (20)$$

now the current $i = Ne BM$ (see equation 2, Chapter V) which, when substituted in equation 20, gives:

$$f = \frac{F/\bar{N}}{\sqrt{2}} \quad (21)$$

Now, if the flame background gives us a current of 10^{-7} amperes then:

$$\begin{aligned} N &= \frac{i}{eBM} \\ &= \frac{10^{-7}}{1.6 \times 10^{-19} \times 10^6} \approx 600,000 \text{ counts/sec.} \end{aligned} \quad (22)$$

Earlier we have taken F (the flame flicker constant) to be approximately $1/10$, now substituting these values into

the equation for $f_{\min}$ we get:

$$f_{\min} = \frac{1/10 \times \sqrt{600,000}}{\sqrt{2}} \approx \underline{55 \text{ Hz}}$$

To see if equation 21, for the frequency of minimum noise, had any practical implications an air/propane premixed flame was placed in front of the monochromator slit and the noise produced by this flame at various frequencies was measured using the a.c. system described in Chapter IV. This was repeated at several different slit widths (in each case the d.c. photoanodic current was measured) so that we now have the actual frequency of minimum noise for various intensities (i.e. photoanodic currents), see Table 5-2. Before any calculations of $f_{\min}$ could be carried out, it was necessary to measure the flicker constant of this flame. To do this the flame was placed in front of the monochromator with the slits wide open to minimise the shot noise contribution; a 100 Hz chopper was placed between the entrance slit and the flame so that the signal intensity could be measured. The chopper was then removed and the noise level at this frequency was measured. The amplifier was tuned to 100 Hz for both the measurements. The signal level was found to be 1150 arbitrary units and the peak to peak noise 3.6 arbitrary units. The bandwidth of the tunable amplifier during this measurement was 10 Hz (i.e. a 'Q' of 10). Normally the rms noise is found by dividing the peak to peak noise by five; however, the phase sensitive detector effectively does this itself. For the flicker

factor $\frac{P}{E}$ to be calculated the measured noise must be corrected for the electrical bandwidth of the measurement system, by dividing the noise by the square root of the bandwidth.

$$\begin{aligned}\text{Now } \frac{P}{E} &= \frac{\text{rms noise/unit bandwidth}}{\text{signal}} \\ &= \frac{3.6/\sqrt{10}}{1150} \approx \underline{0.001 \text{ per Hz}}\end{aligned}$$

Now the flicker constant

$$F = \frac{P}{E} f \text{ (where } f = \text{the frequency that } \frac{P}{E} \text{ was measured at).}$$

$$\therefore F = 0.001 \times 10^2 = \underline{0.1}$$

For the PMT used in this experiment $BM \approx 10^6$, thus as we now have values for the flame background current, the flicker constant and the effective gain of the photomultiplier, we calculated the theoretical values of $f_{\min}$ using formulas 22 and 21. These calculated values of $f_{\min}$ were then compared with the observed values, see Table 5-2. Surprisingly the two values matched fairly closely.

TABLE 5-2

Comparison of observed and calculated values of the frequency for minimum noise of an air/propane flame at various PMT current levels

D.C. PMT current amps.	Cal. frequency of min. noise Hz	Obs. frequency of min. noise Hz
10^{-8}	16.8	22
10^{-7}	54	44
10^{-6}	168	190
10^{-5}	540	480

Thus the frequency at which the total noise in an atomic fluorescence flame spectrometry system is at a minimum varies with the magnitude of the photoanodic current produced by the flame background. However, as stated earlier, the background current is usually 10^{-7} - 10^{-6} amps (depending on the type of flame and the instrumental slit width used), which gives an optimum frequency of between 50 and 170 Hz. This frequency would be the best frequency to use only if the output of the primary source is not frequency dependent. Such behaviour is obtained when the primary source is mechanically chopped. But as mechanical chopping of the primary source produces several problems (see Chapter IV), we use electronic modulation of the source. This type of source modulation produces a signal that is frequency dependent (see Figure 36). To enable us to find the best frequency of modulation (i.e. that frequency which gives the best signal to noise ratio at or near the limit of detection), the signal to noise ratios were measured at different EDL modulation frequencies for the atomic fluorescence signal produced by a 0.005 ppm solution of Cadmium when it was sprayed into an air/propane premixed flame and irradiated with a Cadmium EDL. The largest signal to noise ratio was found to occur at 10 KHz, (see Figure 43). This optimum frequency was different from that obtained for the intensity of the radiation emitted

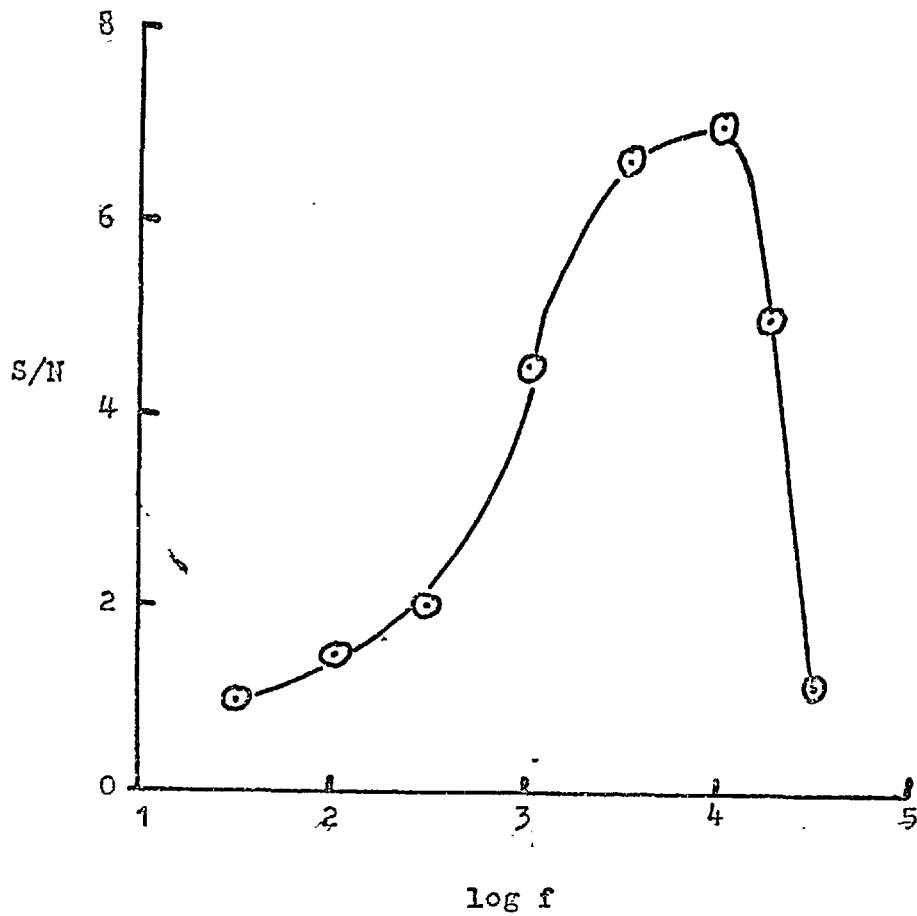


Figure 43

Plot of Signal to Noise vs.
Frequency of Modulation of
a Cadmium EDL used in the
Atomic Fluorescence of Cadmium.
(0.005 ppm solution)

by a modulated EDL (20 KHz) and different from the frequency of minimum noise (50-170 Hz). However, the atomic fluorescence optimum frequency lies between the other two optimum frequencies, as would be expected.

This frequency optimisation for atomic fluorescence measurements was repeated for other elements (As, Sb, Hg, Zn and Mn) and in all cases the optimum frequency was found to be between 9 and 10 KHz.

Now that the a.c. system for measuring atomic fluorescence flame spectrometry has been optimised (at a frequency of 10 KHz, with square wave modulation, and as high a 'Q' setting on the tunable amplifier as is possible without getting frequency drift, i.e. ≈ 250), the limits of detection obtained from a d.c. system and the optimised a.c. system were compared for several elements. In every case the a.c. system gave the lower limits of detection usually by about an order of magnitude over the d.c. system (see Table 5-3). The advantage of the a.c. system was greatest for those elements that fluoresced at the longer wavelengths (i.e. In, Tl and Ga); this was probably due to the higher flame background intensity and thus the higher noise levels at those wavelengths.

TABLE 5-3

A comparison of the limits of detection obtained
for the atomic fluorescence of various elements
using an a.c. and a d.c. system of detection

Element	Wavelength of measurement nm	limit of detection d.c. system ppm	limit of detection a.c. system ppm
Cd	228.8	0.0002	0.00004
Zn	213.9	0.0003	0.00004
Hg	253.7	0.1	0.011
Tl	377.6	0.04	0.002
In	410.5	8.0	0.3
Ga	417.2	10	0.6

5.4 Conclusion

The optimum operating frequency for measurement of atomic fluorescence in flames with an a.c. system has been found to be 10 KHz. The tuned a.c. amplifier should have as narrow a bandpass as possible, which is consistent with being able to keep the detection frequency the same as the modulation frequency. The a.c. system has been found to be superior to the d.c. system of measurement for atomic fluorescence flame spectrometry for all elements investigated.

BIBLIOGRAPHY

1. J.D. Winefordner and T.J. Vickers, Anal. Chem. 36, 161 (1964).
2. B. Budick, R. Novick and A. Lurio, Applied Optics 4, 229 (1965).
3. V.B. Gerard, J. Sci. Instr. 39, 217 (1962).
4. W.E. Bell, A.L. Bloom and J. Lynch, Rev. Sci. Instr. 32, 688 (1961).
5. R.G. Brewer, Rev. Sci. Instr. 32, 1356 (1961).
6. R.J. Atkinson, G.D. Chapman and L. Krause, J. Opt. Soc. Am. 55, 1269 (1965).
7. J.D. Winefordner, M.L. Parsons, J.M. Mansfield and W.J. McCarthy, Spectrochim. Acta, 23B, 37 (1967).
8. H.P. Hoomayers, Spectrochim. Acta 23B, 567 (1968).
9. A.C.G. Mitchell and M.W. Zemansky, Resonance Radiation and Excited Atoms, University Press, Cambridge (1961).
10. A. Unsöld, Physik der Sternatmosphären, Springer, Berlin (1955).
11. J.D. Winefordner and J.M. Mansfield, Paper presented at the 1967 National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.
12. M.L. Parsons, W.J. McCarthy and J.D. Winefordner, Appl. Spectr. 20, 223 (1966).
13. C. Young, Tables for Calculating the Voigt Profile, University of Michigan, Ann Arbor, Mich., (1965).
14. J.D. Winefordner, M.L. Parsons, J.M. Mansfield and W.J. McCarthy, Anal. Chem. 39, 436 (1967).
15. J.D. Winefordner, W.W. McGee, M.L. Parsons, J.M. Mansfield and K.E. Zacha, Anal. Chim. Acta 36, 25 (1966).
16. J.D. Winefordner and R.A. Stabb, Anal. Chem. 36, 165 (1964).
17. Ibid, idem 36, 1367 (1964).
18. J.M. Mansfield, J.D. Winefordner and C. Veillon, idem 37, 1049 (1965).
19. R.M. Dagnall, T.S. West and P. Young, Talanta 13, 803 (1966).
20. H. Prugger, Zeiss Information No. 56, p. 54 (1965) (work by R. Klaus).

21. G.I. Goodfellow, Anal. Chim. Acta 36, 132 (1966).
22. R.M. Dagnall, K.C. Thompson and T.S. West, idem 36, 269 (1966).
23. F. Paschen, Ann. Physik 50, 901 (1916).
24. H. Schüller, Z.f. Phys. 35, 323 (1926).
25. Ibid idem 59, 149 (1930).
26. S. Tolansky, High Resolution Spectroscopy, Methuen, London, (1947).
27. B.J. Russel, J.P. Shelton and A. Walsh, Spectrochim. Acta 8, 317 (1957).
28. W.G. Jones and A. Walsh, Spectrochim. Acta 16, 249 (1960).
29. J.W. Robinson, Atomic Absorption Spectroscopy, Marcel Dekker, New York (1966).
30. J.I. Dinnin and A.W. Heltz, Paper presented at the 1967 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1967.
31. D.N. Armestrout, Anal. Chem. 38, 1235 (1966).
32. J.V. Sullivan and A. Walsh, Spectrochim. Acta 21, 721 (1965).
33. D.C. Manning and J. Vollmer, At. Abs. Newsletter 6, 38 (1967).
34. J. Vollmer, At. Abs. Newsletter 5, 35 (1966).
35. W. Gillies, G. Yamasaki and J.C. Burger, Paper presented at the fifth national meeting of the Society for Applied Spectroscopy, Chicago, Ill., June 1966.
36. Z. Van Gelder, Appl. Spectrosc. 22, 581 (1968).
37. J.I. Dinnin, Anal. Chem. 39, 1491 (1967).
38. J.I. Dinnin and A.W. Heltz, Anal. Chem. 40, 481 (1968).
39. G. Rossi and N. Omenetto, Talanta 16, 263 (1969).
40. A. Walsh, Spectrochim. Acta 7, 108 (1955).
41. N.P. Ivanov and N.A. Kazirava, Zh. Analit. Khim. 19, 1266 (1966).
42. V.A. Fassel, V.G. Mossotti, W.E.L. Grossman and R.N. Kniseley, Spectrochim. Acta 22, 347 (1966).
43. C. Veillon, J.M. Mansfield, M.P. Parsons and J.D. Winefordner, Anal. Chem. 38, 204 (1966).

44. D.C. Manning and P. Heneage, At. Abs. Newsletter 7, 80 (1968).
45. D.W. Ellis and D.R. Demers, Anal. Chem. 38, 1943 (1966).
46. M.S. Cresser and T.S. West, Spectrochim. Acta 25B, 61 (1970).
47. D.R. Demers and D.W. Ellis, Anal. Chem. 40, 860 (1968).
48. L. Klein, Appl. Optics 7, 667 (1968).
49. A. Strasheim, Nature 196, 1962 (1962).
50. A. Strasheim and H.G.C. Human, Spectrochim. Acta 23B, 265 (1969).
51. H.G.C. Human, L.R.P. Butler and A. Strasheim, Analyst 94, 81 (1968).
52. S. Greenfield, P.B. Smith, A.E. Breeze and N.M.D. Chilton, Anal. Chim. Acta 41, 385 (1968).
53. D.J. Smith, Ph.D. Thesis, University of London (1971).
54. C.S. Rann, Spectrochim. Acta 23B, 245 (1968).
55. R.M. Dagnall, K.C. Thompson and T.S. West, Talanta 14, 551 (1967).
56. Ibid, Analyst 92, 506 (1967).
57. Ibid, idem 93, 72 (1967).
58. Ibid, idem 93, 518 (1967).
59. Ibid, idem 94, 643 (1969).
60. R.M. Dagnall, M.R.G. Taylor and T.S. West, Spec. Lett. 1, 397 (1965).
61. J.M. Mansfield, M.P. Bratzel, H.O. Norgordon, D.O. Knapp, K.E. Zacha and J.D. Winefordner, Spectrochim. Acta 23B, 389 (1968).
62. K.E. Zacha, M.P. Bratzel, J.D. Winefordner and J.M. Mansfield, Anal. Chem. 40, 1733 (1968).
63. K.M. Aldous, Ph.D. Thesis, University of Longon (1970).
64. H.G.C. Human and L.R.P. Butler, Spectrochim. Acta 25B, 647 (1970).
65. R. Smith, R.C. Elser and J.D. Winefordner, Anal. Chim. Acta 48, 35 (1969).
66. J. Matousek and V. Sychra, Anal. Chim. Acta 49, 175 (1970).
67. D.A. Jackson, Proc. Roy. Soc. A121, 432 (1928).

68. W.F. Meggers, J. Opt. Soc. Am. 38, 7 (1948).
69. W.F. Meggers and F.O. Westfall, J. Res. Nat. Bur. Std. 44, 447 (1950).
70. W.F. Meggers and K.G. Kessler, J. Opt. Soc. Am. 40, 737 (1950).
71. M. Zelikoff, P.H. Wyckoff, L.M. Aschenbrand and R.S. Loomis, J. Opt. Soc. Am. 42, 818 (1952).
72. C.H. Corliss, W.R. Bozman and F.O. Westfall, J. Opt. Soc. Am. 43, 398 (1953).
73. A.T. Forrester, R.A. Gudmundsen and P.O. Johnson, J. Opt. Soc. Am. 46, 339 (1956).
74. F.S. Tomkins and M. Fred, J. Opt. Soc. Am. 47, 1087 (1957).
75. E. Jacobsen and G.R. Harrison, J. Opt. Soc. Am. 39, 1054 (1949).
76. L. Borey and H. Wise, AERE-R 2976 (1959).
77. E.F. Worden, R.G. Gutmacher and J.G. Concray, Applied Optics 2, 707 (1963).
78. F.C. Fehsenfeld, K.M. Evenson and H.P. Broida, Rev. Sci. Instr. 36, 294 (1965).
79. F.C. Fehsenfeld, K.M. Evenson and H.P. Broida, NBS Report 8701, U.S. Dept. of Commerce (1964).
80. G.D. Chapman, L. Krause and I.H. Brockman, Can. J. Phys. 42, 535 (1964).
81. G.D. Chapman and L. Krause, Can. J. Phys. 43, 563 (1965).
82. D.H. Barling, V. Czajkowski and L. Krause, J. Opt. Soc. Am. 57, 1162 (1967).
83. N.S. Ham and A. Walsh, Spectrochim. Acta 12, 88 (1958).
84. P. Warneck, Appl. Opt. 1, 721 (1962).
85. Y. Tanaka and P.G. Wilkinson, J. Opt. Soc. Am. 45, 1044 (1955).
86. H. Okabe, J. Opt. Soc. Am. 54, 478 (1964).
87. E.W. Sehlag and F.J. Comes, J. Opt. Soc. Am. 50, 866 (1960).
88. P.G. Wilkinson and E.T. Byram, Appl. Opt. 4, 581 (1965).
89. Y. Tanaka and M. Zelikoff, J. Opt. Soc. Am. 44, 254 (1954).
90. J.M. Vaughan, J. Opt. Soc. Am. 54, 318 (1969).

91. N.P. Ivanov, L.V. Minervina, S.V. Boranov and L.G. Pofralidi, Zh. Analit. Khim. 21, 1129 (1966).
92. J.M. Mansfield, Ph.D. Thesis, University of Florida, U.S.A. (1967).
93. R.F. Browner, R.M. Dagnall and T.S. West, Anal. Chim. Acta 45, 163 (1969).
94. B. Fleet, K.V. Liberty and T.S. West, Anal. Chim. Acta 45, 205 (1969).
95. R.F. Browner, R.M. Dagnall and T.S. West, Talanta 16, 75 (1969).
96. K.M. Aldous, R.M. Dagnall and T.S. West, Analyst 94, 347 (1969).
97. D.O. Cooke, R.M. Dagnall and T.S. West, Anal. Chim. Acta, in press.
98. M.D. Silvester and W.J. McCarthy, Anal. Lett. 2(5), 305 (1969).
99. M.D. Silvester and W.J. McCarthy, Spectrochim. Acta 25B, 229 (1970).
100. J.R. Hollanhan, J. Chem. Ed. 43, A401 (1966).
101. M.D. Silvester, Submitted to Anal. Chim. Acta.
102. C. Veillon, Ph.D. Dissertation, University of Florida, August 1965.
103. R.M. Dagnall, M.D. Silvester and T.S. West, Submitted to Anal. Chim. Acta.
104. K.C. Thompson, Ph.D. Thesis, University of London (1968).
105. D.O. Cooke, Ph.D. Thesis, University of London (1971).
106. C. Woodward, Anal. Chim. Acta 51, 548 (1970).
107. S.J. Pratt, Ph.D. Thesis, University of London (1970).
108. D.H. Hingle, G.F. Kirkbright and T.S. West, Analyst 93, 522 (1968).
109. T.S. West and X.K. Williams, Anal. Chim. Acta 42, 29 (1968).
110. R.F. Browner, R.M. Dagnall and T.S. West, Anal. Chim. Acta 46, 207 (1969).
111. J.M. Mansfield, M.L. Parsons, C. Veillon and J.D. Winefordner, Anal. Chem. 38, 204 (1966).
112. D.C. Manning and P. Heneage, At. Abs. Newsletter 6, 124 (1967).
113. T.S. West and X.K. Williams, Anal. Chem. 40, 335 (1968).
114. J. Matousek and V. Sychra, Anal. Chem. 41, 518 (1969).
115. V. Sychra and J. Matousek, Chem. Listy. 63, 177 (1969).

116. J.V. Sullivan and A. Walsh, Spectrochim. Acta 16, 249 (1960).
117. D.C. Manning and P. Heneage, At. Abs. Newsletter 7, 8 (1968).
118. V.G. Massotti, Abstracts Eastern Analytical Symposium, New York, November 1970.
119. Robert D. Moore, Electronics 35(25), 40 (1962).
120. G.A. Morton, Appl. Opt. 7, 1 (1968).
121. M.L. Franklin, G. Horlick and H.V. Malmstadt, Anal. Chem. 41, 2 (1969).
122. D. Alger, R.M. Dagnall, B.C. Sharp and T.S. West, Submitted to Anal. Chem. Acta.
123. F.P. Dickey, S. Kopezynski and G.J. Bell, J. Chem. Phys. 25, 180 (1956).
124. F.P. Dickey and J. Hoffman, J. Chem. Phys. 28, 1253 (1958).
125. W.H. Rogge, F.L. Yarger and F.P. Dickey, J. Chem. Phys. 33, 453 (1960).
126. W. Lang, Mikrochim. Acta 796 (1964).
127. R. Herrmann and W. Lang, Z. Anal. Chem. 203, 1 (1964).
128. W. Lang, K. Rüdiger and R. Herrmann, Z. Angew. Phys. 17, 277 (1964).
129. K.M. Aldous, R.M. Dagnall and T.S. West, unpublished work.
130. R. Herrmann, W. Lang and K. Rüdiger, Z. Anal. Chem. 206, 241 (1964).
131. K. Rüdiger, B. Gutsche, H. Kirchhof and R. Herrmann, Analyst 94, 204 (1969).
132. W. Neu, R. Herrmann and H. Kirchhof, Messtechnik 4, 154 (1968).
133. K.M. Aldous, R.M. Dagnall and T.S. West, Anal. Chem. Acta 44, 457 (1969).
134. W. Trampisch and R. Herrmann, Spectrochim. Acta 24B, 215 (1969).
135. W. Lang, Z. Anal. Chem. 219, 321 (1966).
136. M.G. Jeremić and A.M. Antić-Jovanović, Abstracts of XV Colloquium Spectroscopicum Internationale, Madrid, Spain, No. 340 (1969).
137. A.M. Antić-Jovanović, V. Bojović and M. Marinković, Spectrochim. Acta 25B, 405 (1970).

138. M. Marinkovic and T.J. Vickers, Abstracts of Ninth National Meeting of the Society of Applied Spectroscopy, New Orleans, La., No. E1, October 1970.
139. M. Marinkovic and T.J. Vickers, Anal. Chem. 42, 1613 (1970).
140. B.W. Bullock and S. Silverman, J. Opt. Soc. Am. 39, 200 (1949).
141. R.J. Brehm and V.A. Fassel, Spectrochim. Acta 6, 341 (1954).
142. R.A. Harber and G.E. Sennek, Appl. Opt. 6, 1039 (1966).
143. D.W. Golightly, R.N. Kruseley and V.A. Fassel, Spectrochim. Acta 25B, 451 (1970).
144. C.T.J. Alkemade and J.M.W. Milatz, J. Opt. Soc. Am. 45, 583 (1955).
145. J. Gatehouse and A. Walsh, Spectrochim. Acta 16, 602 (1960).
146. J.A. Bowman, J.V. Sullivan and A. Walsh, Spectrochim. Acta 21, 721 (1965).
147. J.A. Bowman, J.V. Sullivan and A. Walsh, Spectrochim. Acta 22, 205 (1966).
148. R.M. Lowe, Spectrochim. Acta 24B, 191 (1969).
149. N.A. Sebestyen, Spectrochim. Acta 25B, 261 (1970).
150. N.S. Poluektov and S.E. Grinzard, Zavodskaya Laboratoriya 29, 998 (1963).
151. G.F. Box and A. Walsh, Spectrochim. Acta 16, 255 (1960).
152. P.C. Wildy and K.C. Thompson, Analyst 95, 562 (1970).
153. Ibid, idem 95, 776 (1970).
154. K.M. Aldous, D. Alger, R.M. Dagnall and T.S. West, Lab. Prac. 587 (1970).
155. M.S. Cresser, Ph.D. Thesis, University of London (1970).
156. K.M. Aldous, R.F. Browner, R.M. Dagnall and T.S. West, Anal. Chem. 42, 939 (1970).
157. C.F. Bruce and P. Hannaford, Spectrochim. Acta 26B, 207 (1971).
158. G. Gottschalk, "Statistik in der Quantitative Chemischen Analyse Fird". Enke, Stuggart, 1962.
159. P.A. St. John, W.J. McCarthy and J.D. Winefordner, Anal. Chem. 39, 1495 (1967).

160. J.D. Winefordner, W.J. McCarthy and P.A. St. John,
J. of Chem. Ed. 44, 80 (1967).
161. L. De Galan, W.W. McGee and J.D. Winefordner, Anal.
Chim. Acta.
162. Electronics for Scientists and Engineers, R.R. Benedict,
Prentice-Hall, N.J. U.S.A. (1967).
163. Peter Lee, Electronic Data Library (Volume 4), publishers
Morgan-Grampian.