

SOME DEVELOPMENTS IN THE TECHNIQUES OF

ANALYTICAL ATOMIC SPECTROMETRY

by

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ABSTRACT

On a theoretical basis expressions have been derived indicating the parameters affecting the sensitivity of determinations of trace metals by the techniques of atomic emission, atomic absorption and atomic fluorescence.

A preparative scheme is described for the production of microwave excited electrodeless discharge lamps for use as atomic spectral sources for most elements including alternative methods for those metals which attack the silica lamp bulb. Developments in microwave generators and cavities are described which improve the stability and warm-up characteristics of electrodeless discharge lamps.

A new type of long path burner constructed from stainless steel capillary tubing is described and the optical properties and atom profiles in the burning flame gases studied.

A method for the determination of trace quantities of total sulphur in organic and aqueous matrices is proposed utilising the emission from a cool flame of hydrogen.

Preliminary studies in the use of photon counting and solar blind detectors in atomic spectroscopy are reported with reference to the atomic fluorescence determination of zinc.

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CHAPTER I



INTRODUCTION

1.1 HISTORY

In 1663, Isaac Newton began his experimental work in optics by grinding lenses for the construction of telescopes. He was soon faced with the problem of reducing chromatic aberration. In 1666, (having obtained a prism to observe colours) he wrote:-

"Having darkened my chamber, and made a small hole in the window shuts, to let in a convenient quantity of the sun's light, I placed my prism at his entrance, that it might thereby be refracted to the opposite wall".

This experiment was the beginning of spectroscopy, but little progress in its analytical use was made for almost a century. In 1814, Josef Fraunhofer (1787-1826) was faced with the problem of defining more accurately the colour of light used in measuring the properties of glasses. He was led to make a detailed examination of the spectrum of the sun. The spectroscope, as used by Newton, consisted of a slit, lens, prism and screen. Fraunhofer had the excellent idea of using a theodolite telescope instead of the screen and so could make exact angular measurements. He discovered the dark lines in the solar spectrum which provided the first precise standards for measuring the dispersion of optical glasses. Later in 1823 he discovered the transmission grating and constructed the first glass grating by ruling lines with a diamond point. Thus he was able to measure the exact wavelength

of the lines, whereas before only angles had been used.

Although early workers had noted the colours imparted to diffusion flames of alcohol by metallic salts, it was not until the development of the premixed air/ coal-gas burner of Bunsen that atomic emission spectrometry (AE) took real form. Together with Kirchhoff, Bunsen developed a spectroscope of high sensitivity and they were able to demonstrate that the visible lines were not due to compounds but to elements. This resulted in the discovery of several new elements (Cs, Rb, Tl, In, Ga). [1,2]

Due to the sudden interest in arc and spark spectrometry in the early twentieth century interest in atomic flame emission spectrometry remained dormant until Lundegardh demonstrated the merits of the technique in 1928 in a series of papers [3]. These workers used a pneumatic nebuliser together with an air/acetylene flame. Instruments became available in the mid-nineteen forties mainly for the determination of alkali metals with their easily excited resonance lines. It is only comparatively recently, over the past ten or fifteen years, that the range of elements determinable has been extended to encompass most of the periodic table.

Atomic absorption spectrometry (AA) is simply defined as the measurement of absorption of radiation by discrete atoms. The basic principles were established by Kirchhoff [1] in 1860, using the atomic absorption lines discovered by Fraunhofer to deduce the presence of certain elements in the solar atmosphere. The theory of AA was evolved in the early nineteen hundreds

by physicists and astrophysicists. Much of this work has been summarised by Mitchell and Zemansky [4] in their treatise on "Resonance radiation and excited atoms".

The potentialities of AA as an analytical method were virtually overlooked until 1953 when Walsh [5] and later Alkemade and Milatz [6] demonstrated its use as a general analytical tool.

Atomic fluorescence spectrometry (AF) may be defined simply as the measurement of radiation from discrete atoms that are being excited by absorption of radiation from a source which is not seen by the detector. This phenomenon was first reported by Wood [7] in 1905 when he succeeded in exciting fluorescence of the D lines of sodium vapour. Wood called this fluorescence resonance radiation, because it was predicted by the classical theory of a light wave vibrating with the same frequency as the dipole oscillation of the medium. After his initial discovery, resonance radiation was observed for Hg, Li, Cd, Zn and several other elements. These studies again summarised by Mitchell and Zemansky [4] found primary use in astrophysical work for the determination of the composition of solar and stellar atmospheres.

Early studies utilised special quartz cells to confine the atomic vapour usually at low pressure; thus most of the results obtained were not affected by collisional broadening which is an important contribution in flames at atmospheric pressure. The fluorescence of atoms in flames was first

reported by Nichol and Howes [8] in 1923 and then by Badger [9] and Mannkopff [10] who obtained weak signals for Ba, Ca, Cd, Li, Mg, Hg, Na, Ag and Sr when present at high concentration in a flame irradiated by light containing the resonance line of the appropriate metal.

More recently Robinson [11] observed weak fluorescence of the 2852Å Mg line in an oxy/hydrogen flame using a magnesium hollow cathode lamp. In 1962 Alkemade [12] used the atomic fluorescence of sodium in flames to obtain mechanistic insight into excitation and deactivation of atoms and to measure the quantum efficiency of the sodium 5890Å line. He was also the first to point out the possible analytical applications of this technique. The first analytical method was published by Winefordner and his co-workers [13-16] and later by Dagnall, West and Young [17,18] who used commercially available AA equipment. With the recent development of brighter atomic sources the sensitivity of the determinations have been improved, new fluorescence observed and processes of excitation elucidated by Dagnall, Thompson and West for Se, Te, Sb, Bi, As and Ge [19-23]. The limits of detection for several elements have been reported by Winefordner [24].

1.2 THEORETICAL COMPARISON OF AE, AA AND AF FLAME SPECTROMETRY

In the three analytical flame spectrometric methods, a sample solution containing the analyte is introduced, usually in the form of an aerosol, into the flame. In the flame, solvent evaporates from the aerosol to produce solid clottlets of the various components of the sample matrix. The only particles of analytical interest are those containing the analyte atom, and these must undergo dissociation to produce free analyte atoms for measurement by AE, AA or AF flame spectrometry.

Many other equilibrium processes such as ionisation, of analyte atom compound formation with flame products compete with the dissociation process and will affect the final population of analyte atoms in the flame. Because analyte atoms in the flame gases are essential to AE, AA and AF, any kinetic or equilibrium processes influencing the concentrations of analyte atoms in the flame gases will affect each method in exactly the same manner, assuming the flame system is used in each method.

Atomic emission, atomic absorption and atomic fluorescence flame spectrometry therefore differ only in the means of measurement of the characteristic signals. In AA and AF, the atoms are excited by means of an external light source containing radiation characteristic of the analyte atom. The fraction of radiation absorbed by the analyte atoms as a result of radiational excitation is measured in AA, whereas in AF the measured parameter is a portion of the atomic fluorescence, radiation

resulting when a fraction of the excited atoms undergo radiational deactivation. In AE, the analyte atoms are excited by means of collisions with flame gas molecules and a portion of the radiation emitted when a fraction of the excited atoms undergo radiational deactivation is measured. The basic instrumental systems and processes are given in Figure 1.

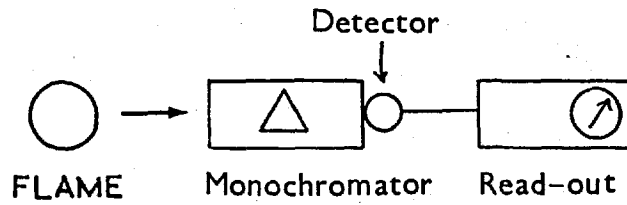
The similarities and differences among AE, AA and AF will be compared, with respect to relative signals and signal to noise ratios, the shape of analytical curves, the limits of detection and later optimal instrumentation.

THERMODYNAMIC EQUILIBRIUM IN FLAMES

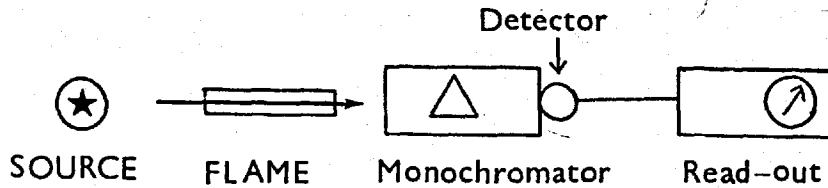
Flame equilibrium is achieved if the flame temperature is the same at all points in the flame body and if all forms of energy are equilibrated among each other. Local differences in temperature do occur in premixed laminar flames because the flame is not truly an adiabatic system. Also the supply of fuel and oxidant is not completely homogeneous because of the radiation of heat to the environment, secondary combustion at the flame boundaries, and convection effects. Therefore net transfer of heat, radiation and mass occur throughout the flame and strictly there can be no thermodynamic equilibrium. However provided transport rates of heat, radiation and mass are small compared with the rate of equipartitioning of energy over the different forms, it is still possible to talk of local thermodynamic equilibrium or flame temperature.

The equilibration of flame energy at a given point over the translational and internal degrees of freedom and for

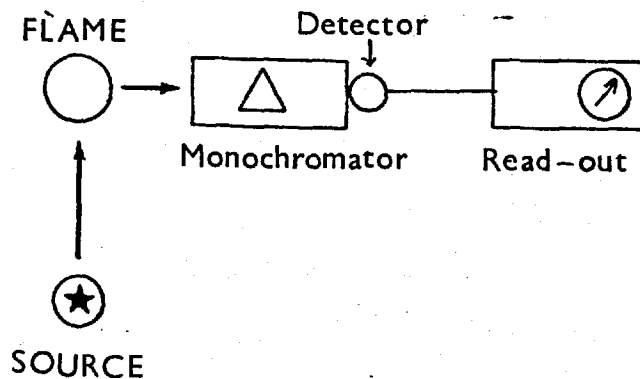
Figure 1 Basic Instrumental Systems for Atomic Emission, Atomic Absorption and Atomic Fluorescence.



Atomic Emission



Atomic Absorption



Atomic Fluorescence

molecular dissociation and atomic ionization require an exchange of energy by means of collisions with the surrounding flame gas molecules. Because the rise velocity of flame gases is of the order of 10m sec^{-1} flame gases undergo about 10^6 collisions before reaching the area of analytical measurement about 1cm above the primary reaction zone. Gaydon [25] has discussed the problem of equipartition of energy among translational, rotational and vibrational degrees of freedom in burnt flame gases, and it may be concluded that thermal equilibrium is established among these in not more than 10^4 collisions corresponding to a 10^{-5} sec or 10^{-1} mm of height above the primary reaction zone in the flame gases. This is significant because of the importance of vibrational energy transfer in excitation of electronic states of atoms in AE.

The equilibration of energy over electronic states of flame molecules requires about 10^4 collisions and so may not be achieved during the 1 millisecond time period. Chemiluminescent OH radiation has been observed [26] for several milliseconds above the primary reaction zones of premixed laminar flames. Although electronic excitation energy is not expected to be important in the excitation of atoms in AE [27], thermodynamic equilibrium with respect to electronic excitation can be considered to hold approximately for regions above the primary reaction zone.

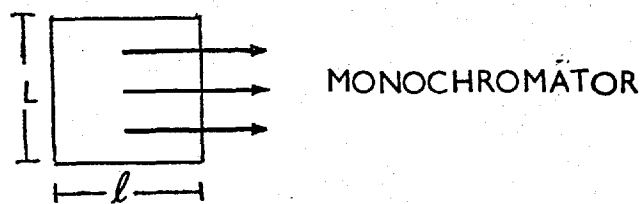
The establishment of thermodynamic equilibrium with respect to molecular dissociation may not be achieved in

1 millisecond above the primary reaction zone, but the general agreement of calculated and measured flame temperatures justifies the assumption that the major constituents in the flame gases are present in their equilibrium concentrations above the primary reaction zones.

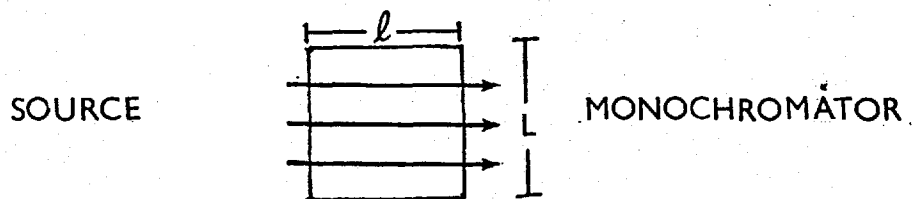
If thermodynamic equilibrium exists, the distribution of energy over the various translational and internal degrees of freedom, the distribution of dissociation and ionization products, and spectral radiation density are governed by a single and universal parameter, T_f , the temperature of the flame. At a given T_f , these distributions depend only upon the temperature and properties of the individual species and not on the type of interaction between them [28]. In analytical flames it will be assumed that there is thermodynamic equilibrium over the small region of measurement.

The five statistical distribution laws for the various forms of energy are the Maxwell Law for the velocity distribution of particles, the Boltzmann Law for the population of various discrete levels of internal energy of a particle, the mass action law relating concentrations of reaction products to those of reactants at equilibrium, the Saha Law relating the concentration of neutral species to those of the corresponding ionic species and free electrons and the Planck Law of radiation for a black body.

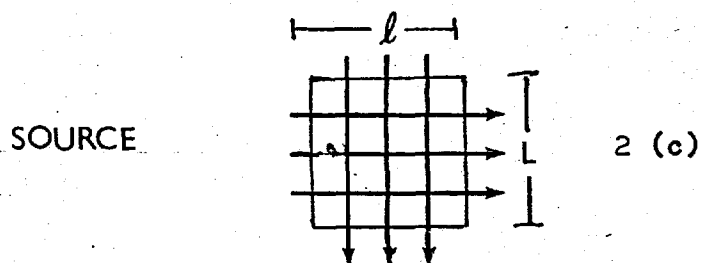
Figure 2 Flame Geometries for Derivation of Line Radiances



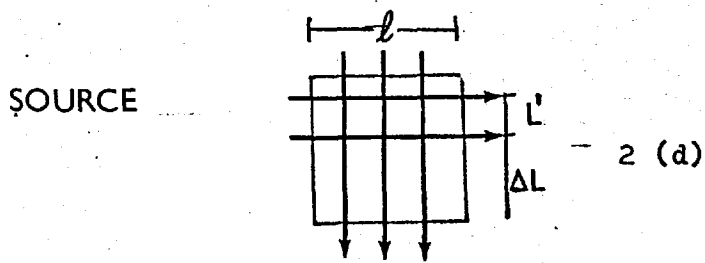
2 (a)



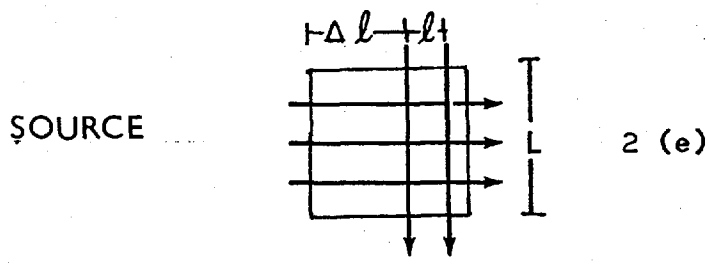
2 (b)



2 (c)



2 (d)



2 (e)

MONOCHROMATOR

1.3 DERIVATION OF LINE RADIANCE [27,29]

In a comparison of theoretical limits of detection and analytical shapes in AE, AA and AF, it is useful to derive expressions for the line radiances (in $\text{ergs sec}^{-1} \text{ cm}^{-2} \text{ ster}^{-1}$), for each flame method. It will be assumed that both the flame temperature (T_f) and the composition are constant throughout the region studied and that thermodynamic equilibrium is attained in this region. It will also be assumed that the same resonance line, broadened mainly by Doppler and Lorentzian broadening, is measured in each method. The flame geometries assumed are shown in Figure 22.

a). Atomic Emission

Assuming the flame to be in thermodynamic equilibrium the radiance B_{AE} , in $\text{erg sec}^{-1} \text{ cm}^{-2} \text{ ster}^{-1}$, in AE is given by Kirchoff's Law:-

$$B_{AE} = B_{B\lambda_0} A_t \quad (1)$$

where $B_{B\lambda_0}$ = spectral radiance ($\text{ergs sec}^{-1} \text{ cm}^{-2} \text{ ster}^{-1} \text{ cm}^{-1}$) of a perfect black body at the flame temperature T_f and at the wavelength λ_0 . $B_{B\lambda_0}$ is given by Planck's Law

$$B_{B\lambda_0} = \frac{8\pi hc^2}{\lambda_0^5} \left[\exp\left(\frac{hc}{\lambda_0 k T_f}\right) - 1 \right]^{-1} \quad (2)$$

A_t is the total absorption and is defined:-

$$A_t = \int_0^\infty a_\lambda d\lambda \quad (3)$$

a_λ is the absorption factor which is wavelength dependant

(a_λ is the fraction of radiation absorbed per unit wavelength interval).

For analytical flames which have temperatures less than 3500°K and at wavelength longer than 2500Å $B_{B\lambda_0}$ is given by Wien's approximation of Planck's Law:-

$$B_{B\lambda_0} \approx \frac{8\pi hc^2}{\lambda_0^5} \exp\left(\frac{-hc}{\lambda_0 kT_f}\right) \quad (4)$$

It is assumed in equation (1) that the black body spectral radiance is essentially constant over the spectral region either side of the line centre. The $B_{B\lambda_0}$ given by equation (4) explains the extreme dependance of intensity of emission on flame temperature. However, the A_t factor, which is only slightly temperature dependant, describes the variation of intensity with the ground state concentration 'n' and depth of flame viewed by the detection optics 'l'. Total absorption ' A_t ' is a function of the products nl and the damping constant or a-parameter which is defined as:-

$$\frac{\Delta\lambda_L}{\Delta\lambda_D} \sqrt{\ln 2} \quad (5)$$

where $\Delta\lambda_D$ and $\Delta\lambda_L$ are the Doppler and Lorentzian half intensity widths of the emission (or absorption) line. However, A_t is dependant on the a-parameter only when self absorption occurs.

Evaluation of the A_t factor

The total absorption of a hot atomic vapour of absorption path length 'l' may be defined as:-

$$A_t = \int_0^{\infty} [1 - \exp(-k_{\lambda} l)] d\lambda \quad (6)$$

k , the absorption coefficient, is a complex function of wavelength and may be described by the following formulae:-

$$k_{\lambda} = k_0 \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2}}{a^2 + (\omega - y)^2} dy \quad (7)$$

$$\text{where } \omega = \frac{2\sqrt{\ln 2} \{\lambda - \lambda_0\}}{\Delta\lambda_D}$$

$$y = \frac{2\delta\sqrt{\ln 2}}{\Delta\lambda_D}$$

The derivation of k_{λ} assumes that Doppler and Lorentzian broadening of the absorption line profile are independent processes and k_{λ} is obtained by considering every infinitesimal wavelength band of the pure Doppler broadened absorption line to be broadened by collisional broadening. Suppose a wavelength band at a distance $\lambda - \lambda_0$ from the centre of an absorption line showing only Doppler broadening is chosen. To represent the collisional broadening of this band, a variable distance δ from the point $\lambda - \lambda_0$ is chosen. The integration is then taken over δ . This model was first proposed by Voigt [30] and the resulting function is termed the Voigt Profile of an absorption or emission line.

b). Atomic Absorption

The spectral radiance $B_{A\lambda}$ (ergs sec⁻¹ cm⁻² ster⁻¹ cm⁻¹) absorbed from a source with a spectral radiance $B_{S\lambda}$ by an atomic

vapour with spectral absorption coefficient k_λ given by:-

$$B_{A\lambda} = B_{S\lambda} [1 - \exp(-k_\lambda l)] \quad (8)$$

The total radiation absorbed B_{AA} (ergs sec⁻¹ cm⁻² ster⁻¹) is given by:- [31,32].

$$B_{AA} = \int B_{A\lambda} d\lambda = \int B_{S\lambda} [1 - \exp(-k_\lambda l)] d\lambda \quad (9)$$

$B_{S\lambda}$ is analogous to $B_{B\lambda}$ in AE above. The limit for integration depends on the absorption line width and source characteristics.

In AA, there are two types of source commonly used to excite the atomic vapour. One can use either a continuum source and monochromator system with a spectral bandwidth 's' greater than the absorption line half width $\Delta\lambda_A$ or a line source and monochromator system with a source line half width $\Delta\lambda_s$ smaller than the absorption line half width. The two cases will be designated as AAC and AAL. If a continuum source is used the integration in equation (9) is over the entire absorption line and $B_{S\lambda}$ is assumed to be constant. If a narrow line source is used, the integration in equation (9) is only over the source line width.

For AAC then:-

$$B_{AAC} = B_{C\lambda_0} A_t \quad (10)$$

where $B_{C\lambda_0}$ is the spectral radiance of the continuum source over the absorption line half width $\Delta\lambda_A$. The great similarity between equation (1) and (10) indicate that the concentration dependance of the line radiance in AAC and AE should be identical because they both are a linear function of A_t , the integral

absorption. Also $B_{C\lambda_0}$ can be given by Planck's or Wien's Law (see equation (2) or (4)) except that T_f must be replaced by the black body temperature of the source T_s .

The integral in equation (9) can be evaluated for the cases of low n_l by:-

$$\int_0^\infty [1 - \exp(-k_\lambda l)] d\lambda = \int_0^\infty k_\lambda d\lambda = \frac{\sqrt{\pi} k_0 l \Delta\lambda_D}{2\sqrt{\ln 2}} \quad (11)$$

and for high values of n_l by:-

$$\int_0^\infty [1 - \exp(-k_\lambda l)] d\lambda = \sqrt{\frac{\sqrt{\pi} k_0 l a \Delta\lambda_D}{\ln 2}} \quad (12)$$

where k_0 = peak absorption coefficient at λ_0 for pure Doppler broadening.

$\Delta\lambda_D$ = Doppler half width

The terms k_0 and $\Delta\lambda_D$ are further defined:-

$$k_0 = \frac{2\sqrt{\ln 2} \pi e^2 \lambda_0^2 n f}{\sqrt{\pi} mc^2 \Delta\lambda_D} \quad (13)$$

f = oscillator strength of the transition.

$$\Delta\lambda_D = \frac{2\lambda_0}{c} \sqrt{\frac{2 \ln 2 k T_f}{M}} \quad (14)$$

M = atomic weight of absorber atom.

Substituting in the above equations (11) and (12) for k_0 the final expressions for intensity in AAC are:-

$$B_{AAC} = \frac{\pi e^2 \lambda_o^2 n f l B_{C\lambda_o}}{mc^2} \quad (\text{low nl}) \quad (15)$$

$$B_{AAC} = B_{C\lambda_o} \sqrt{\frac{2\pi e^2 l \lambda_o^2 n f a \Delta\lambda_D}{mc^2 \sqrt{\ln 2}}} \quad (\text{high nl}) \quad (16)$$

The fraction of radiation absorbed from the source 'a' may then be derived for low and high concentration.

low nl

$$a = \frac{\pi e^2 l \lambda_o^2 n f}{mc^2 s} \quad (17)$$

high nl

$$a = \frac{1}{s} \sqrt{\frac{2\pi e^2 l \lambda_o^2 n f a \Delta\lambda_D}{mc^2 \sqrt{\ln 2}}} \quad (18)$$

For AAL using a line source:-

$$B_{AAL} = \left[1 - \exp(-k_m l) \right] B_L \quad (19)$$

where k_m is the average atomic absorption coefficient at the absorption line peak and B_L is the radiance ($\text{ergs sec}^{-1} \text{cm}^{-2} \text{ster}^{-1}$) of the line source ie:-

$$B_L = \int_{\Delta\lambda_s} B_{L\lambda} d\lambda \quad (20)$$

where $k_m = k_o \delta(a, \omega)$.

The term $\delta(a, \omega)$ is the Voigt profile integral which for a given value of the a -parameter and ω is a constant. The value of ω accounts for the half width of the narrow line source $\Delta\lambda_s$ compared to the half width of the absorption line.

For low concentration of analyte atoms k_m is small (low optical density case) then:-

$$B_{AAL} \approx k_o \delta(a, \omega) l B_L \quad (21)$$

Which when expanded gives

$$B_{AAL} \approx \frac{2\sqrt{\ln 2} \pi e^2 l \lambda_o^2 n f \delta(a, \omega) B_L}{\sqrt{\pi} c^2 \Delta\lambda_D} \quad (22)$$

while for high concentration

$$B_{AAL} = B_L \quad (23)$$

In the latter case all of the radiation of the entire source line is absorbed. The fraction of radiation absorbed may then be derived for the low and high concentration cases.

low n_l

$$\alpha = \frac{2\sqrt{\ln 2} \pi e^2 l \lambda_o^2 n f \delta(a, \omega)}{m c^2 \Delta\lambda_D} \quad (24)$$

high n_l

$$\alpha = 1 \quad (25)$$

The absorbance A is defined by:-

$$A = -\log (1 - \alpha) \quad (26)$$

c). Atomic Fluorescence Flame Spectrometry (AF)

In AF, there are two possible methods of exciting the analyte atomic vapour [28,29], that is using a continuum source (with or without an excitation monochromator) and a line source (with or without an excitation monochromator). The former case will be designated AFC and the latter AFL. In AFC it will be assumed that the source half width, $\Delta\lambda_s$ (or spectral bandwidth of the excitation monochromator if one is used) is much greater than the absorption line half width $\Delta\lambda_A$ and in AFL it will be assumed that $\Delta\lambda_s < \Delta\lambda_A$.

For the case of AF, we will assume an illuminated brick-shaped flame (see Figure 2c) having a path length l cm in the direction of the excitation beam, L cm path length in the direction of the emission monochromator and 1' cm high. It will be assumed that corrections have been made for any thermal emission at or near λ_0 . The line radiance in AF is therefore given by:-

$$B_{AF} = \left(\frac{\Omega_A}{4\pi} \right) B_{AA} \left(\frac{L}{1} \right) \Phi \left[\frac{A_t (nL)}{\int_0^\infty k_\lambda L d\lambda} \right] \quad (27)$$

where B_{AA} is given for AAC and AAL by use of the expressions in AA section, the factor $\Omega_A/4\pi$ is the fractional solid angle of radiation collected from the source and impinging upon the flame assuming the entire area $L \times 1'$ is illuminated as in (Figure 2c), $L/1$ accounts for the flame area excited and the flame area fluorescing in the direction of the emission

monochromator, Φ is the quantum yield for the resonance fluorescence and the final term allows for the reabsorption of the fluorescence by ground state analyte atoms in the direction of the emission monochromator. The final term is simply the fraction of fluorescence radiation absorbed in the emission path length L and for low optical densities (low nL) is given by [29]

$$\frac{A_t(nL)}{\int_0^\infty k_\lambda L d\lambda} = \frac{\int_0^\infty [1 - \exp(-k_\lambda L)] d\lambda}{\int_0^\infty k_\lambda L d\lambda} \approx \frac{\int_0^\infty k_\lambda L d\lambda}{\int_0^\infty k_\lambda L d\lambda} = 1 \quad (28)$$

and for high optical density (high nL)

$$\frac{A_t(nL)}{\int_0^\infty k_\lambda L d\lambda} = \frac{\int_0^\infty [1 - \exp(-k_\lambda L)] d\lambda}{\int_0^\infty k_\lambda L d\lambda} \quad (29)$$

$$\approx \frac{\sqrt{\frac{\sqrt{\pi} \kappa_0 n f L a \Delta \lambda_D^2}{\ln 2}}}{\frac{\sqrt{\pi} \kappa_0 n f L \Delta \lambda_D}{2 \sqrt{\ln 2}}} \quad (30)$$

$$\approx \frac{2 \sqrt{a}}{\sqrt{\sqrt{\pi} \kappa_0 n f L}} \quad (31)$$

It should be pointed out that $\kappa_0 n f$ is generally replaced by k_0 , which is the atomic absorption coefficient at λ_0 for pure Doppler broadening and is expressed in cm^{-1} , in most other references dealing with this subject. The substitution of $\kappa_0 n f$ for k_0 is used in order to indicate explicitly the concentration-oscillator strength terms.

The re-absorption factor is not influenced by the means of excitation but is dependant only on the concentration and

spectral characteristics of the analyte atoms and on the path length L [27]. This re-absorption factor is only slightly dependant on flame temperature. The quantum yield Φ depends not only on the spectral characteristics of the analyte atoms but also on the concentration and type of collisional quenching in the flame. [31 - 35]

In equation (27) right angle illumination is assumed over the entire flame width L and that the fluorescence over the entire width l is collected by the detector optics. However, if only partial illumination of the flame cell occurs then the fluorescence radiation is reduced by re-absorption of the non-illuminated layer. If only fluorescence from deep within the flame cell is observed then an inner filter effect results in a reduction of fluorescence radiance. Alkemade [27] and Hooymayers [29] have given theory and equations for the last two cases which are probably not as common in analytical arrangements.

FINAL EXPRESSIONS FOR RADIANCES

By combining the previous equations, expressions for the radiance of resonance lines in AE, AAC, AAL, AFC and AFL are obtained for low and high concentration regions. In the case of AA the value α , the fraction of radiation absorbed, is also derived (see Table 1). All of the expressions are only valid for low and high concentrations and do not apply to the intermediate region.

The radiances can be converted to instrumental signals

TABLE 1 Radiance Expressions in AE, AA and AF for Low and High Optical Density Regions.

Method	Radiance Expressions	
	Low Optical Density	High Optical Density
AE	$B_{AE} = \frac{B_{B\lambda_0} \Xi \lambda_0^2 n f l}{c}$	$B_{AE} = B_{B\lambda_0} \sqrt{\frac{2 \Xi \lambda_0^2 n f l a \Delta \lambda_D}{c \sqrt{\ln 2}}}$
AAC	$B_{AAC} = \frac{B_{C\lambda_0} \Xi \lambda_0^2 n f l}{c}$	$B_{AAC} = B_{C\lambda_0} \sqrt{\frac{2 \Xi \lambda_0^2 n f l a \Delta \lambda_D}{c \sqrt{\ln 2}}}$
	$\alpha = \frac{\Xi \lambda_0^2 n f l}{c s}$	$\alpha = \frac{1}{s} \sqrt{\frac{2 \Xi \lambda_0^2 n f l a \Delta \lambda_D}{c \sqrt{\ln 2}}}$
AAL	$B_{AAL} = \frac{B_L 2 \sqrt{\ln 2} \Xi \lambda_0^2 n f l \delta(a, \omega)}{\sqrt{\pi} c \Delta \lambda_D}$	$B_{AAL} = B_L$
	$\alpha = \frac{2 \sqrt{\ln 2} \Xi \lambda_0^2 n f l \delta(a, \omega)}{\sqrt{\pi} c \Delta \lambda_D}$	$\alpha = 1$

TABLE I (continued)

Method	Radiance Expressions	
	Low Optical Density	High Optical Density
AFC	$B_{AFC} = \frac{B_{C\lambda_0} \Omega_A \Xi L \lambda_0^2 n f \Phi}{4\pi c}$	$B_{AFC} = \frac{B_{C\lambda_0} \Omega_A \Xi \sqrt{L} \Phi a \Delta \lambda_D}{4\pi \sqrt{\ln 2} \sqrt{1}}$
AFL	$B_{AFL} = \frac{B_L \Omega_A 2\sqrt{\ln 2} \Xi \Phi \lambda_0^2 n f L \delta(a, \omega)}{4\pi \sqrt{\pi} c \Delta \lambda_D}$	$B_{AFL} = \frac{B_L \Omega_A \Phi L \sqrt{2ac \Delta \lambda_D}}{4\pi l' \sqrt{\ln 2} L \Xi \lambda_0^2 n f}$

$$\Xi = \frac{\pi e^2}{m c}$$

by multiplying each radiance by an instrumental constant K , which converts the radiance incident on the monochromator entrance slit to a photomultiplier detector signal. In the case of a magnified image of the source in AA and AF the K factor must be divided by the magnification factor. Because the instrumental systems for AE, AA and AF are assumed to be identical except for the differences in entrance optics already mentioned, the instrumental constant K is therefore identical for all methods in the cases considered.

1.4 SHAPES OF THEORETICAL CURVES [36]

The shapes of theoretical curves of $\log B$ vs $\log n$ can be obtained by using the expressions in Table 1. For AFC and AFL, the method of illumination is as shown in Figure (2). For any given atom, line, and flame the quantities $B_{B\lambda_0}$, a , ϕ , $\Delta\lambda_D$, L , l and κ_0 are constant. For a given source $B_{C\lambda_0}$ and B_L are constant. For any given atom, line, flame and line source δ_0 is constant [37]. Of the above parameters only $B_{B\lambda_0}$ is critically dependant on T_f the flame temperature. The a -parameter [38,39] and ϕ [34] depend less critically upon flame temperature and gas composition. Typical growth curves for Mg in an air/acetylene flame [36] are given in Figures 3+4

a). Atomic Emission ($\log B_{AE}$ vs $\log n$) [40,41]

The slope is 1.0 at low n_l and 0.5 at high n_l assuming homogeneous flame in thermodynamic equilibrium. The shape is identical with that of the growth curves of $\log A_L$ vs $\log n$.

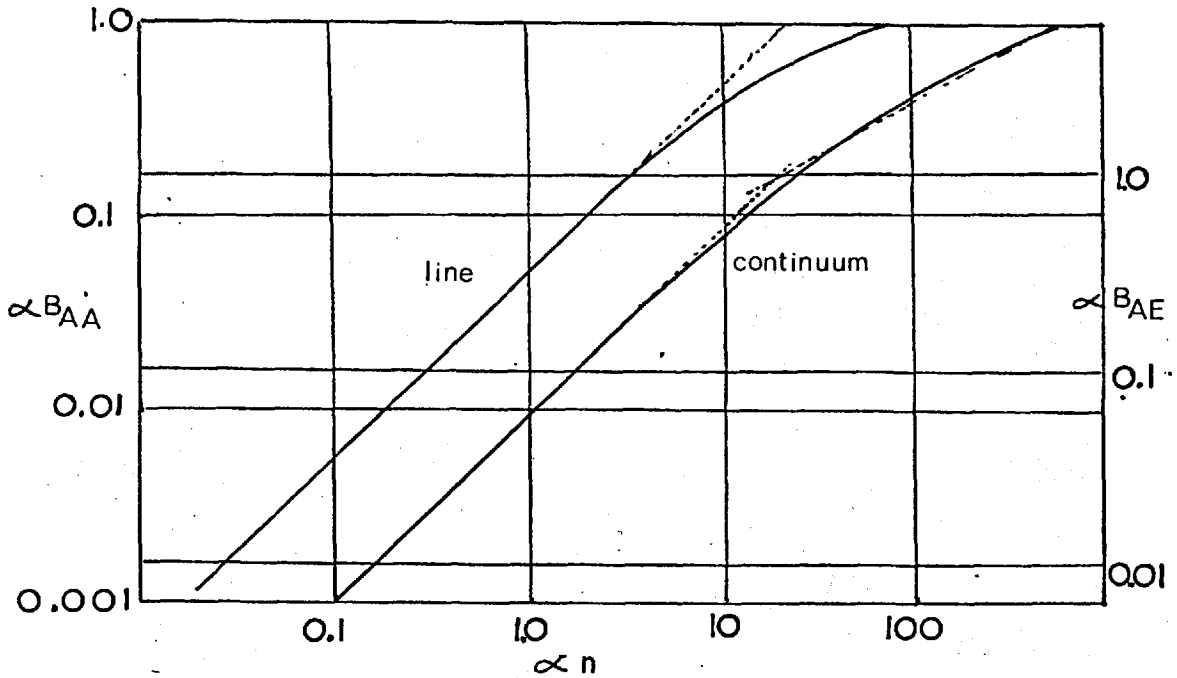


Figure 3 Growth curves for atomic absorption with a continuum source (atomic emission is represented by the same curve, ordinate is of $B_{AE}\sqrt{\ln 2}/B_{B\lambda_0}\Delta\lambda_D$) and with a narrow line source. Data used to calculate curves: $T_f = 2400^\circ K$; $\lambda_0 = 2852\text{\AA}$ (magnesium line); $\Delta\lambda_D = 0.021\text{\AA}$; $a = 0.5$; $L = 1 = 1 \text{ cm}$, $\Delta\lambda_s \leq 0.0025\text{\AA}$; $\delta(a, \omega) = 0.61$, and $s = 0.2A$

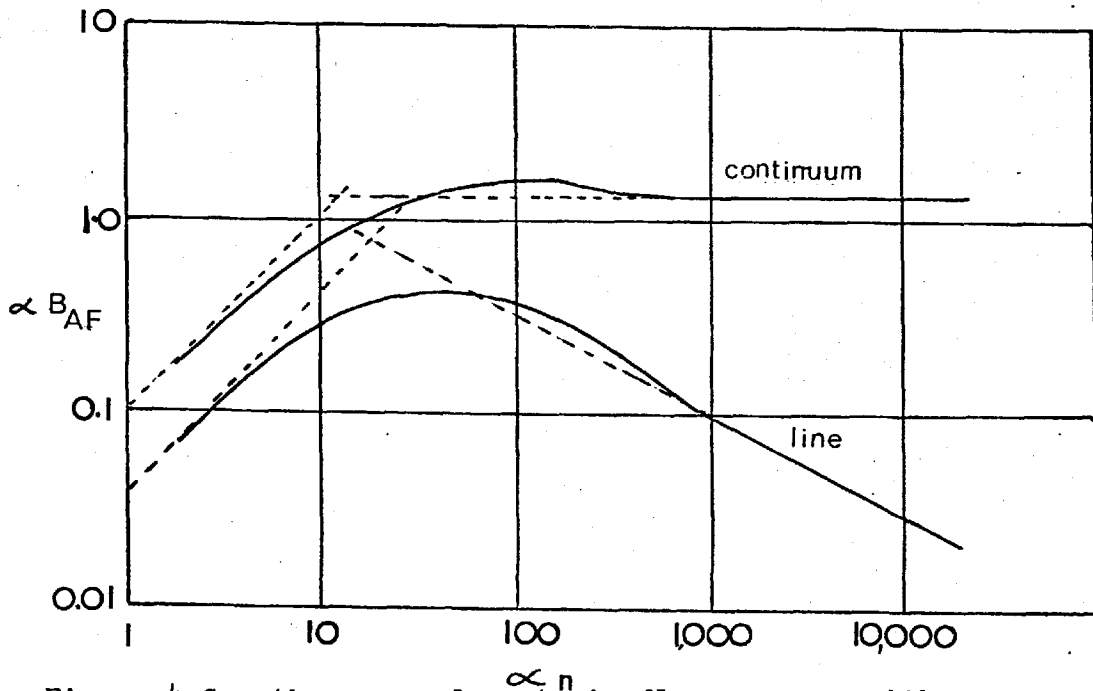


Figure 4 Growth curves for atomic fluorescence with a continuum source (ordinate $B_{AF}/\Phi B_{C\lambda_0}\Delta\lambda_D$), and with a narrow line source (ordinate $B_{AF}/\Phi B_L$). Data used to calculate curves are in caption of Figure 3

b)i Atomic Absorption (Log B_{AAC} vs Log n) [42-45]

The slope of the low and high concentration asymptotes are identical with those in AE. The only difference between curves in AAC and AE is the absolute value of the ordinate for a given n value because of the differences between $B_{B\lambda_0}$ and $B_{C\lambda_0}$, which depend upon T_f and T_s respectively. It is interesting to see that the curve of Log B_{AAC} vs Log n is independent of s , the spectral bandwidth of the monochromator. However, the value α (fraction of radiation absorbed) is usually the measured parameter and the Log α vs Log n does shift and change shape when s is increased. [37,46]

The measured curve for Log B_{AAC} vs Log n will actually approach the shape of the Log B_{AAL} vs Log n at high values of n when using a continuum source and monochromator with fixed spectral bandwidths for AAC, the measured B_{AAC} tends to a maximum value i.e. α approaches 1.0, at high concentrations where the absorption line width exceeds s . Plots of A vs Log n also shift and change form with variation in s .

ii). (Log B_{AAL} vs Log n)

The slope of the low nl asymptote is 1.0, and of the high nl asymptote is zero. At high values of nl, the flame becomes opaque and $B_{AAL} \rightarrow B_L$ and $\alpha \rightarrow 1.0$. Conventional line sources should result in greater α - values (and greater B_{AAL} values) than continuum sources with monochromators having spectral bandwidths $0.1\text{\AA}$ where these expressions are valid. However, because the detector sees the source the background

noise with a continuum source should be less [47] than with line sources so a comparable limit of detection should result.

c)i Atomic Fluorescence ($\log B_{AFC}$ vs $\log n$)

The slope is 1.0 at low n values and 0.0 at high n values. Thus analytical curves in AFC will be of no practical use at high analyte concentrations. Dilution of the sample must be performed to bring the concentration within the linear portion of the curve.

ii). ($\log B_{AFL}$ vs $\log n$)

The slope is 1.0 at low n values and -0.5 at high n values. Again high analyte concentration should be diluted before analysis.

1.5 SHAPES OF ANALYTICAL CURVES

1). Relationship between Concentration of Analyte in Flame (n) to Analyte in Solution (C).

The $\log B$ vs $\log n$ curves determine the shapes of analytical curves, which are plots of $\log S$ vs $\log C$, where S is the detector signal and C the concentration of the metal in solution. The signal S should be directly proportional to B over the entire range of analytically useful concentrations [48-51]. However, n may not bear a constant relationship to C at all values of C because of variation in the degree of ionisation, solute vaporisation, aspirator yield, and solution transport rate with C [36]. The relationship between n (number of metal atoms in ground state cm^{-3}) and C (moles of metal cm^{-3}) is given by [27,36]:-

$$n = 6 \times 10^{23} \left(\frac{F \epsilon \beta C}{Q e_f B(T)} \right) \quad (32)$$

where F is the transport rate of solution as determined by the nebuliser ($\text{cm}^3 \text{sec}^{-1}$), ϵ is the efficiency of producing analyte molecules in the flame, β is the atomisation efficiency [free atom fraction], Q is the supply rate of flame gases ($\text{cm}^3 \text{sec}^{-1}$), e_f is the flame gas expansion factor, $B(T)$ is the normalising partition function.

$$B(T) = \frac{1}{g_0} \sum_i g_i \exp \left(\frac{-E_i}{kT} \right) \quad (33)$$

where g is the statistical weights of the ground (0) and excited (i) states and E_i is the excitation energy of state (i).

2). Atomisation Efficiency (β) [86]

This is defined as the ratio of the concentration of free analyte atoms in the flame to the total concentration of analyte in the various gaseous forms. This factor allows for incomplete dissociation of the analyte clots, for compound formation with flame gas products and for ionisation of the analyte atoms in the flame gases.

3). Aspiration Efficiency (ϵ) [52]

This is defined as the ratio of the number of all gaseous analyte species formed in the flame gases in unit time to the number of analyte atoms taken up by the nebuliser in unit time. The factor accounts for vaporisation of the solvent,

and transport efficiency of the mist into the flame. Many workers assume the constancy of β at all values of the concentration of analyte solution. It is known, however, that great changes in n for a constant C can occur due to change in solution matrix and changes in flame gas composition and temperature.

4). Factors Affecting β .

At low concentrations of metal in solution, β will vary with the concentration C because of variation in the degree of ionisation [53]. Zeegers, Smith and Winefordner [36] have derived an expression for β assuming that no compound formation occurs and that the metal M has M^+ as its only ionisation form. If K_i , which is a function of T_f , is the ionisation constant for the process $M \rightleftharpoons M^+ + e^-$ and if electro-neutrality and material balance are valid

$$n_e = n_{M^+} + n_f \quad (34)$$

n_f = concentration of free electrons due to flame gases (n_f is assumed independent of n_T , the total concentration of M in atomic and ionic forms) and n_{M^+} is the concentration of electrons due to ionisation of M .

$$n_T = M_n + n_{M^+} \quad (35)$$

then:-

$$\beta = \frac{K_i + n_f}{2n_T} + \frac{1 - \sqrt{\frac{K_i^2 + 2n_f K_i + n_f^2 + 4K_i n_T}{n_T^2}}}{2} \quad (36)$$

For non-hydrocarbon flames low in free electrons due to flame gases ($n_T \gg n_f$) and for a low concentration of M in all forms;- ($K_i \gg n_T$ for low n_T)

$$\beta = \frac{n_T}{K_i} \quad (37)$$

$$n = \frac{n_T^2}{K_i} \quad (38)$$

$\log n = 2 \log n_T - \log K_i$ so the limiting slope of analytical curves in flame spectrometry approaches a value of 2, not unity, as the concentration is made smaller. At high total concentration in non-hydrocarbon flames ($n_T \gg K_i$ and $n_T \gg n_f$) or at most M concentrations in hydrocarbon flames ($n_f > n_T$):-

$$\beta \approx 1 \quad (39)$$

and so the analytical curve will have the same slope as the growth curve. At high concentrations of flame gas products compound formation may occur (MO, MOH etc). Assuming that the flame gas product is X, that no ionisation of M occurs, that only the compound MX forms and that its formation can be described by the equilibrium constant K_d (which is a function of T_f).

$$\beta = \frac{K_d}{K_d + n_X} \quad (40)$$

n_X = concentration of flame gas product.

Therefore β is independent of total M concentration n_T if $n_X > n_T$ which is the usual case in flame spectrometry and is dependant only upon the flame gas composition and temperature and the particular compound formed. This compound formation does not change the shape of analytical curves in AE and AA or AF from the shapes of the Log B vs Log n curves.

5). Factors Affecting ϵ .

At high concentrations, the aspiration efficiency can vary non-linearly with the analyte concentration [367]. In conventional flame spectrometric analysis the analyte is supplied to the flame in the form of an aerosol. Evaporation of the solvent may be complete before the analyte reaches the flame, or may be incomplete even after the aerosol has passed through the flame (as with some total consumption burners). The degree of solvent evaporation is almost independent of the solute concentration and will have little effect on the shape of the analytical curves which are obtained with a particular type of aspiration system. The subsequent evaporation of residual solid or molten analyte particles is a very critical step in flame analysis and has an effect on both the shape and position of the analytical curves. The drop size distribution of the aerosol produced by most nebulising systems is independent of the analyte concentration over a very wide range and consequently the dimensions of particles remaining after solvent evaporation will be dependant on the droplet distribution and the solution concentration. If only partial vaporisation

of the residual particles takes place the degree of vaporisation will be lowest at high concentration of analyte ie ϵ decreases with increasing analyte concentration.

At the present time it is not possible to accurately predict the variation of ϵ with concentration of analyte, although the basic theory of aerosol evaporation has been studied [54-62]. If an equation could be derived which considered even the larger particles which do not move with the rise velocity of the flame gases it should be possible to assign the lifetime of any particle in the flame. If then the lifetime of any particles is greater than the time taken for the particles to reach the height of observation in the flame,, the analytical curve will have a smaller slope than the corresponding growth curve.

Over most analytical concentration ranges the aspiration yield and solution transport rate F should be independent of analyte concentration [51]. However, these factors particularly at high concentrations will be functions of viscosity, surface tension and solution density.

6). Minimisation of Chemical and Physical Interferences.

Chemical interferences are generally considered to be those influencing ϵ and β and physical interferences those influencing F and e_f . When measuring resonance lines of atoms in the same flame using AE, AAC, AAL, AFC or AFL, variations of ϵ , β , F and e_f will affect the atomic concentration n in exactly the same manner because all Log B vs Log n curves

in flame spectrometry have the same slope (unity) at low concentrations, any changes in the above parameters in the analytically useful range at low concentration will have identical effects in all flame methods. At high concentrations, the specific Log B vs Log n relationships must be used to determine the importance of variations of ϵ , β , e_f or F.

Solute-vaporisation interferences often termed chemical interferences which effect ϵ are generally the most severe ones in flame spectrometry. Their influence on atom production and thus concentration of analyte n can often be minimised by the use of high temperature flames or flames which have a low rise velocity and thus long residence time for particles [63,64]. Conversely lower temperature flames minimise the effect of ionisation interference which affect β . However, the use of a high temperature flame which avoids reduction in ϵ and an ionisation supressor (eg KCl) is normally the best compromise.

If the flame is in local thermodynamic equilibrium, then compound formation does not affect the shape of the analytical curves of all flame methods. As long as the same flame is used for all measurements, the value of β , which reflects the extent of compound formation will be a constant for all analyte concentrations. By choosing a high temperature flame β can be increased by many orders of magnitude for a given analyte atom, giving rise to a useful analytical method eg many refractory elements in air/acetylene have $\beta < 10^{-5}$ but approach the value of unity for nitrous oxide/acetylene [65].

By careful sample pre-treatment the interferences affecting F and the aspiration yield can often be minimised and in any case only affect the analytical curve at very high concentrations.

1.6 COMPARISON OF THEORETICAL SIGNALS

1). Ratio of Radiances of AA and AF vs AE.

Increase in the sensitivity of a method is one of the main goals of research in analytical chemistry. The actual detection limit in flame spectrometry depends on factors influencing the signal and the noise and so will vary from element to element and from instrumental set-up to instrumental set-up. A comprehensive treatment of detection limits in AE, AA and AF has been derived using complex signal to noise considerations [48-50] by Winefordner. However, these are over complicated for a comparative treatment and so it will be assumed in the following section that the noise level in each method is identical (see page 46 for noise level considerations). It is then the ratio of radiance which is the reciprocal of the limits of detection. The ratios of radiance (signal) levels in AAC, AAL, AFC and AFL to those in AE will be given. These ratios are strictly the signal gains and designated G_{SX} , where X is the flame method of analysis being compared to AE. The evaluation of G_{SX} can be found by using the low optical density (nl) expressions in Table I. The resulting signal gains:-

$$G_{SAAC} = \frac{B_{AAC}}{B_{AE}} \approx \frac{B_{C\lambda_o}}{B_{B\lambda_o}} \quad (41)$$

$$G_{SAAL} = \frac{B_{AAL}}{B_{AE}} \approx \frac{B_L \delta_o}{C_2 B_{\lambda_o} \Delta \lambda_D} \quad (42)$$

$$G_{SAFC} = \frac{B_{AFC}}{B_{AE}} = \frac{B_{C\lambda_o} \Phi \Omega_A}{4\pi B_{\lambda_o}} \quad (43)$$

$$G_{SAFL} = \frac{B_{AFL}}{B_{AE}} = \frac{B_L \delta_o \Phi \Omega_A}{4\pi C_2 B_{\lambda_o} \Delta \lambda_D} \quad (44)$$

where $C_2 = \frac{\sqrt{\pi}}{2\sqrt{\ln 2}}$

The above equations are valid for signal ratios only if the same instrumental system is used for all measurements, if the source is not modulated, if the same flame has a constant temperature and concentration of analyte atoms at all points in the measured value, if the flame area $L \times l'$ in AA and AF is fully and uniformly illuminated by the source image, if the solid angle subtended by the monochromator, $\Omega/4\pi$, in AA is less than that subtended by the entrance optics, if the same spectrally isolated resonance line is measured in all three methods, and if $L = l$ in AF.

2). Discussion of Signal Ratio Expressions

In equations (41) - (44) the oscillator strength f_{ou} , is not explicitly contained in the right hand expressions. In equations (43) and (44) f_{ou} is implicitly contained in the quantum efficiency.

Since:-

$$\Phi = \frac{A_{uo}}{A_{uo} + \sum K_{x_i} n_{x_i}} \quad (45)$$

where A_{uo} is the Einstein coefficient of spontaneous emission in sec^{-1} and is commonly called the transition probability and K_{x_i} is the second order collisional rate constant in $\text{cm}^3 \text{sec}^{-1}$, and n_{x_i} is the concentration of the colliding species in cm^{-3} . The summation is over all quenching species. The relationship between A_{uo} and f_{ou} , the absorption oscillator strength is:-

$$A_{uo} = \frac{6.62 \times 10^{15} f_{ou} g_o}{\lambda_o^2 g_u} = Z f_{ou} \quad (46)$$

where g_o and g_u are the statistical weights of the ground and upper states involved in the resonance transition, λ_o is the peak wavelength. Combining equations (45) and (46) gives:-

$$\Phi = \frac{f_{ou}}{f_{ou} + \sum K_{x_i} n_{x_i} / Z} \quad (47)$$

Thus if the quantum efficiency is small compared to unity it will be proportional to f_{ou} , and if Φ is near unity it will not be a function of f_{ou} . Consequently, if the quantum efficiency is much less than unity the gain factors G_{SAFC} and G_{ASFL} will be dependant on f_{ou} .

The above signal gain factors contain parameter characteristic

of the experimental system ($B_{C\lambda_0}$, B_L , Ω and Ω_A); of the flame alone ($B_{B\lambda_0}$); of the atom and flame ($\Delta\lambda_D$ and Φ); and of the atom, flame and source (δ_0).

3). Evaluation of Parameters in Radiance Ratio Expressions

In equations (41) - (44) approximate values for all the parameters and constants can be given. The constant C_2 is about unity. The term δ_0 is about 0.5 [37] for atoms with spectral lines having an a-parameter of 0.5 $\rightarrow$ 2.0 [for $a=0.5$ $\delta_0=0.61$; for $a=1.0$, $\delta_0=0.42$; for $a=2.0$, $\delta_0=0.26$], this should be characteristic of most lines for atoms in flames. The solid angle $\Omega_A/4\pi$ for atomic absorption measurements is taken to be 0.005 this is 1/10 the value of Alkemade [27] in his estimation of gain factors. Estimation of the source spectral radiance for a 450 Watt Xenon arc continuum are taken from Prugger [66] whose values compare well with those of Klein [67]. Estimates of source radiance for high intensity Hollow Cathode Lamps (HCL) and Electrodeless Discharge Lamps (EDL) are taken from Prugger [66] and Mansfield et al [68] respectively. The quantum efficiency Φ can range from 0 to 1 but is dependant on flame composition. For inert gas diluted hydrogen flames Φ will be about 0.5 [31 - 35] whereas for hydrocarbon flames 0.05. Thus for comparison Φ will be assumed 0.2.

For analytical flames the values of flame temperature of about 2000°K, 2500°K and 3000°K are used and values of $B_{B\lambda_0}$ the back body spectral radiance is given in Table II [69]

TABLE II SPECTRAL RADIANCE VALUES OF A BLACK BODY $B_{B\lambda_0}$ [69]
AND 450-Watt XENON ARC SOURCE $B_{C\lambda_0}$ [66]

WAVELENGTH		SPECTRAL RADIANCE ¹		
(Å)		$B_{B\lambda_0}$		$B_{C\lambda_0}$
	2000 ²	2500	3000	
2000	9×10^{-12}	1×10^{-8}	1×10^{-6}	1×10^{-2}
3000	2×10^{-7}	2×10^{-5}	6×10^{-4}	5×10^{-1}
4000	2×10^{-5}	7×10^{-4}	7×10^{-3}	1×10^0
5000	2×10^{-4}	4×10^{-3}	3×10^{-2}	1×10^0
6000	1×10^{-3}	1×10^{-2}	5×10^{-2}	1×10^0

1. Units of watt $\text{cm}^{-2} \text{ster}^{-1} \text{nm}^{-1}$

2. Temperature of flame, °K

together with the value of $B_{C\lambda_0}$ for the 450 Watt Xenon arc [66] at the same wavelength.

The line sources radiance B_L for high intensity HCL [66] and EDL [68] of resonance lines at about 2000Å (Zn), at 3000Å (Mg), at 4000Å (Ca or In) and 6000Å (Na) are approximately 10^{-4} to 10^{-5} watts cm^{-2} ster^{-1} for HCL and 10^{-2} to 10^{-4} for EDL. The average values are taken for the calculations. The Doppler half width for resonance lines between 2000 and 6000Å in flames of temperature 2000 - 3000°K will be taken as 0.03Å. The final values calculated are shown in Table III the significance will be discussed below.

4). Discussion of Calculated Radiance Ratios

Several interesting conclusions can be drawn from Table III in which the G_s values calculated using equations (41)-(44) and data listed in the previous section. AF always must necessarily result in a smaller signal than AA whether a line or continuum source is used. In fact for the results given in Table III, it can be seen that the AAC signal is 10^3 as large as in AFC and that AAL is 10^3 as large as in AFL. Because atomic fluorescence results from atomic absorption and because the same instrumental system is assumed, the signal in AA (C or L) is greater than AF (C or L) by the factor $\left(\frac{\Omega_A \Phi}{4\pi}\right)^{-1}$. Therefore, if the signals alone are considered, AA should be used for the most sensitive measurement of all analyte atoms having resonance lines shorter than about 6000Å for essentially all flames.

TABLE III APPROXIMATE SIGNAL GAIN FACTORS FOR AAC, AAL, AFC AND AFL vs AE FOR TYPICAL FLAME TEMPERATURES AND RESONANCE LINE WAVELENGTHS USING TYPICAL CONTINUUM AND LINE SOURCES.

2000°K	$G_{SAAC}^{1.}$	$G_{SAAL}^{2.}$	$G_{SAFC}^{1.}$	$G_{SAFL}^{2.}$
2000	1×10^9	2×10^{10} (1×10^8)	1×10^6	2×10^7 (1×10^4)
3000	2×10^6	1×10^6 (5×10^3)	2×10^3	1×10^3 (5×10^{-1})
4000	5×10^4	1×10^4 (5×10^1)	5×10^1	1×10^1 (5×10^{-3})
5000	5×10^3	1×10^2 (5×10^0)	5×10^0	1×10^0 (5×10^{-4})
6000	1×10^3	2×10^2 (1×10^0)	1×10^0	2×10^{-1} (1×10^{-4})
2500°K				
2000	1×10^6	2×10^7 (1×10^5)	1×10^3	2×10^4 (1×10^1)
3000	2×10^4	1×10^4 (5×10^1)	2×10^1	1×10^1 (5×10^{-3})
4000	2×10^3	3×10^2 (2×10^0)	2×10^0	3×10^{-1} (2×10^{-4})
5000	2×10^2	5×10^1 (2×10^{-1})	2×10^{-1}	3×10^{-2} (2×10^{-5})
6000	1×10^2	2×10^1 (1×10^{-1})	1×10^{-1}	2×10^{-2} (1×10^{-5})
3000°K				
2000	1×10^4	2×10^5 (1×10^3)	1×10^1	2×10^2 (1×10^{-1})
3000	1×10^3	3×10^2 (2×10^{-2})	1×10^0	3×10^{-1} (2×10^{-4})
4000	2×10^2	3×10^1 (2×10^{-3})	2×10^{-1}	3×10^{-2} (2×10^{-5})
5000	3×10^1	1×10^1 (3×10^{-3})	3×10^{-2}	1×10^{-2} (3×10^{-5})
6000	2×10^1	4×10^0 (2×10^{-4})	2×10^{-2}	4×10^{-4} (2×10^{-6})

1. Value for 450Watt Xenon arc lamp.

2. First value for electrodeless discharge lamp.
Second value for high intensity hollow cathode lamp.

G_s values calculated using equations (41)-(44) and using data given in text.

In terms of signals only, the combination of AA and AE should be used over the analytically useful range of wavelengths.

Although the signals in AF (C or L) are never as great as those in AA (C or L), the values of G_s for AF vs AE can still exceed unity for short wavelength resonance lines. For example, for a 2000°K flame AF results in a greater signal than AE for resonance lines shorter than about 6000Å; the corresponding figures for flames of temperature 2500°K and 3000°K are about 4000Å and 3000Å respectively. It is also very interesting to note that even if the estimated values for the radiance of the 450 Watt Xenon arc are 10 times too high, the Xenon lamp should give results comparable with line sources for all resonance lines. This however, has not been realised experimentally to date. It should also be stressed that the value of G_{SAA} for either line or continuum sources tends to favour the absorption technique because the solid angle measured in AE is usually much larger than in AA. This could mean values in Table III for G_{SAA} could be an order of magnitude too large.

1.7 COMPARISON OF THEORETICAL DETECTION LIMITS

If all noise sources were identical in AE, AA and AF, then the values in Table III would reflect the ratios of the limits of detection. It is quite reasonable to assume that the noises in AFC, AFL and AE are essentially identical when using the premixed flames produced using burners with chamber type nebulisers.

1). Total Noise in AE, AFL and AFC

The total noise measured N_T at the output of the photodetector is given by:-

$$N_T = \sqrt{N_{\text{shot}}^2 + N_{\text{flame}}^2} \quad (48)$$

where N_{shot} , the shot noise at the photodetector output, is a result of the quantum nature of light and particular nature of electron emission from the photocathode and depends upon the total light flux reaching the photocathode of the detector (see Chapter 4 p.173). The flame noise N_{flame} , often termed the flame flicker noise, is a result of random fluctuation in the background intensity emitted by the flame due to temperature fluctuation in the flame. The noise resulting from fluctuations in atomic concentration in the flame due to uneven solution aspiration will be assumed to be small compared to the above sources of noise as they should be in a well-adjusted spectrometric system.

In high temperature flames ($\text{C}_2\text{H}_2 / \text{O}_2$, $\text{C}_2\text{H}_2 / \text{N}_2\text{O}$ and H_2 / O_2) the flame flicker noise should be considerably greater than the shot-noise. Thus the values given in Table III for AE, AFC and AFL should also correspond approximately to the ratio of the detection limit in AE to the detection limit in AFC or AFL. However, experimentally the same flame would not be used for AE as for AF, the most common flame for AE being the premixed nitrous oxide/acetylene, whereas in AF the low background $\text{H}_2 / \text{O}_2 / \text{Argon}$ flame is ideal for most elements. When using different flames with essentially the same temperature then the

inverse ratio of the limits of detection must also account for the difference in aspiration efficiency and free atom formation in each flame and also the increase in flicker noise for the higher background flame.

2). Total Noise in Atomic Absorption

In atomic absorption there is a further major factor which contributes to the total noise, N_{source} thus:-

$$N_T = \sqrt{N_{\text{shot}}^2 + N_{\text{flame}}^2 + N_{\text{source}}^2} \quad (49)$$

The source flicker noise is due to fluctuations in the source intensity mainly due to temperature fluctuations, fluctuations in vapour concentration and poorly stabilised power supplies. A further factor which contributes to the total noise is the apparent unsteady absorption of source radiation by the flame particularly at low wavelengths eg 2000Å (As, Se). Recent studies [70] show that this may be due in part to the lens effect of the flame and not only to absorption of radiation. In comparing the total noise for AE, AA and AF the shot noise for AA will be greatest because of the much greater light flux directly from the source incident on the photodetector.

3). Evaluation of Total Noise

If the noise components in equations (48) and (49) are assumed to be random (white noise) ie the same power at all frequencies, then the root-mean-square (rms) noise voltage will depend on the square root of the frequency response

bandwidth (Δf) of the detection system. At frequencies below 100 Hz, the low frequency noise (pink noise) is superimposed upon the white noise and so when using dc or wide band ac amplification the pink noise as well as the white noise must be accounted for in the total noise expression. The rms pink noise voltage depends on $\ln \left(\frac{f_L + \Delta f}{f_L} \right)$ where f_L is the lower cut-off frequency of the filter system.

The shot noise in terms of anode current for the photomultiplier tube is given approximately by:-

$$N_{\text{shot}} = \sqrt{2eBMAf (i_d + i)} \quad (50)$$

where e is the electron charge, BM the effective gain of photomultiplier, i_d the dark current and i the total anode current.

For a typical photomultiplier tube (PMT) $2eBMAf$ is about 10^{-13} amperes and i_d is about 10^{-9} amperes. The anode current due to normal flame background will be of the order of 10^{-9} - 10^{-7} amperes for a low background flame (air/hydrogen) at 2000°K and 10^{-7} to 10^{-5} for a high background flame (nitrous oxide/acetylene at 3000°K). The value K in the signal expressions is taken as $1.0 \text{ amp watt}^{-1} \text{ cm}^2 \text{ nm ster}$ for a line source when using a good analytical spectrometric system. Therefore the shot noise current will be of the order of 10^{-11} to 10^{-10} amperes for a low background flame and 10^{-10} to 10^{-9} amperes for a high background flame.

If, in addition to flame background, an external light source were used in AA having intensities such as those listed in Table II, the total photoanodic signal due to flame and source would be impossibly high ie 0.01 to 1 ampere for either low or high background flame with either line or continuum source. This is not surprising in view of the direct admittance of the source radiation from these sources into the monochromator. Experimentally one would reduce the slit width and utilise a smaller monochromator solid angle Ω in order to reduce the signal and thus the noise. However, for comparison purposes, it is necessary to compare all the flame methods under optimal conditions resulting in maximum signal to noise ratios. Therefore for comparison only the photoanodic current of 0.1 ampere in AAC and AAL will be used. The resulting shot noise would be of the order of 10^{-7} to 10^{-8} amperes.

Flicker fluctuations are difficult to estimate because of the presence of a low frequency component as well as the corresponding harmonics and the white noise component [71].

An estimate of flicker noise can be obtained by using

$N_{\text{flicker}} = \sqrt{S}$, $\sqrt{}$ is the measured ratio of rms flicker to signal responsible for it and S is the photoanodic signal upon which the flicker is superimposed. For example, for the low (2000°K) and high (3000°K) temperature analytical flames mentioned above, the flame flicker noise if $\sqrt{} \sim 0.01$ will be 10^{-11} to 10^{-9} for the former flames and 10^{-9} to 10^{-7} for the

latter flames over most of the wavelength region 2000-8000Å. The source flicker noise ($\xi \sim 0.001$) for the continuum and line sources discussed above will be about 10^{-5} amperes.

Obviously the above calculations of total noise level are only approximate and that only the relative values are of much importance, we can see that the total noise (equations (48) and (49)) in AE, AA and AF are related as follows for low background flames:-

$$N_{AE} \approx N_{AFC} \approx N_{AFL} \approx 10^{-5} N_{AAC} \approx 10^{-5} N_{AAL}$$

and for high background flames:-

$$N_{AE} \approx N_{AFC} \approx N_{AFL} \approx 10^{-3} N_{AAC} \approx 10^{-3} N_{AAL}$$

Therefore taking noise factors as well as signal into account the limits of detection should be lower for AFL or AFC than for AAL or AAC at all wavelengths when using low temperature flames. With high temperature flames, the limits of detection should be comparable for AFL or AFC and AAL or AAC at all wavelengths. However, if limits of detection are most important, atomic emission should be used for all analyte atoms with resonance lines above about 3000Å, but AF or AA should be used for all analyte atoms with resonance lines at wavelengths below about 3000Å, with high temperature, high background flames. High temperature flames are the ones of greatest practical analytical use because they minimise solute vaporisation interferences. Thus, on a purely theoretical basis, it

would seem to be immaterial whether atomic fluorescence or atomic absorption were used with high temperature flames. However, because essentially the same spectrometric measurement system can be used for both AF and AE, it would seem that the combination of AF and AE would be ideal for practical work. With low temperature flames AF would be superior to AE.

1.8 COMPARISON OF SELECTIVITY OF AE, AA AND AF

1). Spectral Interference

The spectral interference in AAL and AFL should be less than in the other (AE, AAC, AFC) flame methods, because interference can only occur when there is overlap between analyte resonance line and the interfering absorption line. Although this type of interference is possible [72] in AAL and AFL, it is not too important because the absorption lines are narrow (approximately $0.1\text{\AA}$ with wings only extending a few $\text{\AA}$) and because absorption is relatively small unless the lines overlap significantly or unless the interferent has a very large absorption coefficient even in the line wings where small overlap may occur [65, 72-74].

The spectral interferences in AE, AAC and AFC, should be approximately identical because any substance will interfere in those techniques if it has a spectral line within the spectral bandwidth of the monochromator. In AFC direct line or stepwise-line [4,73] fluorescence can also cause interference, but this should be relatively unimportant compared to the

direct interference of an element with its resonance line within the spectral bandwidth of the monochromator which includes the resonance line of the analyte. These spectral interferences in AE, AAC and AFC become less important as the monochromator spectral bandwidth $\Delta\lambda$ is reduced. With a good monochromator ($\Delta\lambda \sim 0.2\text{\AA}$), spectral interferences should only be slightly greater in AE, AAC and AFC than in AAL and AFL.

2). Chemical Interferences

These affect the free atom fraction (β) and solute vaporisation (ϵ) and therefore have the same effect on all flame methods. They are generally the most severe interferences in flame spectrometry.

3). Interferences due to Flame Temperature Variation

Flame temperature fluctuations has little effect on any of the important parameters except for the Boltzmann factor $\exp\left(\frac{-hc}{\lambda_0 kT_f}\right)$ and the β factor. Assuming that the analysis deals with analyte concentrations in the middle part of the analytical working curve, ionisation is generally negligible and only compound formation needs to be considered. The β factor depends on an exponential term similar to the Boltzmann factor except that hc/λ_0 is replaced by V_d , the dissociation energy of the stable molecule formed between the analyte atoms and the flame gas products X. To a first approximation, the most stable molecular entity for most analytes in most analytical flames is the monoxide (although the monohydroxide may be stable in some cases the final result is the same).

In AE the relative change in signal, dS_{AE} , with flame temperature dT_f is found [75] to be:-

$$\frac{dS_{AE}}{S_{AE}} \approx \left(\frac{E_u + V_d}{kT_f} \right) \frac{dT_f}{T_f} \quad (51)$$

where E_u is the excitation energy of the resonance transition ($E_u = \frac{hc}{\lambda_0}$). For AAL, AAC, AFL and AFC it can be shown [51] that:-

$$\frac{dS_{AA}}{S_{AA}} = \frac{dS_{AF}}{S_{AF}} = \left(\frac{V_d}{kT_f} \right) \frac{dT_f}{T_f} \quad (52)$$

The above equations are valid only if $V_d \geq 2.5\text{eV}$ for analytical flames of temperature 2000°K 3000°K . Because nearly all elements form oxides with dissociation energies greater than 2.5eV , the above equations can be used to give estimates of temperature sensitivity. Assuming the same flame and analyte the ratio of sensitivity with respect to temperature change is given by:-

$$\Psi = \frac{dS_{AE} / S_{AE}}{dS_{AA} / S_{AA}} = \frac{dS_{AE} / S_{AE}}{dS_{AF} / S_{AF}} = \frac{E_u + V_d}{V_d} \quad (53)$$

If the value of V_d is of the order 6eV (monoxide of Al, Be, Ce, Dy, Er, Gd, Ge, Hf, Ho, La, Lu, Nb, Pr, Sc, Si, Sm, Sn, Ta, Tb, Th, Ti, Tm, U, V, Y, Zr), the relative sensitivity factor Ψ will vary from less than $10/6$ for a line at $4000\text{\AA}$ to less than $7.5/6$ at $8000\text{\AA}$. In other words, AE is really

not much more sensitive to flame temperature variation than either AA or AF methods. If ionisation is also a problem, the temperature dependence of ionisation and compound formation may be such that β is essentially a constant, and so under such unusual circumstances, AE is much more temperature sensitive than AA or AF; because ionisation can be suppressed by the use of an ionisation buffer such as KCl, this situation is seldom important. The problem of interference due to temperature variation in AE has been grossly overstated by many authors when stressing the advantage of AA and limitations of AE.

4). Physical Interferences

These are interferences that affect the aspirator yield ϵ , and F the solute transport rate and therefore have exactly the same effect on all flame methods.

5). Scattering and Band Absorption of Exciting Radiation in AA and AF.

These result in an increased absorption and fluorescence signal and a slight increase in total noise in the instrumental system. Because these interferences are spectrally continuous, the increased signal can be compensated for in AAC and AFC by simply scanning the wavelength region containing the spectral line. The signal increases in AA are primarily a result of molecular absorption because of the use of premixed flames and efficient nebulisers, although in AF the signal increase does

occur to some extent even with premixed flames [79].

The magnitude of the absorption [AA] or scattered signal [AF] can be experimentally determined using a line close to the resonance line of interest.

6). Quenching Interferences in AE

Quenching of excited atoms due to change in flame gas composition as a result of the nebulised sample solution into the flame can only produce interference in AF. In AE, there are as many exciting collisions as quenching collisions as long as thermal equilibrium exists. In AA the mechanism of deactivation is irrelevant to the measured parameter. However, it is well known that the substitution of argon for nitrogen as a diluent in a premixed oxy-hydrogen flame gives rise to enhanced fluorescence signals as a result of the lowest quenching cross-section of argon [183]. Therefore it might be assumed that quenching could result in a specific interference in AF. However, it can be shown that even if the aspirated interferent had the same quenching cross-section as nitrogen it would have to be in excess of 10^4 ppm in the sample solution to cause even a measurable quenching interference.

1.9 COMPARISON OF EXPERIMENTAL SENSITIVITY IN AE, AA AND AF

In Table IV, tabulation of the best lowest experimental limits of detection by AFL, AAL and AE found in the literature, and Table V a similar listing is given for AFC, AAC and AE. It is evident from these tables that at the present time the

TABLE IV COMPARISON OF EXPERIMENTAL LIMITS OF DETECTION
IN AAL, AFL AND AE

Part I Elements Determined by AAL, AFL and AE

ELEMENT	WAVELENGTH (Flame) ¹			LIMITS OF DETECTION (ppm)		
	AAL	AFL	AE	AAL	AFL	AE
Ag	3281 (A/A)	3281 (A/H)	3281 (N/A)	5×10^{-4}	1×10^{-4}	2×10^{-2}
Al	3962 (A/N)	3962 (N/H)	3962 (N/A)	1×10^{-1}	5×10^1	5×10^{-3}
As	1937 (A/H)	1937 (A/H)	2350 (O/A)	1×10^{-1}	1×10^{-1}	5×10^1
Au	2428 (A/A)	2676 (A/H)	2676 (N/A)	2×10^{-2}	5×10^{-2}	4×10^0
Be	2349 (N/A)	2349 (N/A)	2349 (N/A)	2×10^{-3}	1×10^{-2}	1×10^{-1}
Bf	2231 (A/A)	2231 (A/H)	2231 (O/A)	5×10^{-2}	5×10^{-2}	2×10^0
Ca	4227 (A/A)	4227 (A/H)	4227 (N/A)	2×10^{-3}	2×10^{-2}	1×10^{-4}
Cd	2288 (A/H)	2288 (O/H)	3261 (N/A)	1×10^{-2}	1×10^{-6}	2×10^0
Co	2407 (A/A)	2407 (A/H)	3454 (N/A)	5×10^{-3}	1×10^{-2}	5×10^{-2}
Cr	3579 (A/A)	3579 (A/H)	4254 (N/A)	5×10^{-3}	5×10^{-2}	5×10^{-3}
Cu	3247 (A/A)	3247 (A/H)	3247 (N/A)	5×10^{-3}	1×10^{-3}	1×10^{-2}
Fe	2483 (A/A)	2483 (A/H)	3720 (N/A)	5×10^{-3}	8×10^{-3}	5×10^{-2}
Ga	2874 (A/A)	4172 (A/H)	4172 (N/A)	7×10^{-2}	3×10^{-1}	1×10^{-2}
Ge	2652 (N/A)	2652 (A/H)	2652 (N/A)	1×10^0	2×10^1	5×10^{-1}
Hg	2537 (A/A)	2537 (A/H)	2537 (O/A)	5×10^{-1}	2×10^{-2}	4×10^1
In	3039 (A/A)	4511 (A/H)	4511 (N/A)	5×10^{-2}	1×10^{-1}	2×10^{-3}
Mg	2852 (A/A)	2852 (A/A)	2852 (N/A)	3×10^{-4}	1×10^{-3}	5×10^{-3}
Mn	2795 (N/A)	2795 (A/H)	4031 (N/A)	2×10^{-3}	6×10^{-3}	5×10^{-3}
Ni	2320 (A/A)	2320 (A/H)	3415 (N/A)	5×10^{-3}	3×10^{-3}	6×10^{-1}
Pb	2833 (A/A)	4058 (A/H)	4058 (N/A)	1×10^{-2}	1×10^{-2}	2×10^{-1}
Rh	3435 (A/A)	3692 (A/H)	3692 (A/H)	3×10^{-2}	3×10^0	3×10^{-1}
Sb	2175 (A/A)	2311 (A/P)	2598 (O/A)	1×10^{-1}	5×10^{-2}	2×10^1
Se	1960 (A/H)	1960 (A/A)		1×10^{-1}	1×10^0	
Sn	2246 (A/H)	3034 (A/H)	2840 (N/A)	3×10^{-2}	5×10^{-2}	3×10^{-1}
Sr	4607 (A/A)	4607 (A/H)	4607 (N/A)	1×10^{-2}	3×10^{-2}	2×10^{-4}
Te	2143 (A/A)	2143 (A/A)	2383 (O/A)	1×10^{-1}	5×10^{-2}	2×10^2
Tl	2768 (A/A)	3776 (A/H)	3776 (N/A)	3×10^{-2}	8×10^{-3}	2×10^{-2}
Zn	2138 (A/A)	2138 (A/H)	2138 (O/A)	2×10^{-3}	4×10^{-5}	5×10^1

TABLE IV (Continued)

Part II Elements determined by AAL and AE

ELEMENT	WAVELENGTH (Flame) ¹		LIMITS OF DETECTION (ppm)	
	AAL	AE	AAL	AE
B	2498 (N/A)	2498 (N/A)	6×10^0	3×10^1
Ba	5536 (N/A)	5536 (O/A)	5×10^{-2}	2×10^{-3}
Ce		5697 (O/A)		1×10^1
Cs	8521 (A/A)	8521 (O/A)	5×10^{-2}	8×10^{-3}
Dy	4212 (N/A)	4046 (N/A)	2×10^{-1}	7×10^{-2}
Er	4008 (N/A)	4008 (N/A)	1×10^{-1}	4×10^{-2}
Eu	4594 (N/A)	4594 (N/A)	4×10^{-2}	6×10^{-4}
Gd	3684 (N/A)	4402 (N/A)	4×10^0	2×10^0
Hf	3073 (N/A)	3682 (O/A)	8×10^0	8×10^1
Ho	4104 (N/A)	4054 (N/A)	1×10^{-1}	2×10^{-2}
Ir	2640 (A/A)	3800 (O/A)	2×10^0	1×10^2
K	7665 (A/A)	7665 (O/A)	5×10^{-3}	3×10^{-3}
La	5501 (N/A)	5791 (N/A)	2×10^0	2×10^0
Li	6708 (A/A)	6708 (N/A)	5×10^{-3}	3×10^{-5}
Lu	3312 (N/A)	3312 (O/A)	3×10^0	2×10^{-1}
Mo	3133 (A/A)	3903 (N/A)	3×10^{-2}	1×10^{-1}
Na	5890 (A/A)	5890 (O/A)	2×10^{-3}	1×10^{-4}
Nb	3344 (N/A)	4059 (N/A)	3×10^0	6×10^{-2}
Nd	4634 (N/A)	4925 (N/A)	2×10^0	2×10^{-1}
Os	2909 (N/A)	4420 (O/A)	1×10^0	1×10^1
Pd	2476 (A/A)	3635 (N/A)	3×10^{-2}	5×10^{-2}
Pr	4951 (N/A)	4951 (N/A)	1×10^1	1×10^0
Pt	2660 (A/A)	2660 (N/A)	1×10^{-1}	2×10^0
Rb	7800 (A/A)	7800 (O/A)	5×10^{-3}	2×10^{-3}

TABLE IV (Continued)

ELEMENT	WAVELENGTH (Flame) ¹		LIMITS OF DETECTION (ppm)	
	AAL	AE	AAL	AE
Re	3460 (N/A)	3460 (N/A)	1×10^0	1×10^0
Ru	3499 (A/A)	3728 (O/A)	3×10^{-1}	3×10^{-1}
Sc	3912 (N/A)	3912 (N/A)	1×10^{-1}	3×10^{-2}
Si	2516 (N/A)	2516 (O/A)	1×10^{-1}	5×10^0
Sm	4297 (N/A)	4760 (N/A)	2×10^0	2×10^{-1}
Ta	2715 (N/A)	4813 (O/A)	5×10^0	2×10^1
Tb	4327 (N/A)	4319 (N/A)	2×10^0	4×10^{-1}
Th		5761 (O/A)		2×10^2
Ti	3643 (N/A)	3999 (N/A)	1×10^{-1}	2×10^{-1}
Tm	3718 (N/A)	3718 (N/A)	2×10^{-1}	2×10^{-2}
U	3515 (N/A)	5915 (O/A)	3×10^1	1×10^1
V	3184 (N/A)	4379 (N/A)	2×10^{-2}	1×10^{-2}
W	4009 (N/A)	4009 (N/A)	3×10^0	5×10^{-1}
Y	4077 (N/A)	3621 (N/A)	3×10^{-1}	4×10^{-2}
Yb	3988 (N/A)	3988 (N/A)	4×10^{-2}	2×10^{-3}
Zr	3601 (N/A)	3601 (N/A)	5×10^0	5×10^1

1. Flame Types - A/A = air/acetylene; N/A = nitrous oxide/acetylene; O/A = oxy-acetylene; A/H = air/hydrogen; O/H = oxy-hydrogen; A/P = air/propane.

TABLE V COMPARISON OF LIMITS OF DETECTION IN AAC, AFC AND AE.

ELEMENT	WAVELENGTH (Flame) ¹			LIMITS OF DETECTION (ppm)		
	AAC	AFC	AE	AAC	AFC	AE
Ag	3281 (O/A)	3281 (A/H)	3281 (N/A)	2×10^{-1}	1×10^{-3}	2×10^{-2}
Al	3944 (O/A)		3962 (N/A)	2×10^0		1×10^{-2}
Au		2676 (O/H)	2676 (N/A)		4×10^0	5×10^{-1}
Ba	5536 (O/A)		5536 (O/A)	9×10^{-1}		3×10^{-2}
Bi	3068 (O/A)	3068 (O/H)	2231 (O/A)	4×10^0	2×10^0	4×10^1
Ca	4227 (O/A)	4227 (A/H)	4227 (N/A)	3×10^{-2}	1×10^{-1}	1×10^{-4}
Cd	2288 (O/A)	2288 (O/H)	3261 (N/A)	1×10^{-2}	8×10^{-2}	2×10^0
Co	3527 (O/A)	2407 (A/H)	3454 (N/A)	3×10^0	5×10^{-1}	5×10^{-2}
Cr	3579 (O/A)	3579 (A/H)	4254 (N/A)	2×10^{-1}	1×10^1	5×10^{-3}
Cs	8521 (O/A)		8521 (O/A)	2×10^{-1}		8×10^{-3}
Cu	3247 (O/A)	3247 (A/H)	3247 (N/A)	5×10^{-2}	2×10^{-2}	1×10^{-2}
Dy	4212 (O/A)		4212 (O/A)	5×10^{-1}		1×10^{-1}
Er	4008 (O/A)		4008 (O/A)	1×10^0		3×10^{-1}
Eu	4627 (O/A)		4594 (O/A)	4×10^{-1}		3×10^{-3}
Fe	3720 (O/A)	2483 (A/H)	3720 (A/H)	1×10^0	1×10^0	5×10^{-2}
Ga	2814 (O/A)	4172 (A/H)	4172 (N/A)	2×10^0	5×10^0	1×10^{-2}
Gd	4079 (O/A)		4520 (O/A)	6×10^{-1}		2×10^0
Ho	4163 (O/A)		4104 (O/A)	2×10^0		1×10^{-1}
In	3039 (O/A)	4150 (A/H)	4511 (N/A)	2×10^{-1}	2×10^0	5×10^{-3}
Ir		2544 (A/H)	3800 (O/A)		1×10^2	1×10^2
K	7665 (O/A)		7665 (O/A)	3×10^{-2}		3×10^{-3}
Li	6708 (O/A)		6708 (N/A)	4×10^{-3}		3×10^{-6}
Lu	3312 (O/A)		3312 (O/A)	5×10^1		2×10^{-1}
Mg	2852 (A/O)	2852 (A/H)	2852 (N/A)	1×10^{-2}	1×10^{-2}	5×10^{-3}

TABLE V (Continued)

ELEMENT	WAVELENGTH (Flame) ¹			LIMITS OF DETECTION (ppm)		
	AAC	AFC	AE	AAC	AFC	AE
Mo	3133 (O/A)		3903 (N/A)	8×10^{-1}		1×10^{-1}
Na	5890 (O/A)		5890 (N/A)	3×10^{-2}		1×10^{-4}
Nb	4059 (O/A)		4059 (N/A)	3×10^1		1×10^0
Nd	4925 (O/A)		4925 (O/A)	4×10^1		1×10^0
Ni	3415 (O/A)	2320 (A/H)	3415 (N/A)	7×10^{-1}	1×10^0	6×10^{-1}
Pb	2833 (O/A)	4058 (A/H)	4058 (N/A)	2×10^0	3×10^0	2×10^{-1}
Pd		3405 (A/H)	3635 (N/A)		5×10^1	5×10^{-2}
Pr	4951 (O/A)		4940 (O/A)	6×10^1		2×10^0
Pt		2660 (A/H)	2660 (N/A)		5×10^2	4×10^1
Rb	7800 (O/A)		7800 (O/A)	4×10^{-2}		2×10^{-3}
Re	3460 (O/A)		3460 (N/A)	5×10^0		2×10^{-1}
Rh		3692 (A/H)	3692 (O/A)		1×10^1	3×10^{-1}
Ru		3728 (A/H)	3728 (O/A)		1×10^2	3×10^{-1}
Sb		2311 (A/H)	2598 (O/A)		3×10^2	2×10^1
Sc	3912 (O/A)		3912 (N/A)	1×10^0		3×10^{-2}
Sn	2863 (O/A)		2840 (N/A)	6×10^0		3×10^{-1}
Sr	4607 (O/A)		4607 (N/A)	6×10^{-2}		2×10^{-4}
Tb	4327 (O/A)		4327 (O/A)	3×10^1		1×10^0
Ti	3653 (O/A)		3999 (N/A)	5×10^0		2×10^{-1}
Tl	2768 (O/A)	3776 (A/H)	3776 (N/A)	6×10^{-1}	7×10^{-2}	2×10^{-2}
Tm	4094 (O/A)		4106 (O/A)	1×10^{-1}		2×10^{-1}
V	3184 (O/A)		4379 (N/A)	6×10^{-1}		1×10^{-2}
Y	4077 (O/A)		4077 (N/A)	1×10^1		1×10^0
Yb	3988 (O/A)		3988 (O/A)	2×10^{-1}		5×10^{-2}
Zn	2138 (O/A)	2138 (A/H)	2138 (O/A)	2×10^{-2}	3×10^{-2}	5×10^1

limits of detection are much lower with line sources than with continuum sources in AA and AF. This is somewhat surprising having calculated signal ratios and signal-to-noise ratios. There seems to be no logical explanation for the relatively poor detection limits with continuum sources especially in AAC. Even if estimates of source intensity were 10 times too high and geometry 10 times less favourable than assumed, it would seem that a continuum source in AA and AF should give lower limits of detection than line sources. This indicates that intensities quoted for line and continuum sources should be checked to see if this is causing the error in the calculations.

From the results in Table IV it is seen that AE and AFL or AAL are the useful combinations ie AE is complimentary with AFL and AAL when using high-temperature flames. Also since AE and AFL can use the same instrumental systems and can result in lower detection limits when using low temperature flames, the combination of AE with AFL seems to be the most ideal at the present time. However, if experimental limits of detection in AFC ever approach the theoretical values, then the ideal system would be AE and AFC where a single scanning spectrometric system could possibly be used for all elements with resonance lines between 2000 — 8000Å.

At the present time many limits of detection in AFL (as well as AFC) and AE do not approach the theoretical values. The main reason being that for many elements, intense stable

line sources are not available, and that only recently have high temperature premixed flames (C_2H_2 / N_2O) been used in AE [80,81,82] and AF [83, 84, 85].

The theoretical expressions have been derived and with these in mind developments in each of the basic units have been attempted in this study. These are 1) the preparation of intense atomic line sources; 2) the construction of a laminar flame atom reservoir; 3) a preliminary study in the application of solar blind photomultiplier tubes and photon counting as detection systems in atomic spectrometry.

CHAPTER II



SOURCES IN ATOMIC SPECTROMETRY

The flame techniques of atomic absorption and atomic fluorescence require an external source of radiation for excitation of the analyte atoms in the flame cell or atom reservoir. The main requirements of these sources are:-

- 1). They emit radiation over the region of the absorption line profile for the analyte atom and
- 2). The spectral radiance is stable with respect to long and short term fluctuations.

Requirements of Sources used in Atomic Absorption

The intensity of sources for atomic absorption is not a prime concern as the sensitivity is independent of source intensity provided an adequate signal is obtained from the photodetector. With continuum sources a high resolution monochromator is required with spectral band pass ' $\Delta\lambda$ ' $\leq 0.2\text{\AA}$. This is because the fraction of radiation absorbed is inversely proportional to the spectral bandwidth of the monochromator, (see Table I).

Atomic line sources have been generally accepted for use in AA as they provide radiation which is peculiar to the element to be determined and the monochromator serves only to isolate this line from other source lines and unwanted background. Thus, the monochromator used in conjunction with an atomic line source in AA need not have as high a resolution ($\Delta\lambda \approx 0.5\text{\AA}$) as would be required with a continuum source. The

quality of the spectral line determines the sensitivity of the determination and for this reason the emission profile from the source should be sharp and not self-reversed or broadened so that maximum overlap can take place (see Figure 5).

Requirements of Sources used in Atomic Fluorescence

The intensity of the continuum or line source in AF determines the sensitivity of the analysis as the fluorescent emission is directly proportional to the source radiance, (see Table I). Here the quality of the atomic line emission is not so important but if self-reversal is present in the line source the emission profile is deficient in energy at the wavelength where peak absorption takes place for the analyte atoms. Thus the source with self reversal gives poor detection limits. The monochromator in AF does not see the source radiation so a medium resolution instrument which is able to isolate the fluorescent line from unwanted flame background is sufficient. It would be useful here to note the broadening processes which may affect the shape of atomic spectral lines.

1). Natural Broadening ($\Delta\lambda_N$)

Natural broadening is due to the finite lifetime of the atom in the excited state (ie Heisenberg's uncertainty principle). For resonance lines this width is of the order of $10^{-4}\text{\AA}$.

2). Doppler Broadening ($\Delta\lambda_D$)

Doppler broadening is caused by the absorbing or emitting atoms having different component velocities along the line of

observation.

3). Lorentz Broadening (also known as Pressure or Collisional Broadening) ($\Delta\lambda_L$)

This is due to the perturbation of the absorbing or emitting atoms by foreign gas atoms. The effect of this type of broadening varies from different foreign gases and for different atomic states. Owing to these factors the calculation of collisional half intensity line widths $\Delta\lambda_L$ is very difficult and the results obtained are not always consistent.

4). Resonance Broadening (also known as Holtzmark Broadening) ($\Delta\lambda_R$)

Resonance broadening is due to the perturbation of absorbing or emitting atoms by atoms of the same type. This type of pressure broadening whilst generally negligible in analytical flames unless extremely high concentrations are used can however be appreciable in some types of spectral source.

5). Stark and Zeeman Broadening

Stark and Zeeman broadening are caused by electric and magnetic fields respectively. Although Stark broadening can cause lines to become diffuse in the arc, both these effects are negligible in flames, but an important factor within hollow cathode sources used in AA.

6). Hyperfine Structure

Hyperfine structure is due to nuclear spin and/or presence of several isotopes and results in the fact that each line consists of a number of separate hyperfine components each

behaved as an independant line. The total separation of the various components ranges from a few tenths to a few hundredths of a wavenumber λ^{-1} , for most spectral lines the influence of isotopes and the nuclear spin on the line width is negligible λ^{-1} .

The total half-intensity width $\Delta\lambda_T$ is related to the half-intensity widths caused by the broadening processes by the following equation:-

$$\Delta\lambda_T = \sqrt{\Delta\lambda_D^2 + (\Delta\lambda_L + \Delta\lambda_R + \Delta\lambda_N)^2} \quad (54)$$

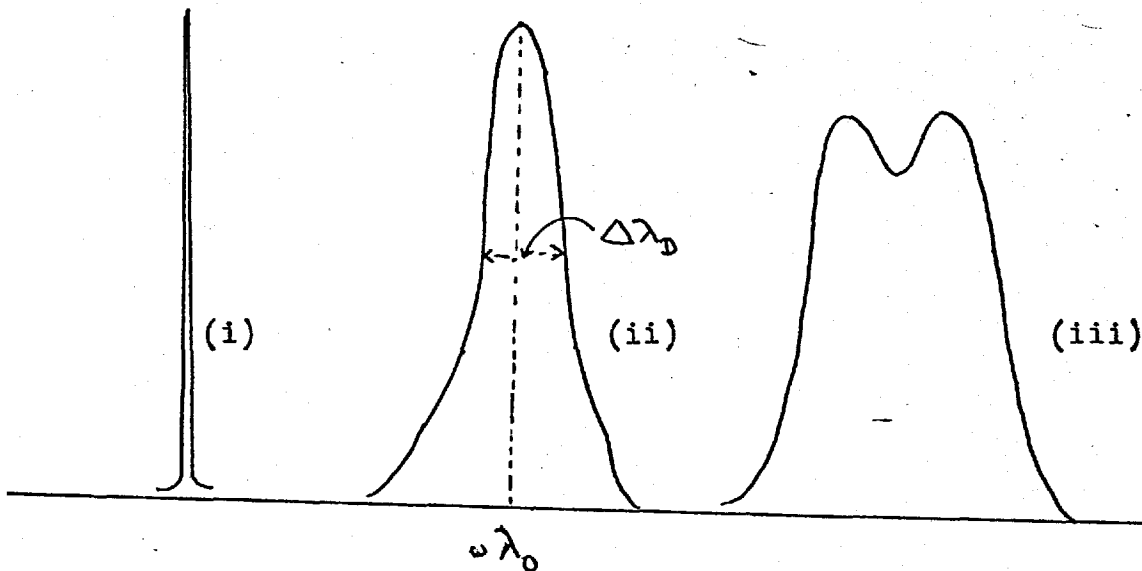


Figure 5 (i) Natural width
(ii) Doppler broadened line
(iii) Self-reversed line

2.2 TYPES OF SOURCES

1). Continua

Walsh in his original paper [5] expressed doubt in the use of spectral continua as sources for AA, however, recently work has been published where a Xenon arc [88,89], tungsten filament lamp (650Watt) [89], and hydrogen arc [88] have been used as continuous sources for AA in conjunction with high resolution monochromators.

Because of the theoretical superiority of the continuum when used for AF several workers have evaluated its performance although have not yet reached theoretically predicted limits of detection [90,91,92]. Interference studies in AF using a continuum source (500Watt Xenon arc) have been reported [93,94] and detection limits for thirteen elements in air/acetylene flames given [93]. The possibility of increasing the light output by running high pressure Xenon arcs at 2kW dc or 11kW [67] pulsed operation may improve considerably the sensitivity in AFC.

2). Metal-Vapour-Discharge Lamps (VDL)

These sources used initially in AF by Winefordner [14,16,79] for the determination of Zn, Cd, Hg, Tl, Ga and In and later by West [18,96] who compared for Cd the sensitivity with AA using the same apparatus, were found to suffer from self-reversal and resonance broadening if operated at recommended currents. However, their intensity was sufficient to make them useful sources for AF but they tend to give poor sensitivity

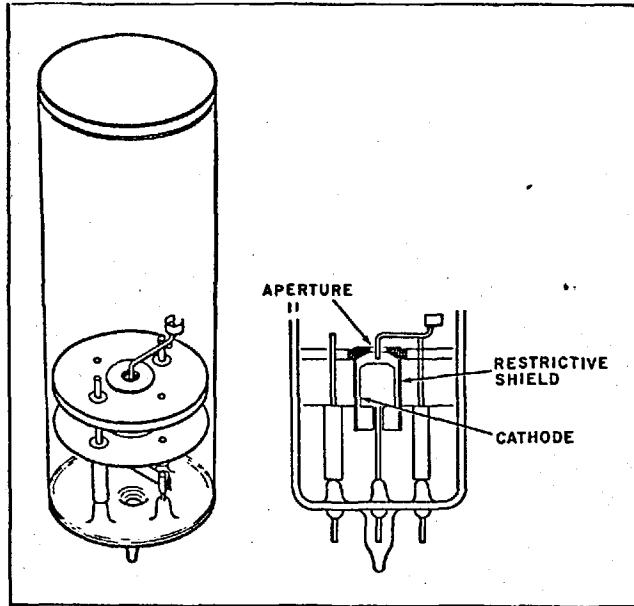


Figure 6 Diagram of restrictive shield hollow cathode lamp, used for volatile or molten metals.

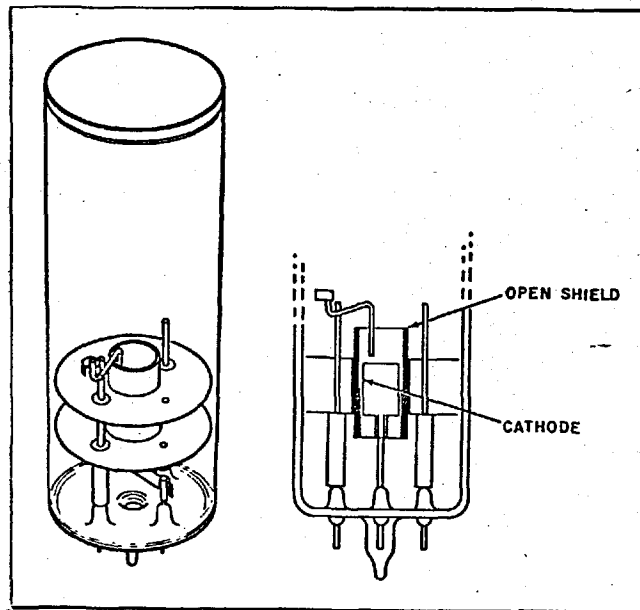


Figure 7 Diagram of an open shield hollow cathode lamp used for metals difficult to sputter.

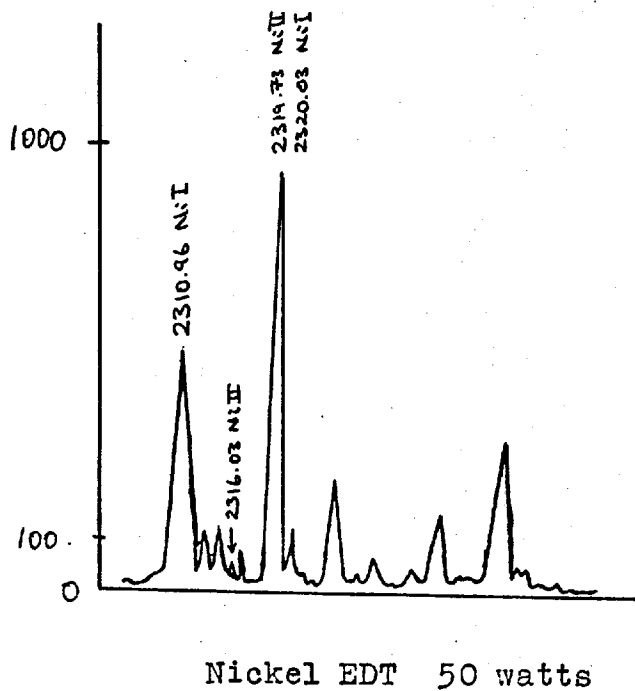
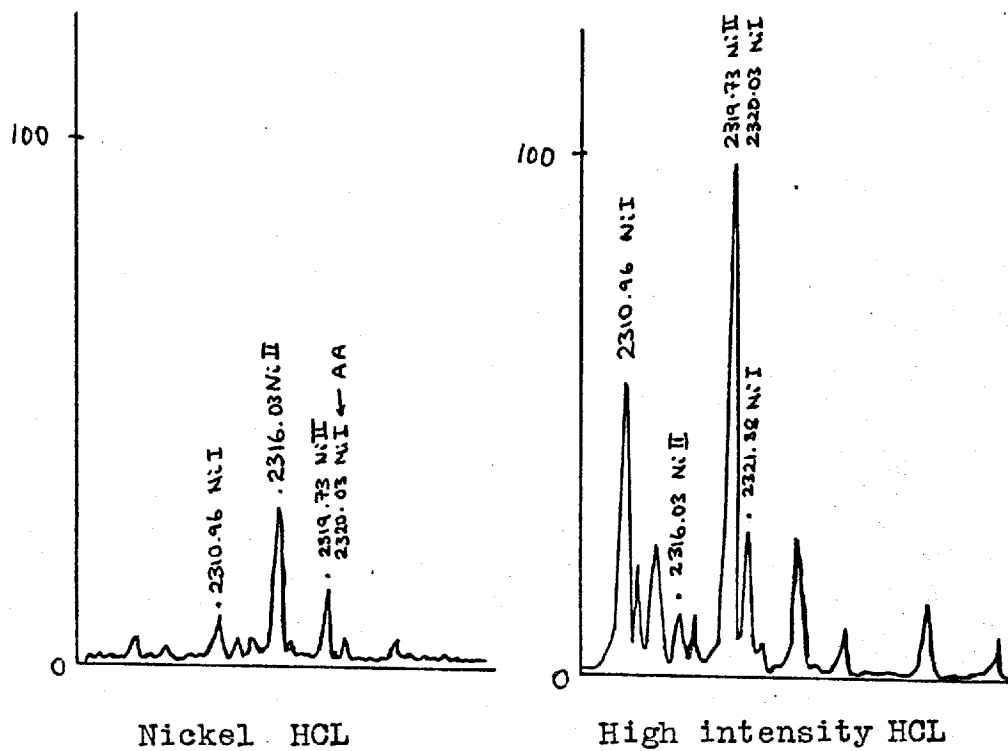
in AA due to the self-reversed emission profile [97].

Unfortunately intense VDL sources are only manufactured for a limited number of fairly volatile elements.

3). Hollow Cathode Lamps (HCL)

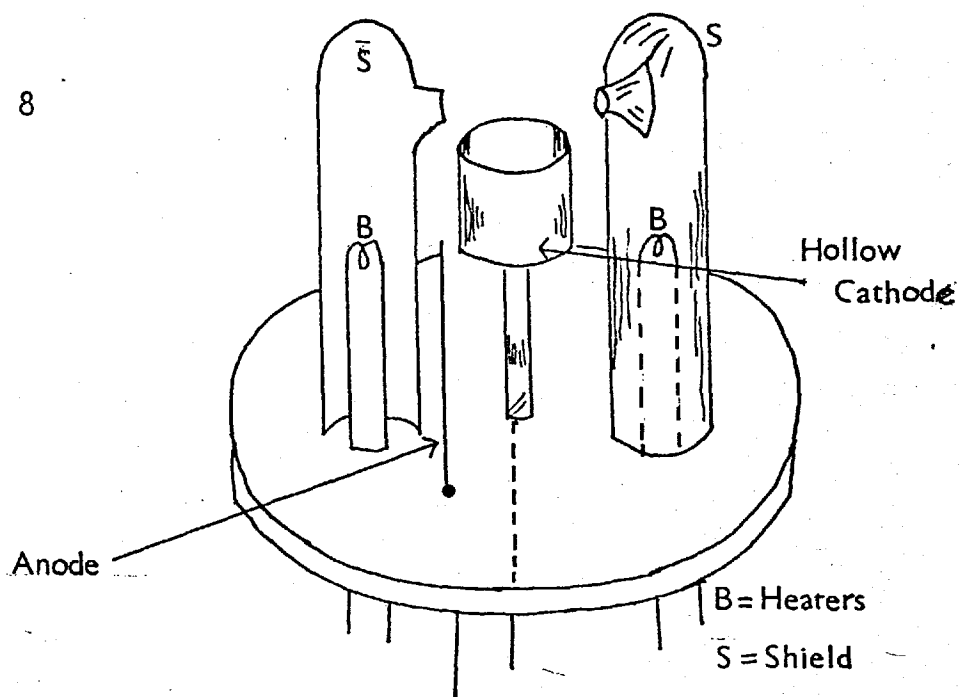
Figure 6.7 shows diagrams of the recently developed 'Intensitron' HCL developed by Perkin-Elmer [98,99]. These ceramic shielded hollow cathodes designed for either molten or normal sputtering operation give intensities much greater than the earlier HCL [100,101] and are capable of producing atomic fluorescence for several elements [91]. The intensity is comparable to the high intensity HCL developed earlier by Sullivan and Walsh [102] Figure 8. This lamp has a more elaborate electrode assembly and requires an auxiliary power supply. It is basically a simple hollow cathode discharge producing by sputtering the optimum pressure of atomic vapour around the outlet of the cathode and a second electrical discharge, isolated from the first to provide an excitation of the atomic cloud. In this way the excitation, and therefore the intensity, can be increased without increasing the vapour pressure and thus there is no accompanying increase in self-reversal or resonance broadening. A 10 to 100 fold increase in radiation results at the same time ionic radiation is suppressed Figure 9. A spectral comparison is given in Figure 9 for a nickel hollow cathode lamp, high intensity HCL and an electrodeless discharge lamp EDL (see following section), showing the improvement in spectral quality and intensity.

Figure 9 Spectra of Nickel atomic sources



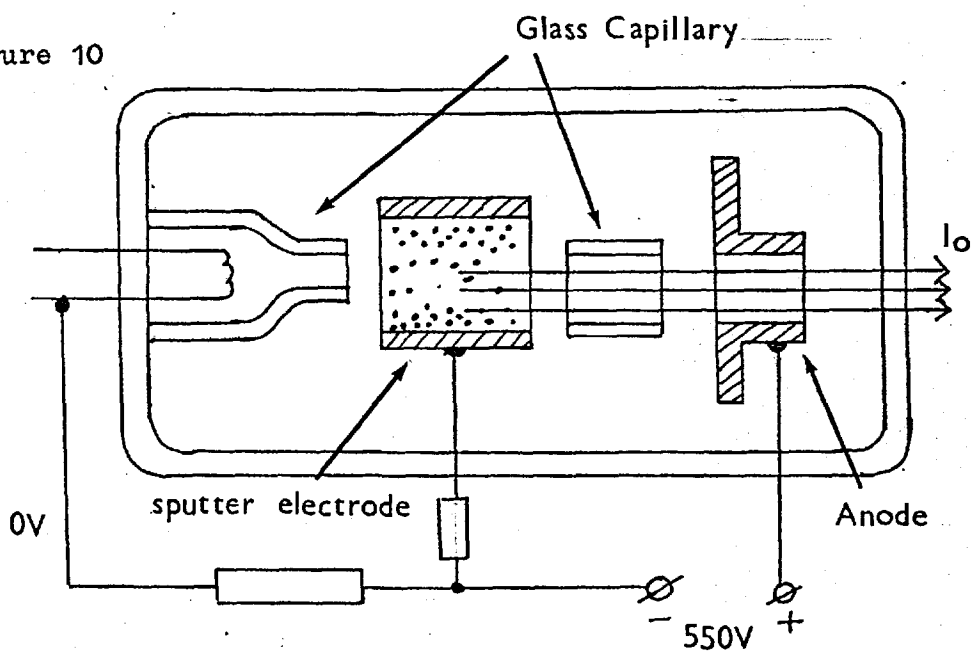
note the suppression of the 2316.03 Å ion line

Figure 8



High Intensity Hollow Cathode Lamp

Figure 10



Modified Hollow Cathode Lamp of van Gelder

A modified HCL which gave increased intensity at the resonance line without appreciable broadening was described by Van Gelder [103] Figure 10. This novel design is similar to the high intensity lamp but has the added advantage of being capable of selective modulation (see section 4.2.9)

4). High Current or Pulsed Operation of HCL's

Rossi and Oménetto [104] described a demountable water cooled HCL capable of high current operation up to $\frac{1}{2}$ ampere. This gave greater intensities than usual HCL's and they were able to excite fluorescence of several elements. Hot cathode lamps have been described by Dinnin [105, 106] who reported AF results for several elements in the air/hydrogen flame. There is some question as to the validity of the values for detection limits quoted for refractory elements [107].

Katskov, Lebedev and L'vov [108] measured the spectral characteristics of pulsed HCL used for AA studies. Emission intensities, line widths and line profiles were measured at different dc and pulsed current levels. At the same average current, the line widths were slightly greater, but the intensities were much greater (20 $\rightarrow$ 130 times) when using pulsed operation.

5). Miscellaneous Primary Sources

Strasheim [109] has demonstrated the feasibility of an electrical discharge as a source in AA. By using a time resolved system in which the detector only sees the emission

remaining when the discharge from a spark ceases. The line profile is reasonably narrow and sensitivity for AA is good. In a recent paper [110] the determination of Cu, Ca, Mg and Zn were reported. The advantage of this source is its convenience for simultaneous multielement analysis however, because of its poor precision it is not envisaged to be of any great use in AA.

A gas stabilised dc arc [111] has been used as a primary source for AA. A solution containing the elements of interest is nebulised into the nitrogen gas used to stabilise the arc, and the resonance lines excited. The concentration of the solution was found to be the only source parameter appreciably affecting the sensitivity of the determination. This device offered the same convenience as the time resolved spark for multielement analysis, and the precision was as good as with a hollow cathode lamp as primary source. The sensitivity was somewhat poorer than that achieved with hollow cathode sources.

A high frequency plasma torch has been used as a primary source of radiation in AA [112]. It was reported that the line profiles obtained (when solutions containing the test elements were nebulised into the plasma) had a half width of about $0.05\text{\AA}$ and were of very high intensity. Although no work has been published using this source for AF there is no reason why it should not be ideal for this purpose [149].

Rann [113] has taken a look at the utility of a flame

as the radiation source for AA measurements. From both a theoretical and experimental treatment he concluded that the sensitivity was reduced by a factor of two if a flame replaced the hollow cathode source.

6). Electrodeless Discharge Lamps (EDL)

The most effective and intense source at present available for AA and AF is the electrodeless discharge lamp. They are known to emit very sharp and intense spectral lines, and they can be made with a minimum of equipment. The absence of electrodes lead to long-life of an EDL as no electrode burn-away can occur and there are no glass to metal seals which are a potential source of leaks. Also the pure spectral output cannot be contaminated by the appearance of the electrode spectrum.

a). Development of Electrodeless Discharge Lamps

The high frequency electrodeless discharge was discovered by Hittorf [114] in 1884. This was followed in 1891 when J.J. Thomson [115] published two papers on 'the discharge of electricity through exhausted tubes without electrodes'. The spectra of many species were observed using a Wimshurst machine coupled to a coil of copper wire surrounding an evacuated glass vessel. Jackson, [116] in 1928, used an EDL operated from a 10 MHz oscillator to obtain the spectrum of Caesium in order to study its hyperfine structure. Meggers et al [117-119] in 1948-50, described the preparation of an

EDL of mercury 198 and proposed it as a secondary wavelength standard, as there was no hyperfine structure owing to absence of nuclear spin and isotopic shifts. The wavelength of the lines were quoted to $10^{-4}\text{\AA}$. More recently these lamps have been used to study the spectra of the lanthanides and the actinides and their isotopes. [120-124]. Tomkins and Fred [122] have shown that as little as $0.1\mu\text{g}$ of a given element was sufficient to produce strong emission in an EDL. It can be seen that for radioactive elements and isotopes [120-125] these sealed sources are much safer and more economical than the commonly employed dc arc. The advent of the laser caused a great deal of interest in EDL's for optical pumping studies [126].

Radio frequency EDL's have been used as spectral sources for the alkali metals [127] and for excitation of atomic resonance fluorescence of the alkali metals [128-129]. Ham and Walsh [130] describe 2450MHz powered sodium and mercury sources for use in Raman work. Microwave excited EDL's have been used to obtain continuous sources in the vacuum U.V. using argon, hydrogen, krypton and xenon filler gases [131-136]. A microwave discharge can easily be operated at low temperatures and Vaughan [137] used a helium discharge cooled by liquid helium to obtain spectral lines with an effective Doppler temperature of 10^0K .

The preparation of metal EDL's has been described in

many publications [117-125, 127-130, 138,139], but these sources were prepared primarily for spectral elucidation studies. Certain EDL's have also been prepared as spectroscopic standards where absolute cleanliness of preparation was essential [117-119, 140]. However, until recently, there has been little work on the production of EDL's solely for use as sources in AA and AF. Ivanov et al [141] report the use of lamps with high-frequency excitation for use as sources in AA, and Goodfellow [142] has made some AF measurements using a continuous flow microwave system. This type of continuous flow system has also been proposed as a spectroscopic source by Richards [143]. Winefordner [14,95] has used some commercially available EDL's (Ophos Instrument Co., Rockville, Ma., U.S.A.) for AF studies, with rather poor results mainly because of the EDL design. These sources were not of high intensity or stability since they were marketed primarily for use in interferometry and wavelength calibration studies. The real potential of EDL's as sources for AF and AA was realized by Dagnall, Thompson and West [145] and they have described the preparation for several elements. The author has further extended this initial work to enable sources to be prepared for over 60 elements.

b). Basic Principles of Microwave Discharge

The excitation of a discharge by radio and microwave fields is very efficient as these fields accelerate electrons over a confined region thus maintaining an emitting plasma

without internal electrodes within the plasma. The discharge is equivalent to a cold plasma owing to its non-isothermal nature [146]. This means that the effective temperature of the atoms and molecules is much less than that of the electrons. The theory of these discharges is rather complex but a brief kinetic and thermodynamic description of low pressure electrodeless discharges has been given [146].

The frequency range mostly used has been 30-3000 MHz and a wide variety of power supplies and resonant cavities have been described in the literature. Because of the difficulties associated with the preparation of two identical discharge lamps, many conclusions which have been reached in the past concerning optimum preparative and excitation conditions are subject to question or modification. In general, however, microwave frequencies have been found to be the most efficient in converting electrical power into luminous power. Jacobsen and Harrison [147] reported a 16 fold increase in intensity of the 5461Å Hg line at 3000 MHz over that obtained for the same power at 150 MHz, while Forrester et al [148] found 95 Watts of RF power at 2450 MHz to give a source radiance ten-times greater than was possible using a 1k Watt generator at 70 MHz for the same emission line. In addition, there is evidence [118,147] that the lifetime of the EDL is extended with increase of the frequency excitation.

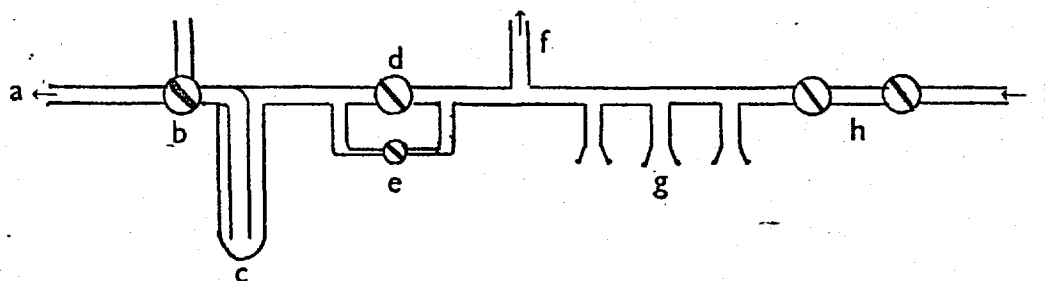
The use of microwave frequencies (> 100 MHz) for excitation is attractive not only for those reasons mentioned above, but

also because of the availability of comparatively inexpensive medical diathermy units. These units (intended only for medical use) supply a continuous microwave power at 2450 MHz, usually up to about 200 Watts rf power, and they can be used with a wide range of different cavities and antennae. In addition, because of the thermally uniform nature of this type of discharge, the emitted radiation is comparatively free of self-reversal effects.

c). Preparation of Electrodeless Discharge Lamps

i). Vacuum System

The vacuum system used by the author consisted of a two stage rotary pump, a cold trap, a means of introducing argon (or other gas) and several B10 outlets on the manifold. (See Figure 11) [145].



- a — Two-stage rotary pump
- b — Three-way tap
- c — Cold-trap
- d,h — Two-way taps
- e — Capillary leak
- f — Vacuostat gauge (10^{-2} - 10 torr)
- g — B10 connections
- i — Argon supply

Whilst being perfectly adequate for the general preparation of EDL's (having been used to prepare over 500 EDL's) a more

elaborate vacuum system is suggested for the further evaluation of lamp parameters. (See Chapter V)

ii). Lamp Dimensions

The lamp blank is made from transparent quartz tubing (Jencons Ltd.) 8mm internal diameter and nominally 1mm wall thickness. This was found to be most suitable with the cavities employed for excitation although slightly wider tubing can be used up to 13mm external diameter. About a 25cm length of this tubing was taken and thoroughly washed with detergent solution, actone and finally distilled water to remove any loose particulate matter and grease. When dry, the clean tubing was formed into two lamp blanks using an oxy-coal gas Scoria burner. After marking the centre of the length of tubing with a slight constriction two constrictions were formed (2mm id), about 5cm either side of the centre mark. The tubing was then allowed to seal at the centre mark and whilst still molten the two halves were drawn apart. The final rounding off of the individual lamp bases could then be performed. This procedure was found to be the most economical and rapid way to fabricate the lamp blanks. Because of the intense continuous emission from quartz at its softening temperature protective goggles should always be worn and the whole operation performed in a fume cupboard to prevent the inhalation of vaporised silica. Surface etching of the quartz tubing can be removed by heating the lamp blank to just below its softening point in the oxy-coal gas flame.

Lamp blanks can be made of any length but for most elements either at 4 or 5cm bulb length appears to be optimal (see TableVI).

iii). General Procedure

The lamp blank was connected to a B10 cone with medium pressure tubing, (Apiezon M grease was used for all ground glass joints and taps), and the whole attached to one of the outlets on the vacuum-line. The system was pumped down to about 0.1 torr. Argon (B.O.C. Compressed gas) was introduced into the system and again re-pumped to 0.1 torr. The lamp bulb was baked out at a temperature just below its softening point (using an oxy-propane hand torch) for about a minute, during which time argon was flushed through the system to remove any released gases. The degree to which the inner quartz surfaces are degassed is thought to play a part in the spectral purity of the output and also the lamps useful lifetime. However, the above procedure was found to be adequate for degassing the quartz.. The bulb was allowed to cool under vacuum and then was removed from the vacuum line. A few milligrams of the required substance or substances were introduced into the bulb which was then reconnected to the system.

The amount of substance has been found to be critical [149,150] less than 5mg being reported as optimum for Cd [149]. Too large a charge weight causes instability and plating-out in operation and ideally all the charge should be in the vapour phase at the lamps operating temperature [151].

The tube was evacuated as before, flushed out with argon and re-evacuated to a pressure of about 0.1 torr. Gentle heat from a micro-burner, depending on the volatility of the substance, was then applied to the base of the tube to drive off any moisture or occluded gas in the charge used. After a further two flushings of inert gas the pressure in the system was set generally to 3 torr (see Table VI) and the constriction was sealed by means of an oxy-propane hand torch.

In some instances (Hg, Se and Br) the lamps were sealed under as low a pressure as could be achieved whilst being continuously pumped. The material placed in the tube must have a well defined vapour pressure of about 1mm at 400-500°C in order to achieve maximum stability and intensity when operated with the power unit and cavities described below. It was this property which determined for most elements whether the metal itself or the corresponding halide was employed. In general the metal iodide was the most useful and it was normally formed in situ by the addition of a few mg of iodine to the degassed metal such that a sub-stoichiometric amount of iodine was present. This ensured complete formation of the required iodide. If an excess of iodine was present in the tube the metal spectrum was almost completely absent and a continuous iodine spectrum observed. By the above techniques lamps have been prepared for over 40 elements viz. Al, As, Bi,, Co, Cr, Fe, Ga, Ge, In, Mo, Nb, Nd, Pb, Sb, Si, Sn, Te, Ti, Tl, Tb, Th, U, Zr (as metal iodide) and A, Br, Cd, Cl, Cs, H,

He, Hg, I, K, Kr, Na, Ne, N, O, P, Rb S, Se, Xe, Zn (as element).

However, several elements do not fit this preparative scheme and they will be discussed in detail below.

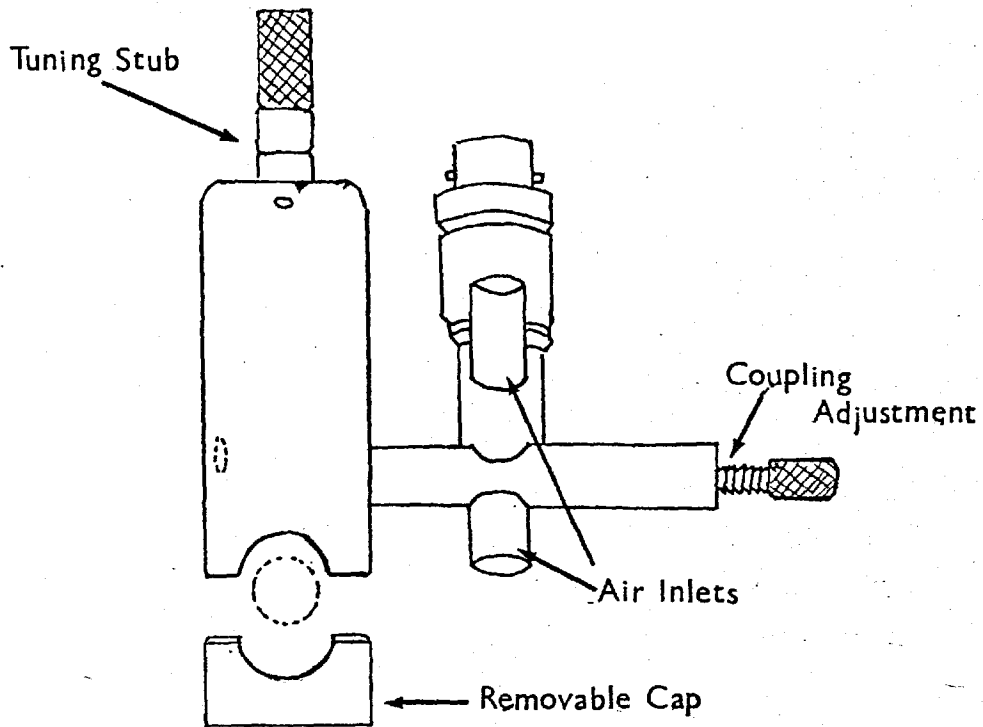
d). Operation of Electrodeless Discharge Lamps

Excitation of the lamps was achieved with a 'Microtron 200' generator (Electro-Medical Supplies Ltd. W1) in conjunction with several cavities. The output of the generator was 2450 MHz (12.5cm wavelength) at a power of 20-200 Watts. A reflected power meter can be used to facilitate tuning and to ensure the safe level of reflected power is not exceeded and thus damage to the Magnetron valve is averted. Initiation of the discharge, which relies on the production of free electrons in the lamp, was achieved with a simple Tesla coil vacuum tester.

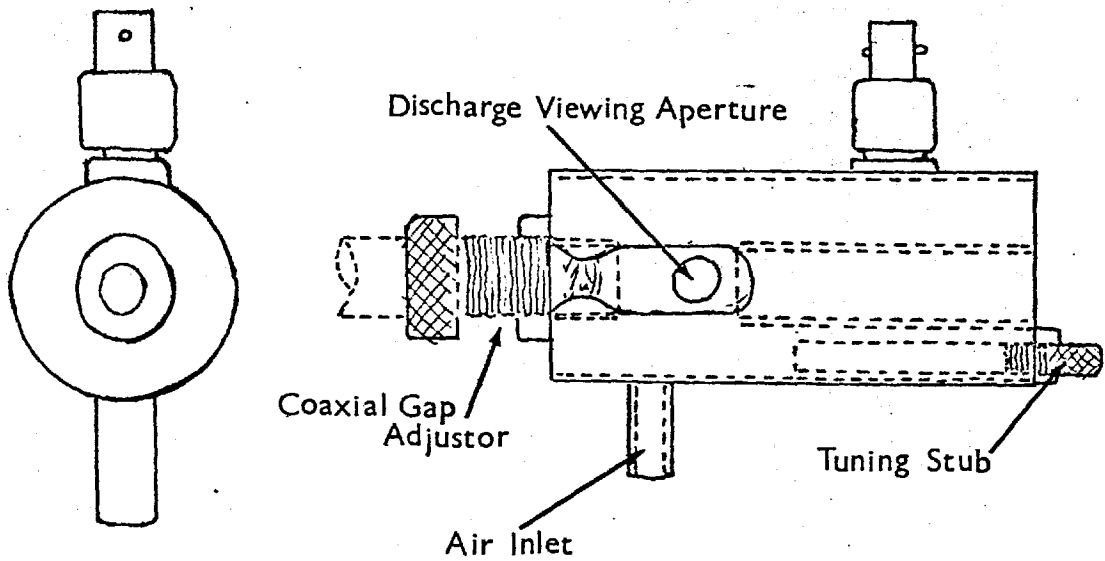
Two resonant cavities were initially studied [151] the foreshortened $\frac{1}{4}$ wave coaxial (Evenson) cavity and the foreshortened $\frac{3}{4}$ wave coaxial (Broida) cavity. (Figure 12). The $\frac{1}{4}$ wave cavity was the most efficient and had external dimensions 2.5 cm diameter and 6 cm length, with variable coupling at right angles to the longitudinal axis of the cavity. The coaxial input connection was integral with the cooling air inlets and the main tuning probe was in line with the axis of the cavity. The end cap of this cavity was removed in order to view the lamp side-on.

The $\frac{3}{4}$ wave cavity was less efficient, but had the advantage of totally enclosing the lamp and not being sensitive to tuning. It was cylindrical in shape about 5cm diameter by 13 cm length,

Figure 12.



The foreshortened $\frac{1}{4}$ wave coaxial cavity



The foreshortened $\frac{3}{4}$ wave coaxial cavity

had an adjustable re-entrant gap, coaxial with the discharge lamp, and a tuning probe off-set and parallel to the discharge lamp. The cavity could be air cooled and possessed adequate viewing apertures either at right angles or in line with the lamp which was completely enclosed. Because of the thermostating effect of the cavity better stability of spectral output was obtained and higher overall lamp operating temperatures could be achieved and for this reason it was particularly effective for relatively involatile substances.

In general it was found that the $\frac{1}{4}$ wave cavity gave optimum results when a low pressure of argon fill gas was used (< 3 torr) whilst the $\frac{3}{4}$ cavity gave optimum results with higher pressures (1-10 torr). This difference in operating pressures was attributed to the high localised density of radiation in the centre of 2.5 cm diameter $\frac{1}{4}$ wave cavity around the tuning stub which excited the discharge, which was in turn transferred by excited atoms and electrons away to the ends of the tube. This transfer over the length of the tube would be more efficient at lower pressures as the quenching collision frequency would be less at low pressures than high. The $\frac{3}{4}$ wave cavity give an even distribution of energy along the whole length of the lamp, thus the length of the discharge is less dependant on the fill pressure. The lower efficiency of the $\frac{3}{4}$ wave cavity to couple to the gas discharge results in longer warm-up periods before stable spectral output is reached for each lamp.

e). Spectral Characteristics of Electrodeless Discharge Lamps

All lamps when first prepared need a running-in period of about 1 hour before stability is reached. This is particularly important for lamps made by the addition of iodine to the metal in situ as the equilibrium conditions are reached during this initial period of operation. Once the lamp has reached equilibrium a warm-up time of about 5 minutes is usually sufficient. To accelerate the warm-up the lamp may be gently pre-heated to about 250°C before use thus reducing the stabilisation period (see Figure 17). When in operation the lamps exhibit no observable inert gas background emission or continuum from iodine if used. However, the $2061\text{\AA}$ iodine line was observed in all iodide lamps. Mercury was often present at $2537\text{\AA}$ as an impurity line from the vacuum system. If a continuous emission was observed this was usually due to excess of iodine (over that required to form the metal iodide) which was clearly visible in the lamp on gently heating.

The stability of spectral output was generally found to be comparable with that of hollow cathode lamps when measured under similar conditions. In order to ensure good EDL stability it is imperative that the lamp be thermally stable and protected from draughts or cooled with a constant supply of air.

TABLE VI Preparation and Operating Conditions for EDL's

Element	Compound(s) used	Size cm	Argon Torr	Power Watts	Wavelength Å AA
Al	Al + I ₂	5	3	50	3093
Sb	Sb + I ₂	5	3	40	2176
As	As + I ₂	5	3	40	1937
Ba	BaCl ₂	4	3	80	5535
Be	Be + I ₂	5	3	45	2348
Bi	Bi + I ₂	4	3	40	2231
B	B + Cl ₂	5	3	50	2497
Br	Br	5	-	40	-
Cd	Cd	4	3	60	2288
Cs	Cs (pyrex glass)	4	3	45	8521
Ca	CaCl ₂	4	3	80	4227
Cl	Cl ₂ (4 Torr)	8	-	35	-
Cr	Cr + Cl ₂ (CrCl ₃)	4	3	60	3579
Co	Co + I ₂ (CoCl ₂)	4	3	60	2407
Cu	Cu + I ₂ (CuCl ₂)	4	3	60	3247
Ga	Ga + I ₂	4	3	40	2874
Ge	Ge + I ₂	5	3	40	2652
Au	Au + Cl ₂	4	3	50	2428
Hf	Hf + Cl ₂ (HfI ₄)	4	3	60	3072
In	In + I ₂	4	3	50	3040
I	I ₂	5	1	30	2061
Ir	Ir + Cl ₂	4	3	60	2850
Fe	Fe + I ₂ (FeCl ₂)	4	3	55	2483
La	La + Cl ₂ (LaCl ₃)	4	3	80	5501
Pb	Pb + I ₂ (ratio 1:1.5)	4	3	50	2833
Li	LiCl	4	3	100	6708
Mg	Mg (X93 glass)	4	3	45	2852
Hg	Hg	5	1	35	2537
Mo	Mo + Cl ₂	5	3	45	3133
Ni	NiCl ₂	4	3	55	2320
Nb	Nb + I ₂	4	3	50	3349
Pd	Pd + Cl ₂ (PdCl ₂)	4	3	60	2448
Pt	Pt + Cl ₂	4	3	60	2659
K	K (X93 glass)	4	3	45	7665

TABLE VI (continued)

Element	Compound(s) used	Size cm	Argon Torr	Power Watts	Wavelength A
P	P	4	3	45	—
Pr	PrCl ₃	4	3	100	4951
Rh	Rh + Cl ₂	4	3	60	3434
Rb	Rb (pyrex glass)	4	3	40	7800
Se	Se	5	1	35	1961
Si	Si + I ₂	5	3	50	2516
Ag	AgCl	4	3	40	3280
Na	Na (X93 glass)	4	3	45	5890
Sr	SrCl ₂	4	3	90	4607
S	S (cool for atomic lines)	4	3	45	1900
Ta	Ta + I ₂	4	3	50	2714
Te	Te + I ₂	5	3	40	2143
Tl	Tl + I ₂ (TlCl)	4	3	55	2768
Th	Th + I ₂	5	3	45	3719
Sn	Sn + I ₂ (ratio 1:3)	5	3	40	2246
Ti	Ti + I ₂	5	3	50	3643
W	W + Cl ₂	4	3	60	2551
U	U + I ₂	5	3	45	3585
V	V + I ₂ (VCl ₃)	5	3	70	3184
Zn	Zn (ZnCl ₂)	4	3	65	2138
Zr	Zr + I ₂	5	6	50	3601

Operating conditions for $\frac{3}{4}$ wave cavity

Alternative preparation given in parenthesis

2.3 PREPARATION OF ELECTRODELESS DISCHARGE LAMPS FOR PALLADIUM, SILVER, PLATINUM AND GOLD

The comparative involatility of these noble metals and their compounds indicates that previously published preparation methods [145, 152] for electrodeless discharge lamps will not produce satisfactory sources. Lamps prepared from the elements alone give no emission apart from the carrier gas and they merely 'plate out'. The metal plus iodine method of preparation was attempted in this study, but the iodides are either difficult to prepare (eg. gold) or they are too involatile (eg silver), and some molecular metal iodide band emission is observed at normal operating powers.

The need to operate such lamps at high temperatures and, therefore, at high powers results in the lamp-life often being short because of the tendency for the compound to dissociate irreversibly. The use of the $\frac{1}{4}$ wave (Evenson) type of cavity accelerates this behaviour, and so the $\frac{3}{4}$ wave (Broida) cavity because its tuning characteristics are not critical and because it acts as a thermostat for the discharge lamp, which generally results in increased stability, has been used. This type of cavity is less efficient than the $\frac{1}{4}$ wave cavity, and it therefore necessitates the use of a different set of preparative conditions.

This section describes, with special reference to palladium, silver, platinum and gold, a general method of preparing electrodeless discharge lamps from the corresponding

metal chlorides, which are suitable for the $\frac{3}{4}$ wave cavity. It has been found that this particular cavity is useful in atomic fluorescence spectroscopy because it prevents radiation from the source from being directly reflected into the monochromator, thus resulting in improved limits of detection. Although it is much larger than the $\frac{1}{4}$ wave cavity, there is no difficulty in using it for atomic absorption and atomic fluorescence studies in most types of commercial atomic absorption equipment.

a). Palladium

Palladium discharge lamps were made by introducing about 5 mg of palladium metal (as foil) into a quartz bulb about 4 to 5 cm in length. The bulb and metal were de-gassed at red heat under vacuum with an oxy-propane hand torch. (Palladium has a high melting point (1552°C), so that vacuum evaporation does not occur). The lamp was removed from the vacuum line, and chlorine gas from a cylinder was then introduced at atmospheric pressure into the quartz bulb. The metal chloride was formed with a minimum of heat to prevent loss of the chloride by volatilisation, and the chlorination process was stopped while there was still an excess of palladium metal in the quartz bulb. The tube was then cooled, re-evacuated and any free chlorine flushed out with argon. The lamp was then sealed under an argon pressure of 3 torr.

Lamps produced in this way initiated readily when placed in either of the microwave cavities used in this study.

The optimum excitation powers were about 40 Watts in the $\frac{1}{4}$ wave cavity and about 60 Watts in the $\frac{3}{4}$ wave cavity, with 2 and 5 Watts reflected power, respectively. The higher power level required with the latter cavity arises because of its less efficient nature (lower Q value).

TABLE VII Palladium Discharge Lamp Spectrum¹

Wavelength Å	Recorder reading ²
2447*	18
2476*	16
2763*	12
3027	3
3065	7
3114	6
3242*	63
3251	14
3258	7
3302	24
3373	11
3404*	100
3421	20
3433	22
3441	10
3460	13
3481	14
3489	12
3516	37
3553	28
3571	9
3609*	62
3634*	92

1. Lamp operated at 40 Watts, with 2 Watts reflected power in the $\frac{1}{4}$ wave cavity. * denotes lines recommended for atomic absorption spectroscopy.
2. Slit width 0.015 mm and gain 3,0; uncorrected for instrument response characteristics.

Under these conditions, and in the absence of cooling, a stable, intense discharge showing no background emission from either argon or chlorine was obtained. The colour of the discharge was blue, and observation about 10 cm from the entrance of the Unicam SP 900A flame spectrophotometer showed that it contained

all of the expected atomic lines for palladium, their relative intensities being similar to those obtained in the arc, rather than spark, spectrum [153].

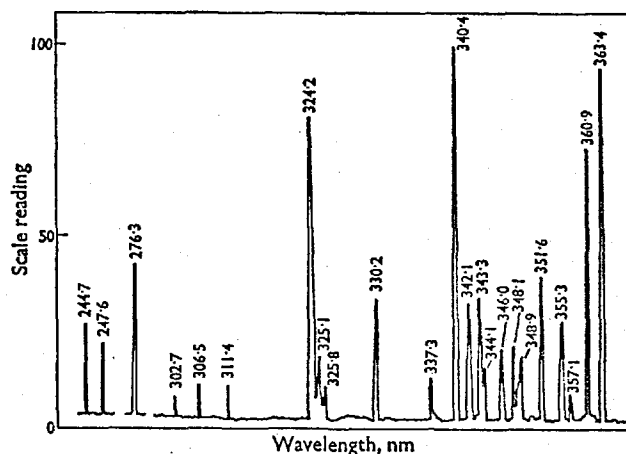


Figure 13 Emission spectrum of palladium discharge lamp. Excitation at 2450 MHz and 40 Watts power in the $\frac{1}{4}$ wave cavity. Recorded on Unicam SP 900A spectrophotometer with slit width 0.015 mm and gain 3.0.

Table VII and Figure 13 show the principal spectral lines that are to be observed near those lines which have been recommended for AA.

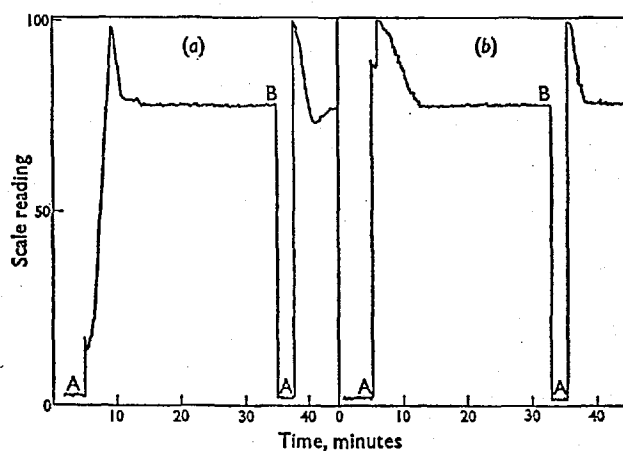


Figure 14 Stability and warm-up period. (a), Palladium discharge lamp; and (b), platinum discharge lamp. A denotes power on and B power off.

The EDL's required an initial 'running-period' of about 1 hour before good stability was reached. After this they would warm up in about 30 minutes, although this could be reduced to between 10 and 15 minutes by gently warming the tube before initiation (Figure 14). The stability with the $\frac{3}{4}$ wave cavity showed less than ± 2 per cent. variation in response, while with the $\frac{1}{4}$ wave cavity it was about ± 5 per cent. This indicated that better thermal stability was obtained in the former cavity because of the delocalised microwave field.

Lamps prepared from palladium and iodine produced a stable, but very weak, discharge.

b). Silver

A quartz bulb, about 4 cm in length, was de-gassed at red heat under vacuum. When cool, about 5 mg of silver powder were introduced and, after flushing with argon, the lamp was re-evacuated and the metal evaporated, by using an oxy-propane hand torch, to form a mirror on the inside walls of the quartz lamp. This had the combined effect of de-gassing the metal and also providing a large surface area for chlorination.

The quartz lamp was then removed from the vacuum line and the metal chloride formed by direct combination with chlorine gas at atmospheric pressure. When some of the chloride had formed and while there was still an excess of metal, chlorination was stopped and the lamp was then flushed with argon to remove free chlorine. The lamp was finally sealed under an argon pressure of about 3 torr.

The silver discharge was purple in colour, and was best operated in the $\frac{3}{4}$ wave cavity at about 40 Watts, without cooling. The stability of these lamps was good and they possessed a clean spectrum free from band emission. (Figure 15)

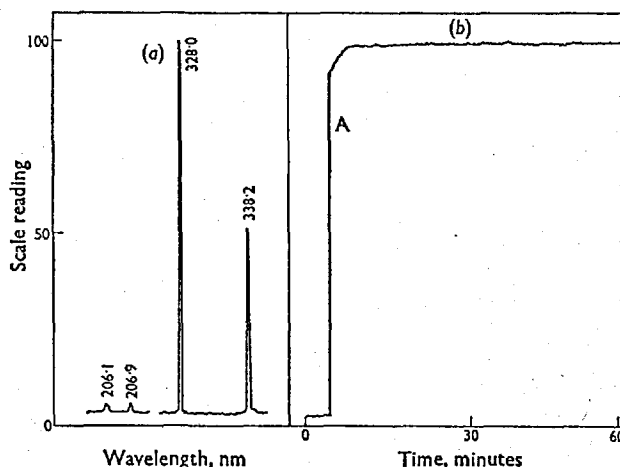


Figure 15 Emission characteristics of silver discharge lamp. (a), emission spectrum; (b), stability and warm-up period. A denotes power on. Excitation at 2450 MHz at 40 Watts power in $\frac{3}{4}$ wave cavity. Measurements made on Unicam SP 900A spectrophotometer with slit width 0.015 mm and gain 3,5.

A silver discharge lamp was also made in the usual manner with a substoichiometric amount of iodine. Although this initially gave an intense emission, after running for about 2 hours the emission from silver iodide molecular species caused high background radiation around the silver resonance line at 3280Å

TABLE VIII Silver Discharge Lamp Spectrum¹

Wavelength Å	Recorder reading ²
2601	<1
2609	<1
3280*	100
3382*	50

1. Lamp operated at 40 Watts, with 3 Watts reflected power in the $\frac{3}{4}$ wave cavity. * denotes the lines used in AA.

2. Slit width 0.015 mm and gain 3,5; uncorrected for response characteristics of Unicam SP 900A spectrophotometer.

The resonance lines at 2061 and 2069Å were observed by using the Unicam SP 900A spectrophotometer but, mainly because of a poor photomultiplier response at these wavelengths, their intensities were only weak in both metal chloride and iodide lamps (Table VIII).

Silver electrodeless discharge lamps, prepared as the chloride, required a 'running-in' period of about 2 hours when first prepared. After this, their performance was reproducible and stable, and they required only a short stabilisation period of about 5 minutes (Figure 15).

c). Platinum

Platinum is a very unreactive metal and will not undergo direct halogenation with iodine, even at high temperatures. Also, its reaction with chlorine is slow, and it was found difficult to produce much of the chloride by using fine platinum wire under the conditions previously described. Because platinum has a high melting point (1769°C), it does not form a mirror under these conditions, and hence an alternative method was used to give a platinum mirror that would facilitate the above chlorination procedure. This was based on the observation that the platinum chlorodiammine complex $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ on heating under vacuum deposited a platinum mirror on the quartz lamp walls. The ammonium chloride formed could be sublimed out of the lamp by using an oxy-propane hand torch. The following procedure proved successful. After de-gassing a lamp blank, 4 or 5 cm in length, at red heat, about 10 mg

of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ were introduced into the lamp and a platinum mirror formed by heating it under vacuum with a micro burner. The metal mirror was then de-gassed at red heat, and the large surface area of metal produced in this way was then chlorinated at atmospheric pressure, and at red heat, with chlorine gas from a cylinder.

The process of chlorination was not allowed to proceed to completion, being stopped while there was still an excess of metal in the lamp. Care was taken not to volatilise the chloride out of the lamp during heating. The lamp was then re-evacuated and flushed with helium to remove excess of chlorine and sealed under a helium pressure of about 1 torr. Helium was used as carrier gas because it gave a lower background emission than argon around the platinum resonance line at $2659\text{\AA}$. Also the higher ionisation potential of helium in comparison with argon caused a more intense emission of platinum resonance lines.

Platinum lamps made in this way were examined with the Unicam SP 900A spectrophotometer, as before, and were found to give all of the expected atomic lines for platinum (Figure 16 and Table IX).

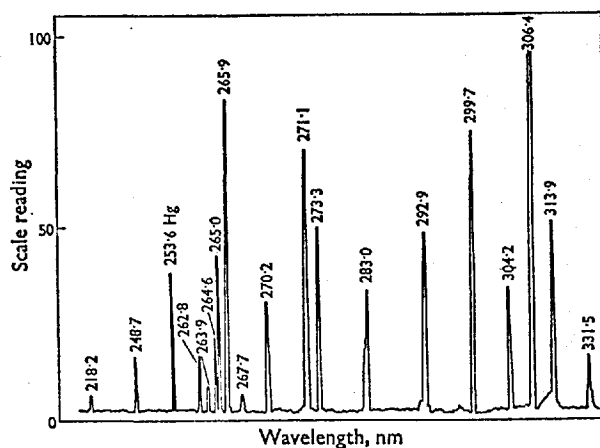


Figure 16 Emission spectrum of platinum discharge lamp. Excitation at 2450 MHz at 40 Watts power in the $\frac{1}{4}$ wave cavity. Measurements made on Unicam SP 900A spectrophotometer, with slit width 0.02 mm and gain 3,5.

The optimum running conditions were 40 Watts in the $\frac{1}{4}$ wave cavity (reflected power 2 Watts) or 50 Watts in the $\frac{3}{4}$ wave cavity (less than $\pm$ 2 per cent. variation in signal response).

Cooling the lamp via a compressed air line caused a reduction in the intensity of the platinum emission and a corresponding increase in helium background emission. The colour of the discharge was orange-red, and the lamp required a 'running-in' period of about 2 hours when first prepared. When the lamp was gently heated in a bunsen flame it subsequently stabilised in about 15 minutes. (Figure 14)

TABLE IX Platinum Discharge Lamp Spectrum¹

Wavelength Å	Recorder reading ²
2182	5
2487	13
2628	15
2639	6
2646*	24
2659*	83
2677	5
2711	75
2733	53
2830	32
2929	50
2997*	76
3042	34
3064*	100
3139	55
3315	23

1. Lamp operated at 40 Watts, with 2 Watts reflected power in the $\frac{1}{4}$ wave cavity.

2. Slit width 0.02 mm and gain 3,5; uncorrected for instrument response characteristics.

*Lines recommended for atomic absorption spectroscopy.

d) Gold

Gold electrodeless discharge lamps were made in a manner similar to that for silver. A quartz bulb, 4 to 5 cm in length, was de-gassed at red heat under vacuum, and gold wire (about 5 mg) was introduced and vacuum evaporated on to the quartz lamp walls. this effected the de-gassing of the metal and gave a large surface area for formation of the chloride.

The chlorination procedure was performed at red heat at atmospheric pressure, and was allowed to continue until a sub-stoich iometric amount of chlorine had reacted with the gold metal.

The tube was then re-evacuated, flushed with argon to

remove unreacted chlorine and finally sealed under an argon pressure of about 3 torr.

These lamps required only a short 'funning-in' period of about half an hour, after which time a stable intense emission was obtained under optimum operation conditions of about 40 Watts power in the $\frac{1}{4}$ wave cavity (reflected power 1 Watt) or 60 Watts in the $\frac{3}{4}$ wave cavity (reflected power 5 Watts). No cooling of the lamp was necessary.

Stability was better than ± 2 per cent. fluctuation in intensity at the resonance line at $2675\text{\AA}$ in the $\frac{3}{4}$ wave cavity and about ± 3 per cent. fluctuation in response in the $\frac{1}{4}$ wave cavity.

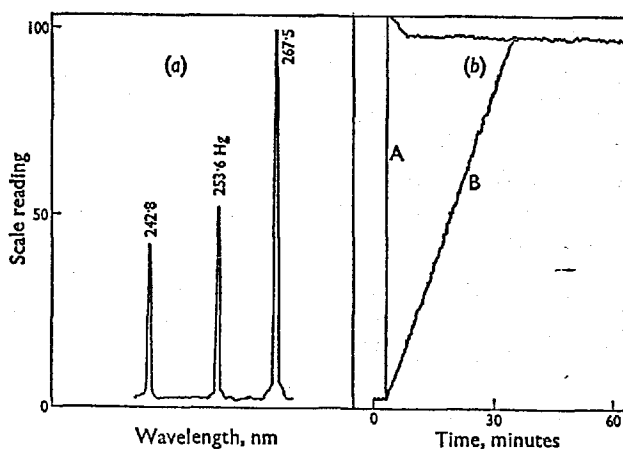


Figure 17 Emission characteristics of gold discharge lamp. (a), emission spectrum; (b), stability and warm-up period. A denotes operation after heating lamp and B operation from cold. Operating and measuring conditions as for Figure

The spectrum obtained with the Unicam Sp 900A flame spectrophotometer was found to contain the expected gold atomic

lines, together with mercury lines that arose from the mercury in the vacuostat gauge. Figure 17 shows the spectrum recorded at slit width 0.02 mm and gain 3,5 in a manner similar to that described above. Both of the gold atomic lines indicated have been recommended for AA measurements. Figure 17 shows the stability and warm up period for a gold lamp operated after warming in a bunsen flame (A) and from cold (B).

The metal chloride method of preparation can be used for several elements whose vapour pressure is too low at the operating temperature of the EDL or whose iodide is unstable in the plasma eg Co, Ni. Where pure metal chlorides are available these may be used directly after the evaporation of any water of crystallisation and gentle sublimation in the lamp bulb before sealing to remove any occluded gases.

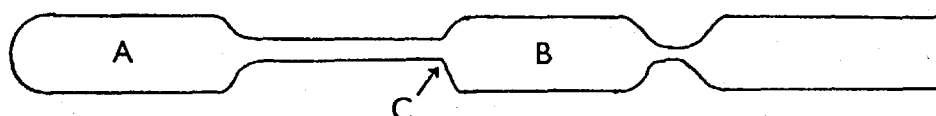
The three preparative methods described above 1) Metal 2) Metal + Iodine and 3) Metal + Chlorine allow the manufacture of most of the analytically useful sources. However, certain elements under the operating condition within an EDL attack the quartz inner surface causing reduction in light transmission and failure of the lamp. These elements notably the alkali and alkaline earth elements require a further consideration.

2.4 PREPARATION OF ELECTRODELESS DISCHARGE LAMPS FOR ALKALI AND SOME ALKALINE EARTH ELEMENTS

a). Rubidium and Caesium

The attack of these elements on silica tubing under normal operating conditions is only slow and if pyrex tubing

is used (borosilicate glass) the lamps can be operated for 50 to 100 hours without any appreciable reduction in signal at the resonance lines. Because of the highly reactive nature of these elements the metals were prepared in situ in a lower reaction bulb and the metal chased into the lamp blank (Figure 18) using a micro burner.



The anhydrous metal chloride is placed in the reaction bulb A together with a piece of calcium turning which has been washed in ethanol to remove any excess liquid paraffin. The reaction proceeds on heating to give free alkali metal and calcium chloride. The metal is chased up the tube into B and the reaction vessel sealed C and drawn off leaving the conventional lamp blank containing the required alkali metal. The method of thermal decomposition of the azide is also possible but because of its unstable nature the above method is preferred. Lamps produced in this way were very intense and stable atomic line sources for Rb and Cs.

b). Sodium and Potassium

Sources prepared for sodium and potassium from the element in silica or pyrex lamp blanks maintained a discharge for several hours but only at the expense of a rapidly darkening inner glass surface. This produced a gradually decreasing intensity, especially at the sodium 3302Å doublet. Ham and

Walsh [130] report that pyrex can be used for about 10 hours for sodium before darkening became too serious, but this is not the author's experience if sources are used with microwave power supplies. The attack on silica was very much more rapid with sodium than potassium and lithium attacked silica and pyrex more rapidly than any other alkali metal.

In consequence, two preventive methods were examined, the first involved boration of the inner surface of the silica tubing [154]. This was achieved by wetting the inner walls of the source bulb with a saturated solution of boric acid, followed by heating to white heat to form a protective layer of borate glass. The second, which is effective only with pyrex (boro-silicate) glass, involved washing the inner surfaces with a 40 per cent. solution of hydrofluoric acid [128]. This removed a layer of silicon thereby leaving a boron-rich glass. The recommended 10 per cent. HF wash was ineffective unless several hours was allowed for the reaction to take place. Both methods are basically the same and rely on the fact that sodium will not attack borate glass so quickly to displace elemental boron because of the stability of the B-O bond in comparison to the weaker Si-O bond.

These methods were effective in slowing down the attack by alkali metals, but neither was effective for more than a few hours of operation. Eventually attack in the former method was caused when the borate glass protective surface

cracked, probably because of the differences in the expansion properties of borate and silica glasses. The borated silica was, however, found to be adequate for potassium and only slight discolouration was noted after more than 25 hours of operation.

Quite obviously, a different approach is necessary. One such method, which appears not to have been described previously for the preparation of microwave-excited electrodeless discharge lamps, is based on the use of a two-ply glass; the inner ply consists of a sodium vapour-resistant silica-free glass and an outer ply of normal soda glass. Such a glass is commercially available in various sizes, although only the narrowest diameter (nominal external diameter 13 mm and 0.8 mm wall thickness) is suitable for use in conjunction with most commercial resonant cavities. Sources were prepared from this glass in the usual manner and it was found that even after 50 hours of operation there was no attack whatsoever from potassium or sodium. The two-ply glass must not be drawn out to a smaller diameter tubing otherwise the inner ply sodium-resistant glass may be broken and surface attack then readily occurs. In addition, prolonged heat causes devitrification. The sealing procedure is more difficult than when silica glass is used, because of the very low melting point of the two-ply glass, hence only a micro burner was used during preparation. The $\frac{3}{4}$ wave cavity which does not cause 'hot-spots' at low powers, is recommended for operation of these sources. Lithium still showed very severe

attack after only a few minutes and in this instance it is considered advisable to prepare the sources in silica glass from lithium chloride and not the metal. These sources show no surface attack at all because of the inability of lithium chloride to remain dissociated under these conditions (3 torr argon carrier gas). The only disadvantage is that the source must be operated at relatively high temperatures because of the comparative involatility of lithium chloride. It has been found that the $\frac{1}{4}$ wave cavity is the most suitable with operating powers of 75-100 Watts (reflected power ~ 2 Watts)

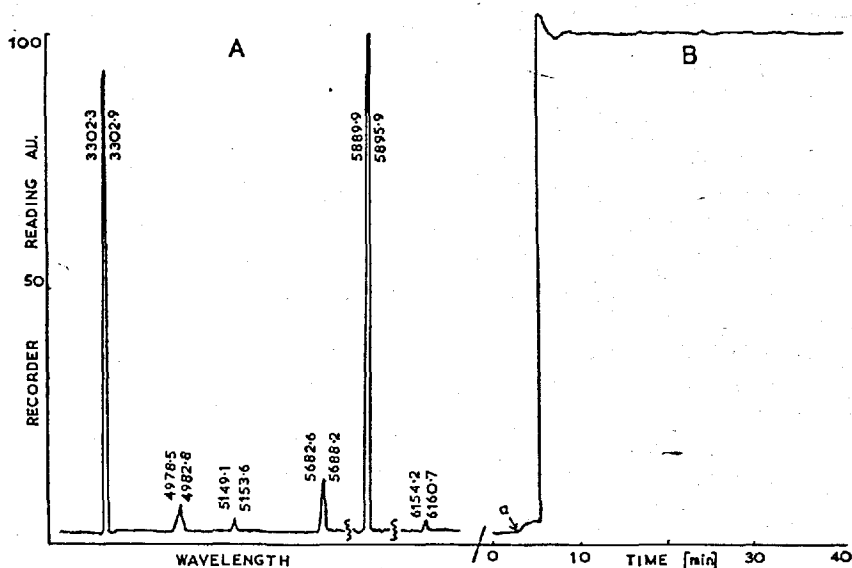


Figure 19 Spectral intensity and stability curves for sodium discharge lamp. A) slit width 0.01 mm, gain 2,0, electrical bandwidth 1. Intensity of 5890, 5896 Å doublet has been divided by 10. B) (a) denotes microwave power on.

The spectral transmission of the X93 two-ply glass is limited in the ultraviolet region; little transmission occurs below about 3000 Å, but it is linear between 3500 and

8000Å. Figure 19 shows the spectral and stability curves for the sodium discharge lamp prepared from a few mg of sodium metal and sealed under about 3 torr of argon. The $\frac{3}{4}$ wave cavity was used and the lamp was operated at about 35 Watts. The stability was better than 2 per cent. at the 5890, 5896Å doublet. Under these conditions this source was 10 times more intense than a Wotan vapour discharge lamp operated at 850 mA. The spectral evaluation was carried out using a Unicam SP 900A flame spectrophotometer which was not capable of resolving the 5890, 5896Å doublet.

The Wotan VDL and the EDL were compared for their analytical sensitivity in AA. Growth curves for sodium and potassium are shown in Figure 20 for AA measurement in the air-propane flame. The Unicam SP 900A was operated in the absorption mode and the light from the source was mechanically chopped at 100 MHz, the standard 5 cm long-path air-propane burner was used. The curves show the EDL's give better sensitivity and steeper analytical curves due to the better line profile obtained under these conditions. Table X gives the sensitivities obtained under the conditions of measurement given in Figure 20 for the two types of source.

TABLE X

Element	Source	Wavelength	Sensitivity for 1% absorption
Na	EDL	5890, 5896Å	0.025 µg/ml
Na	VDL	5890, 5896Å	0.035 µg/ml
K	EDL	7665Å	0.060 µg/ml
K	VDL	7665Å	0.090 µg/ml

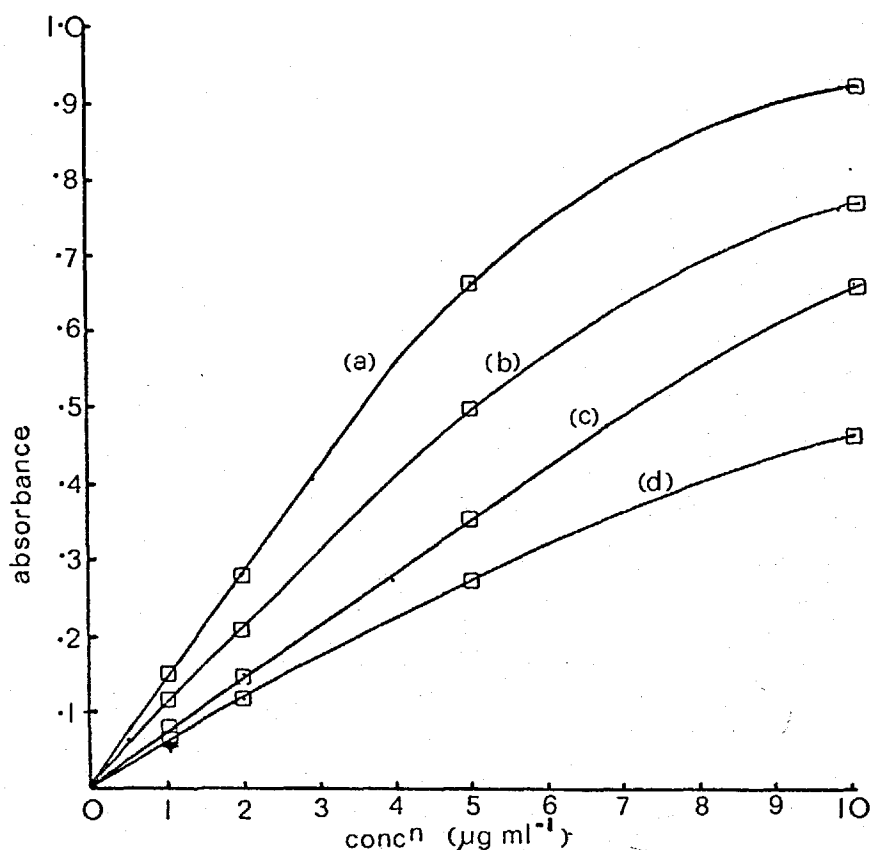


Figure 20 Calibration Curves for Sodium and Potassium in air-propane flame.

- 1) Sodium 5890, 5896 Å; Slit 0.008 mm (a) EDL 40 Watts (b) VDL 850 mA
2) Potassium 7665 Å; Slit 0.02 mm (c) EDL 40 Watts (d) VDL 1500 mA.

c). Magnesium

Magnesium vapour rapidly attacks silica and borosilicate glass within a few minutes of lamp operation. The inner surface becomes dark brown and the transmission of visible light is considerably reduced whether metal or metal iodide is used. However the use of sodium vapour resistant two-ply glass (type X93 available from Glass Tubing and Components Ltd., Chesterfield, England) as in the case of sodium and potassium gave satisfactory results for over 25 hours of operation.

The major resonance line for magnesium is the $2852\text{\AA}$ which is below the good spectral transmission of the X93 glass. Nevertheless the discharge lamp gave sufficient intensity to be a useful source for AA. For AF measurement the lamp was made from X93 tubing with a quartz flat sealed on to the open end of the glass tube (with eg Araldite) and then prepared in the usual manner sealing at an argon pressure of 3 torr. The lamp would subsequently be operated in the horizontal position with the end of the lamp containing the quartz flat out of the cavity area. It is the author's experience that magnesium vapour only attacks heated portions of the silica glass and thus lamps prepared and operated in this way are longlived and sufficiently intense for AF purposes.

In operation the lamps appear bright green due to intense emission of the magnesium triplet $5167, 5172$ and $5183\text{\AA}$. The radiance at $2852\text{\AA}$ of the normal EDL made in X93 glass, the silica windowed EDL and a Higer and Watts HCL are given in Table XI. The EDL's were operated at 45 Watts (or 2 Watts reflected power) in the $\frac{3}{4}$ wave cavity and the HCL at the recommended current of 8 mA.

TABLE XI

Source	Relative Intensity
EDL (silica window)	100
EDL (X93 glass)	8
HCL (silica window)	5

Although electrodeless discharge lamps can be prepared in

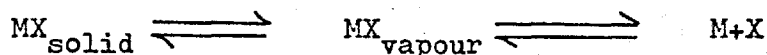
silica for Ca, Sr, and Ba from the chlorides because of the very involatile nature of these compounds the lamps have to be operated at very high powers (>100 Watts) and thus at high temperatures. The resulting emission is unstable, the tube lifetime relatively short and for these reasons the sources are unsuitable in this form for AA and AF routine measurements. However, if used with double-beam instruments for AA they may be of use for rapid determinations.

The major cause of lamp failure, however, seems to be due to reactions between the quartz inner wall and the vapour in contact with it (especially at high running temperatures) together with the thermal decomposition of the compound used. EDL's containing Cd, Zn, Cu and Au (Cu and Au as chlorides) the metal can be seen to plate-out on the inner walls of the lamp after several hours operation. This can cause a steady reduction in UV transmission of the quartz and affect the coupling of the microwave energy to the gas discharge due to preferential absorption by the metal film. The decomposition of the compounds introduced into EDL's usually results in the metal plating-out leaving excess halogen. If the metal iodide is used there is an increase in the continuum level due to the predominance of iodine emission. If the metal chloride is used the excess chlorine gas tends to quench the physical size of the discharge and make subsequent initiation difficult and eventually impossible.

It is known that the emission characteristics of EDL's

vary with vapour pressure of the fill element or compound. At low vapour pressures the sources emit predominantly first spectrum lines and the strongest of the second spectrum [123]. The profile of the resonance lines under these conditions is found to be narrow and as a result favourable sensitivities are obtained in AA [155]. The apparent intensity of the source may be increased by operating it at a higher vapour pressure (increased microwave power) when the first spectrum lines are enhanced relative to the second. Under these conditions line broadening takes place and self-reversal eventually reduces the analytical sensitivity of AA or AF. This is particularly noticeable for elements which exhibit a high vapour pressure, eg mercury and such sources must normally be cooled with a jet of air to give suitable line profile for atomic spectrometry.

The intensity of the discharge may be influenced by various parameters. For example when metal halides are used as charge the following equilibrium occurs:-



where X is usually chlorine or iodine. In these instances there can be a competition for the discharge between MX (giving rise to molecular bands) and M and X. This is particularly noticeable if the second equilibrium is only partly reversible and excess halogen is left in the lamp. Also at low operating pressure when the vapour pressure of MX is low it is possible to observe emission due to sputtering of metal-atoms from

the solid phase as in the hollow cathode type of discharge.

In consequence it may be said that the intensity derived from an EDL is subject to many lamp invariables, most of which cause changes in vapour pressure and may result ultimately in source instability. These effects can in some instances be rectified by proper choice of charge material together with microwave operating power. Provided the charge compound exhibits a high vapour pressure (1 mm Hg) at low temperatures (about 400°C) and dissociates reversibly, then stable and reliable EDL's can be produced easily.

2.5 VACUUM JACKETED ELECTRODELESS DISCHARGE LAMPS

For more involatile compounds slight variation in temperature may result in considerable instability which can usually only be tolerated on double beam instruments in atomic absorption [156]. The use of vacuum jacketed EDL's provides an alternative method by which increased stability may be obtained for relatively involatile compound used as charge. In addition this method of preparation provides a source with a reduced warm up time and allows the use of even more involatile charges (eg some rare earth elements) as a result of an increased operating temperature. The operation of EDL's in vacuum jackets has been described previously [24] but this method required the permanent use of a vacuum pump.

Lamp blanks were prepared as shown in Figure 21. These were de-gassed by strong heating of the outer tube wall in the normal way. The internal diameters of the tube used in the

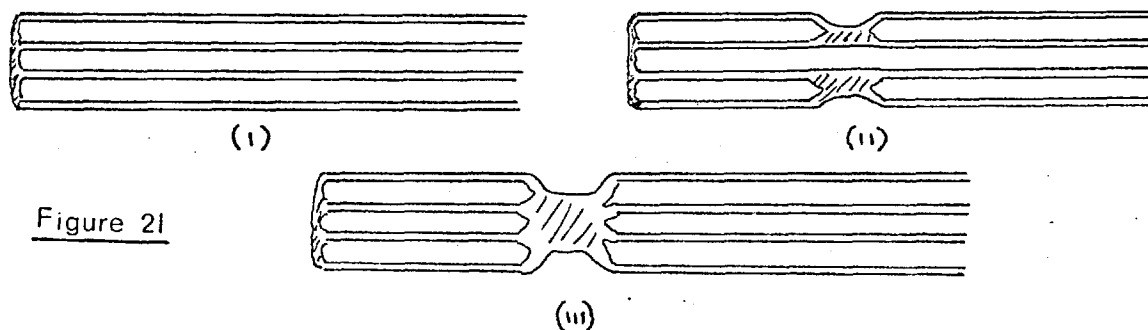
present investigation were 3mm and 8mm respectively. The vacuum jacket can be sealed under continuous pumping to give the appearance of Figure 21. This can be readily achieved by heating about 5 cm from the base of the lamp with the oxy-propane hand torch while rotating the B10 seal on the vacuum line. The centre tube can now be considered as a normal EDL blank and prepared in the usual manner. Because the separate sections are sealed separately the annular space could be filled and used as a source thus a multielement lamp can be produced in this way. (The least volatile compound must be placed in the inner tube).

The advantages of these sources may be summarised as follows:-

1). The microwave power required to give a stable, intense source for a single element is about 25 per cent less than that required for the more conventional type.

2). Because the inner tube can acquire a high running temperature it is possible to use comparatively involatile elements or compounds, eg thallium or lead in place of thallos chloride or lead iodide.

3). The warm-up times for a single element vacuum jacketed EDL is considerably less than the non jacketed source and the emitted radiation is more stable (Table XI).



It must be emphasised however that the material used in the inner tube must be relatively involatile because even at low operating microwave powers the temperature of the inner tube may be high about 800°C. Under these conditions self reversal effects may become apparent in poor sensitivities obtained in atomic absorption and fluorescence spectrometry.

TABLE XII

Element	Power (Watts)	Stability ¹	Warm-up time (minutes)
Pb	60	4.5	20
Pb v.j.	60	0.7	3
Tl	75	5.0	20
Tl v.j.	75	1.0	2.5
Zn	60	3.0	15
Zn v.j.	60	1.5	1.5

1. Stability expressed as $\pm$ % per hour after initial running in period. v.j. denotes vacuum jacketed lamp.

2.6 MICROWAVE GENERATORS

Most of the experimental work involving the evaluation of EDL's has been carried out using commercially available microwave generators. These are mostly designed specifically for medical diathermy and their stability and quality of power output is not always optimum when such units are used as power supplies for spectral sources.

Many generators exhibit up to 50 per cent mains frequency modulation and frequently have unstabilised power supplies to the magnetron oscillator. These units therefore have an inherent mains ripple superimposed on the microwave output,

and this unwanted amplitude modulation can often cause trouble when using a.c. amplifiers with mains derived synchronous demodulation. The dynamic impedance of a magnetron is low, therefore small variations in the applied voltage can cause appreciable changes in operating current.

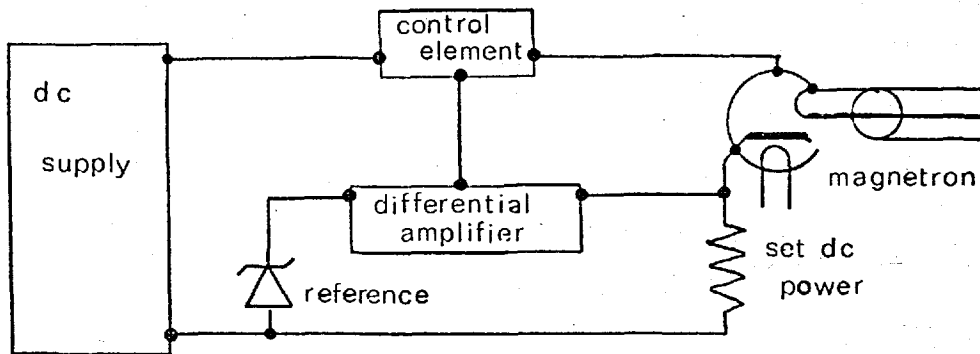


Figure 22 Schematic diagram of current stabilised supply for magnetron

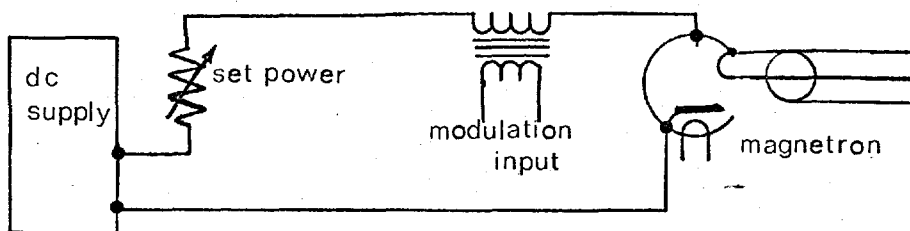
The characteristics of the Mullard Magnetron (JP2-02) used in the Electro-Medical Supplies 'Microtron 200' indicate that a voltage change from 1.60 - 1.65 kV may vary the anode current from 50 - 200 mA. The anode current with power output is almost linear and a milliammeter in the anode circuit reads to a near approximation the output power in Watts. For this reason it is advisable to use a current stabilised power supply for the magnetron. In this way mains frequency modulation is eliminated and a stable unmodulated microwave output is obtained. A standard series valve or semiconductor control element can be used to regulate and thus stabilise the anode current of the magnetron. Figure 22.

However, it must be remembered that the stability of spectral output does not only depend on the power supply, but also on the unchanging efficiency with which the power is converted into spectral radiation.

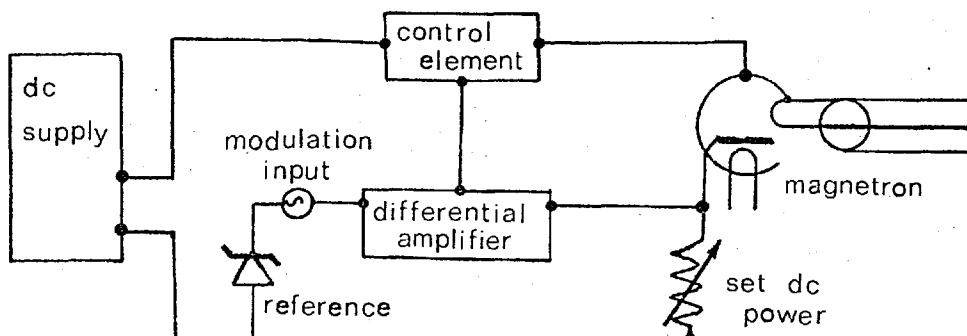
2.7 MODULATION

Modulating the excitation source in atomic fluorescence spectrometry is very attractive because it enables the distance between the source and atom reservoir to be reduced by eliminating the need for a mechanical chopper [157]. The reduction in distance allows a larger solid angle of radiation to reach the atomic population and thus the limit of detection is improved. Modulation in amplitude of the microwave energy may be achieved electrically in two basic ways.

1). By the use of a modulation transformer in the anode circuit of the magnetron.



2). If the power supply is stabilised, by adding a modulation waveform to the reference of the stabilising element.

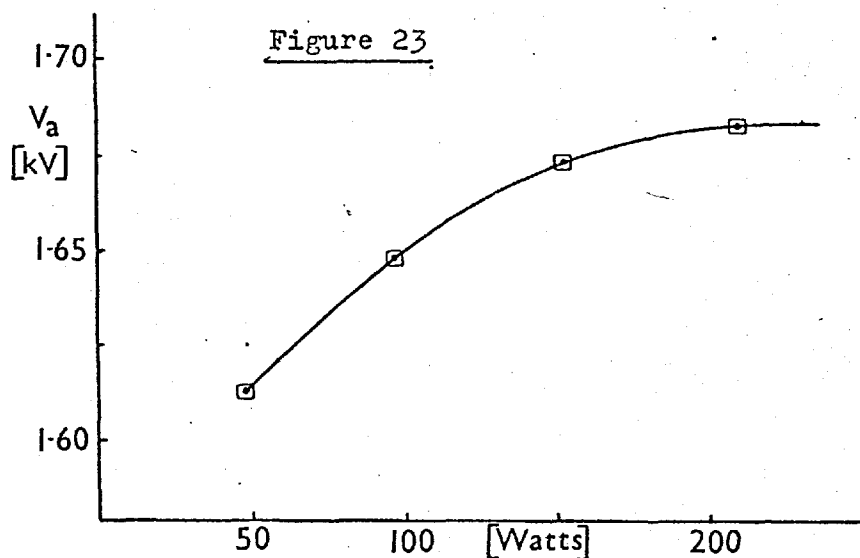


Both methods are acceptable, but the first using a step-up modulation transformer has certain disadvantages. Because the secondary of the transformer is in the anode circuit, the high d.c. current may cause saturation of the core material and the modulation wave applied to the primary of the transformer may not be faithfully reproduced on the microwave output. Also the frequency and function that can be used are limited by the use of a transformer which in general is most efficient at low frequency sinusoidal waveforms. These difficulties can be overcome for particular cases by careful design, but for a flexible system which can be used at several frequencies and waveforms the second method of modulation is to be favoured.

In this instance the reference element of the stabilised power supply can be modulated easily with a low power signal or function generator which may be of sine, square, triangle or pulse waveform at frequencies up to about 500 kHz. The waveform from the generator can also be used to synchronize the a.c. amplification system in phase with the modulation. This is necessary with all phase sensitive detection systems, as used for example in the Perkin-Elmer 290, Techtron AA4 and AA5 and most other commercial atomic absorption spectrometers.

The depth of modulation in both types of modulator is controlled by the amplitude of the modulating waveform. The percentage modulation that can be applied to an EDL and still

maintain a discharge depends on the type of EDL (ie element and fill gas) and also the modulating frequency. At high frequencies (about 50 kHz) modulation can approach 100 per cent, but at low frequencies (about 100 Hz) because of the finite lifetime of the ions in the discharge the percentage modulation may only be of the order of 70 per cent and still maintain a discharge. Because the voltage vs power output for the magnetron is not linear (see Figure 23) the voltage required to give the same depth of modulation varies with power output.



In practice this means that if the same percentage is to be maintained then the modulation depth must be readjusted each time the power is varied. If the modulation is optimised at a relatively high microwave power output, it may be observed that the source goes out due to overmodulation when the power applied is reduced.

There has been some confusion in the literature as to whether any phase shift occurs between the modulated microwave

supply and the light output. Browner, Dagnall and West [157] infer that a phase shift did occur as they report a different setting of the phase shift control for some elements when used in conjunction with the Perkin-Elmer 290 spectrometer modulated at 50 Hz sinewave. However, Wildy and Thompson [158] observed no phase-shift with all the lamps they investigated modulated at 180 Hz square wave. Although the experimental systems were different the results indicate that a careful study of the modulation characteristics of EDL's should be made. The author using a modulated microwave supply employing a stabilised supply has not observed any phase shift for Zn and Tl EDL's at frequencies between 100 Hz — 20 KHz for square waves or 100pps-20 k pps for pulses (mark space ratio 1 : 10).

The use of pulse modulation may offer a more intense source output for the period of pulsing. Initial studies have shown this to be possible and provided the power for the duty cycle does not exceed the normal running power the lamps appear to run with reasonable stability.

2.8. CAVITY DESIGN AND EFFICIENT COUPLING OF MICROWAVE POWER

Most of the early work done on microwave excited EDL's used antennae to direct the power to the lamps [24]. These were simple $\frac{1}{4}$ wave length antennae with a parabolic reflecting element. The reflected power using these devices were minimal and they offered no tuning facilities apart from the location of the lamps relative to the antenna. The first cavity to be used was the tapered rectangular waveguide type [160],

this was large and bulky approximately 25 x 10 cm its only advantage being that it did not radiate rf power as does the antenna. This cavity is still used because of its simplicity as part of the microwave emissive detector for gas liquid chromatography [161].

The first $\frac{3}{4}$ wave coaxial cavity was described by Zelikoff et al [138] and a review of cavities operating at 2450 MHz has been given by Broida et al [151].

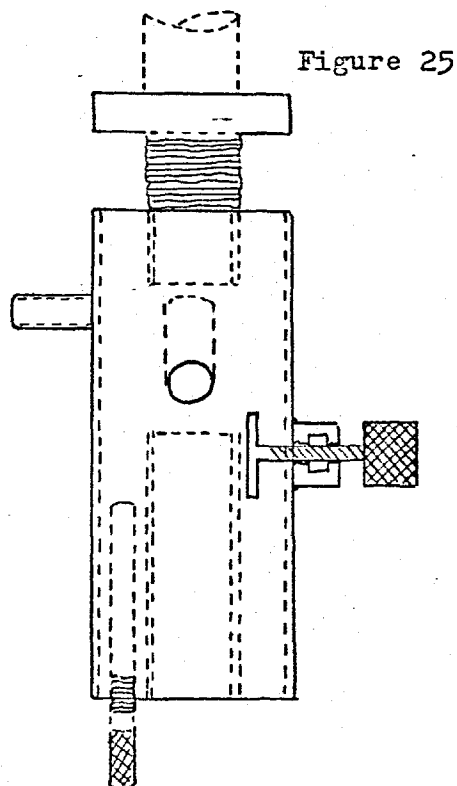
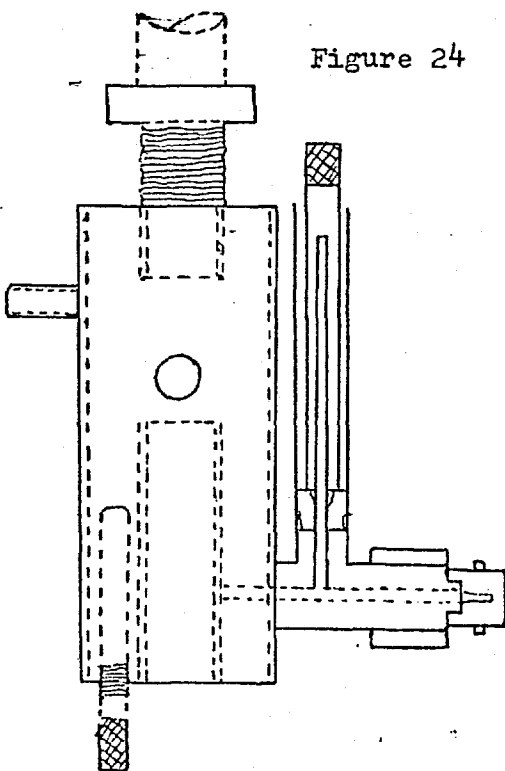
Of the cavities studied it was evident that the thermal stability offered by the $\frac{3}{4}$ wave cavity and uniformity of the microwave field obtained was achieved only at the expense of high coupling efficiency of microwave power to the gas discharge.

The purpose of a gas discharge cavity is to transfer power from the microwave generator to the gas which is contained in the quartz tube at low pressure. A resonant cavity is used to increase the electrical field in the gas and a coupling device is used to match the impedance of the cavity to that of the coaxial line of the microwave generator. When the resonant frequency of the cavity is tuned to that of the generator unit (ie 2.45 GHz) and the impedance is matched, then the reflected power from the cavity is at a minimum (ideally the voltage standing wave ratio should equal 1). This minimum value varies with different types of cavity and the more efficient the cavity the lower the reflected power.

The presence of a discharge in the cavity changes its

resonant frequency and also changes the loaded Q factor. The properties of the discharge change with pressure and with different gases and it is therefore necessary to provide both tuning and matching adjustments to obtain efficient operation over a wide range of discharge conditions. The $\frac{3}{4}$ wave cavity used showed poor tuning and no matching adjustments and this was thought to lead to slow warm up times and poor efficiency of operation.

Although the designers in their original description of the foreshortened $\frac{3}{4}$ wave cavity mentioned the lack of matching available in their design it is only recently that workers appear to have realised the importance of the coupling efficiency of the gas discharge cavity. Broida and his colleagues report that the percentage reflected power can be reduced [151] six times by the addition of a matching stub located on the coaxial connector. This modification has been studied and



(Figure 24) and found to be an improvement over the standard $\frac{3}{4}$ wave cavity in terms of increase in stability and warm up times for many elements [155]. However, the modification to existing cavities is difficult and the matching stub very sensitive to operation.

Better power matching with the $\frac{3}{4}$ wave cavity can be realised by using capacitative tuning stubs [159]. This has been found to improve the warm up times and also the quality of the spectral output from a wide range of EDL's. The modification to the EMS Limited $\frac{3}{4}$ wave cavity is quite simple and can be achieved quickly by most workshops. It involves making and fitting a single plate tuning stub to the outer cylinder of the cavity which changes the capacity between the inner and outer concentric cylinders as seen by the coaxial line feeder (Figure 25). The plate may be made of brass (1.5 cm diameter and 0.2 cm thick) held on a brass rod about 3 cm in length threaded up to the plate. This threaded section passes through a tapped hole (2 BA) in a stud and is silver soldered to the outside cylinder about 5 cm from the coaxial gap tuning end of the cavity. An insulated 'tufnol' knob may be secured to the end of the brass rod for manual tuning.

This cavity can be operated in the usual way and the reflected power may be trimmed until it reaches a minimum. Under these operating conditions the available power is efficiently consumed in the gas discharge and the warm up period is considerably reduced (Table 113)

TABLE 13

Element	Warm-up time (minutes)	
	Untuned $\frac{3}{4}$ wave cavity	Tuned $\frac{3}{4}$ wave cavity
Pb	20	4
Pb v.j.	3	2
Tl	20	2
Tl v.j.	2.5	1.5
Zn	15	2.5
Zn v.j.	1.5	1.0

CHAPTER III



FLAMES AND OTHER ATOM RESERVOIRS

3.1 FLAMES

Ever since the development of the Bunsen burner in 1859, flames have been used for the production of atomic vapour. At their present state of development they may be divided into two distinct types.

a). Turbulent Flow Flames

The characteristic feature of this type of burner is that fuel gas and the combustion supporting gas are not mixed until the point at which they enter the flame, and the solution to be nebulised is also introduced at this point. Thus, the device is a combination of nebuliser and burner; it is known as a total consumption or direct injection burner, since all the liquid aspirated enters the base of the flame and is converted to spray at this point by the shearing effect of the flame gases. This type of burner has been used in many emission flame photometers, since it is particularly safe in operation even with high burning velocity gas mixtures such as oxy-hydrogen and oxy-acetylene. It has been used to some extent in atomic absorption following early work by Robinson [163,164].

b). Laminar Flow Flames

In this type of system the combustion supporting gas aspirates the liquid sample and produces the liquid aerosol which passes into a spray chamber where the larger droplets (about 85 per cent by weight) settle out. The fuel gas may be added before or after the spray chamber and the mixture of fuel and support gas carrying the sample aerosol pass into the burner where it is burned. This is known generally as the

premixed type burner and was used by Lundegardh in his early emission studies in air/acetylene flames [3].

c). Relative Merits of Turbulent and Laminar Flow Burners

Both types of burner have been extensively used and their relative merits discussed.

The turbulent flow burner gives a stiff flame which is tall and narrow; while being suitable for emission studies it provides a short light path for AA and hence poorer sensitivity even using a multipass system [165]. over the longer path premixed laminar flames.

Solution uptake rate is generally less with a turbulent flow burner but because all the sample reaches the base of the flame the aspiration efficiency ϵ should be greater. However, there is evidence that some of the larger liquid droplets produced in this total consumption burner pass through the flame without being vaporised [52, 166]. This factor may contribute to severe scatter signals in AF [24] and also chemical interferences, as a result of large sample droplets, are worse than in the laminar premixed burners [167].

There is no doubt that the turbulent burner is safer in operation because the fuel and oxidant do not mix until the actual point of entry into the flame, and thus flash-back is impossible. As a result of this the turbulence produces an unpleasant loud audible noise as well as a fluctuating atomic

population because of the presence of large droplets in the flame. The premixed laminar burner while producing a silent steady flame only uses about 10 per cent of the sample aspirated. It is prone to flash-back especially when using high-temperature, high burning velocity flames. However, the author feels that the laminar premixed type of flame still affords one of the best and reproducible atom reservoirs for the techniques of AE, AA and AF.

d). Diffusion Flames

Recently there has been interest shown in the diffusion flames of hydrogen as an atom reservoir for certain elements notably Sn, As, Se, [168] and also for the chemiluminescent molecular emission of certain non-metals and halide species such as S_2 , HPO, SnH and InCl [169-172]. These types of flame are laminar in nature and differ only in that there is no oxidant premixed with the hydrogen before combustion. Instead the aerosol mist is produced by using an inert diluent gas such as nitrogen or argon and thus the primary flame front is at the outer mantle of the gas column where atmospheric oxygen is acting as a supporter of combustion. The inner region of this type of flame has been found to be highly reducing because of the absence of any oxidising species and yet quite cool (about 400°C). Under these conditions certain molecular species are formed in an excited state, which emit radiation on deactivation. This chemiluminescent emission has been used as a basis of several methods for the sensitive determination of certain

non-metals eg S, P and the halogens. (See page 151).

e). Flame Gas Mixtures

Premixed flames of air/hydrogen (2000°C), air/propane (1925°C) and air/acetylene (2325°C) together with the recently introduced nitrous oxide/acetylene flame ($173, 174$), are now used for routine AE and AA determinations. Elements not satisfactorily atomised in the air supported flames tend to be elements which form refractory oxides. The nitrous oxide/acetylene flame (about 2800°C), characterised by a red zone above the primary reaction zone, appears to give good sensitivities in AA for almost all the metals which form refractory oxides and had proved difficult or impossible to atomise with lower temperature flames. Its ability to atomise metals has been attributed to the high concentration of CN radicals in the red feather zone thought essential in the dissociation of metal monoxide species [180]. However, since the flame is in thermal equilibrium, it is sufficient to say simply that the absence of O-species within the red zone promotes dissociation of the metal oxides. e

The possible analytical utility of the nitrous oxide/hydrogen flame has been examined [181, 182]. Having a flame temperature only about 200°C less than nitrous oxide/acetylene its atomisation efficiency was much poorer than the hydrocarbon flame for most elements. However because of its low radiative background and high temperature it may have use in AE and AF studies.

Hydrogen flames supported by air or inert gas diluted oxygen have found considerable use in atomic fluorescence [184-186] because of their low radiative background and low quenching of excited states [183]. Argon is preferred to nitrogen as diluent because of its smaller quenching cross-section. These types of flames have been used in the turbulent form [184] or as laminar premixed types [185,186] the latter giving lower quenching of excited atoms because of lower entrainment of nitrogen from air.

Hotter flames of oxy-acetylene and oxy-hydrogen have been used mainly with turbulent burners for atomic emission studies [187-189]. Because of the high burning velocity of these gas mixtures they have generally not been used in AA or burned as true premixed laminar flames.

f). Separated Flames

Laminar premixed flames can be separated either mechanically or using an inert gas sheath. The process of separation involves the occlusion of atmospheric oxygen from the products of the primary reaction zone. In this way the interconal area where most of the free atomic population exists can be studied without the interference of the secondary combustion zone's radiation. These types of separation have been described recently by Kirkbright, West et al [190-192] for the silica separated nitrous oxide/acetylene and air/acetylene emission burners and long-path air/acetylene AA burner. The disadvantage of these types of separators, whilst giving good reduction in

flame background for those flames, was that they soon became etched and discoloured. The inert gas sheath (N_2 or argon) around the normal emission or absorption burner gave similar results with the added advantage that a much wider range of flame stoichiometries could be used [193]. Separation of the nitrous oxide/acetylene flame also increases the size of the reductive red zone by preventing aerial oxidation of the CN radicals. Thus the atomisation efficiency of the flame is enhanced on separation.

3.2 NON-FLAME ATOM RESERVOIRS

Several devices have been described for the production of free atoms without the use of flames, but most of them are relatively complex and require expensive apparatus, though in most cases they are considerably more efficient than flames. Gatehouse and Walsh [175] described the use of a hollow cathode sputtering chamber for the direct atomic vaporisation of solid samples. A sample of the metal or alloy was shaped in the form of a hollow cathode and mounted in a suitable chamber, capable of being purged with a gas such as argon. An improved flow-through cathode sputtering chamber was subsequently described by Walsh [176]. Atomic vapour is produced within the hollow cathode and consequently can attenuate the signal from a conventional hollow cathode lamp source in the usual way. Samples must be suitable for machining into the form of a cathode, although it has been shown by Goleb and Brody [177] that solutions could be analysed by evaporating the solution evenly on the walls of a suitable cathode. The method is

interesting, but at present appears to be beset by difficulties.

Vidale [178] described a modified King furnace method in which the sample is placed in a sealed quartz cell within a quartz tube which is itself placed within an electrically heated furnace at about 1100°C . The tube is purged with argon and evacuated before atomisation. Amounts down to 10^{-10} g were determined with a precision of about 20 per cent. The method is, however, cumbersome and limited in application, though useful for specific problems.

Nelson and Kuebler [179] analysed solid samples such as wire, ribbon or powders by placing them on quartz or graphite strips supported in an enclosed silica chamber purged by an inert gas. The sample was vaporised by an intense flash (10 kw/cm^2) heating from a capacitor discharge lamp wound round the cell.

A spark-in-spray method has been described by Robinson [194]. The liquid sample is sprayed into an electrical discharge. The method is efficient in producing atoms of those metals which form refractory oxides in flames, but the spray becomes highly charged and strong electrical and magnetic fields upset the electronic circuitry of the detecting system. The strong emission from the discharge is also very troublesome.

David [195], Brech [196] and Hagenah [197] et al have suggested the possibility of laser-shot evaporation, and recently the technique has been employed by Mossotti, Laqua and Hagenah [198]. Their experiments revealed that with some elements the

number of free atoms outlasting the laser plume emission was sufficient to permit semi-quantitative atomic absorption at submicrogram levels, but there appears to be a considerable matrix effect. The small sampling area of the laser shot poses additional problems and, although the method scarcely requires sample preparation, it is highly dependent upon experimental parameters.

Undoubtedly, the two most promising methods are the L'vov [199,200] adaptation of the King furnace and the carbon tube method of Massmann [201,202]. The L'vov furnace utilises an electrically heated carbon tube lined with tantalum to prevent too rapid a diffusion of atomic vapour into the carbon walls of the tube. The sample in the form of a few microlitres of solution is placed on a carbon plug which fits into a hole in the tube and an electrical discharge is struck additionally to heat this plug, from an auxiliary electrode. Elements such as titanium and aluminium were determined in this way in the range 1 - 50 ppm and sensitivities down to 10^{-8} and even $5 \cdot 10^{-11}$ g were obtained. Nikolaev [203] similarly obtained limits of $4 \cdot 10^{-9}$ g at 3075.9 Å and 10^{-12} g at 2138 Å for zinc.

Massmann's [201,202] device uses a heated carbon tube for atomic absorption or fluorescence and yields similar results, but his device is perhaps simpler to operate than that of L'vov. The laser and carbon tube furnaces all require rapid response recorders and are restrictive in their application as well as being experimentally bulky and cumbersome.

A simpler device has been described by West and Williams [203] utilising a small electrically heated carbon rod. Sample is placed on the rod from a microlitre pipette (1-5 μ l) after the solvent has been evaporated at low temperatures the sample is vaporised when a large current heats the rod to incandescence. The carbon rod can be operated in an enclosed glass vessel purged with argon at atmospheric or reduced pressure or more simply without the glass cover provided the rod is sheathed by a laminar flow of inert gas. Detection limits in AF for silver of 10^{-13} g have been achieved with a precision of ± 5 per cent.

An extension of this system is the platinum loop described by Winefordner [204]. The sample solution was placed on the loop by immersing it in the solution or by transferring a known volume from a hypodermic syringe. The loop was heated in a stream of inert gas and the atom cloud measured by AF or AA.

The main advantage of these types of atom reservoir is their negligible background and thus the detection limits achieved for the more volatile elements are in the ppb range for AF determination.

Plasma cells have been used in AE for the sensitive determination of many metals particularly the refractory elements. The recent paper by Dickinson and Fassel [205] reviews the previous work published on induction coupled plasmas and gives a comparison of detection limits for 26 elements with flame

emission, atomic absorption and other plasma emission sources. They employed a 30 MHz, 2.5 kWatt rf generator to produce an argon plasma fed with aerosol from an ultrasonic droplet generator. The detection limits obtained for refractory oxide forming elements were generally 3 order of magnitude lower than by other spectroscopic methods.

3.3 THE DESIGN OF CAPILLARY BURNERS FOR ATOMIC SPECTROMETRY [208]

The high temperature high burning velocity premixed flames of nitrous oxide/acetylene and oxy-argon-hydrogen while being very useful atom reservoirs for AA, AE and AF have tended to be prone to flash-back especially on conventional meker and slot type burner head. The possibility of producing a safer burner system was investigated based on the use of stainless steel capillary tubes.

The production of a stationary flame requires that the stream velocity of the fuel oxidant mixture through the burner port be at least equal to the burning velocity. If this condition is not met, the flame is liable to flash back down the burner port and cause an explosion in the spray chamber. In practice, both to ensure a margin of safety and achieve a reasonably stiff flame, ie. one which is not unduly disturbed by air currents in its neighbourhood, the burner is designed so that the stream velocity is several times the burning velocity. The flame is prevented from flashing back at the walls of the burner port, where the stream velocity is zero, by the quenching effect of the walls, and since the quenching effect extends some distance out from the walls, there is a limiting size of burner port below which the flame of a given gas

mixture will not flash back. Unfortunately, however, this size is usually so small for high temperature flames that it is not practicable to rely on the quenching effect alone to avoid flash back.

The burning velocity of a fuel oxidant mixture is a function of its composition, and usually, though not always, reaches its maximum value near the stoichiometric ratio. Thus, it can be seen why a moderately fuel rich flame may burn satisfactorily at a burner but flash back when it is extinguished by the usual procedure of cutting-off the fuel supply. During this process the flame will pass momentarily through the stoichiometric condition, where, if the gas stream velocity is too low, flash back will occur. If the fuel gas comprises an appreciable part by volume of the total gas mixture, the reduction in stream velocity when the fuel is shut off may be sufficient to cause flash back.

The problems of designing burners for high temperature flames arise principally from the fact that gas mixtures having high flame temperatures usually have high burning velocities. This requires limitation of the size of the burner port, with the attendant disadvantage of easier blockage by deposits of salt or carbon. If a large burner port is desired, it is necessary to use large flow rates of gas mixture and either design a nebuliser to operate on the whole of the oxidant or else introduce part of the oxidant as an auxilliary supply direct to the spray chamber. It may be noted also that for

some gas mixtures the burning velocity increases with the temperature of preheating, [206] so that the burner top should be kept sufficiently cool; it must in any case be kept well below the ignition temperature of the gas mixture.

A premixed burner system, with the flame stabilised at a head constructed from a bundle of stainless steel capillary tubing has been described by Padley and Sugden [207]. These workers used this system to burn mixtures of oxygen/nitrogen/hydrogen for flame kinetic studies. However, work described in this section suggests that this type of burner system has a much wider application for flame studies of a variety of gas mixtures.

a). Burner Design

Two types of burner are in general used in flame spectrometry the emission burner usually giving a cylindrical gas column and the long-path absorption type burner. However, recent work by Koirtz and Pickett have shown that the long-path nitrous oxide/acetylene flame is particularly suited to flame emission [80-82].

Stainless steel hypodermic tubing (Accles and Pollock Ltd.) was cut into 2 cm lengths. This could be done easily by scoring the tube wall with a small triangular file and breaking in a similar manner to glass tubing. Because of the high temper of the tube it would snap-off cleanly without distorting the wall. The tubes were smeared with high temperature epoxy resin (Araldite type AY105 with hardener HY953F, Ciba Ltd.)

Figure 26 Long path capillary burner and gas separator

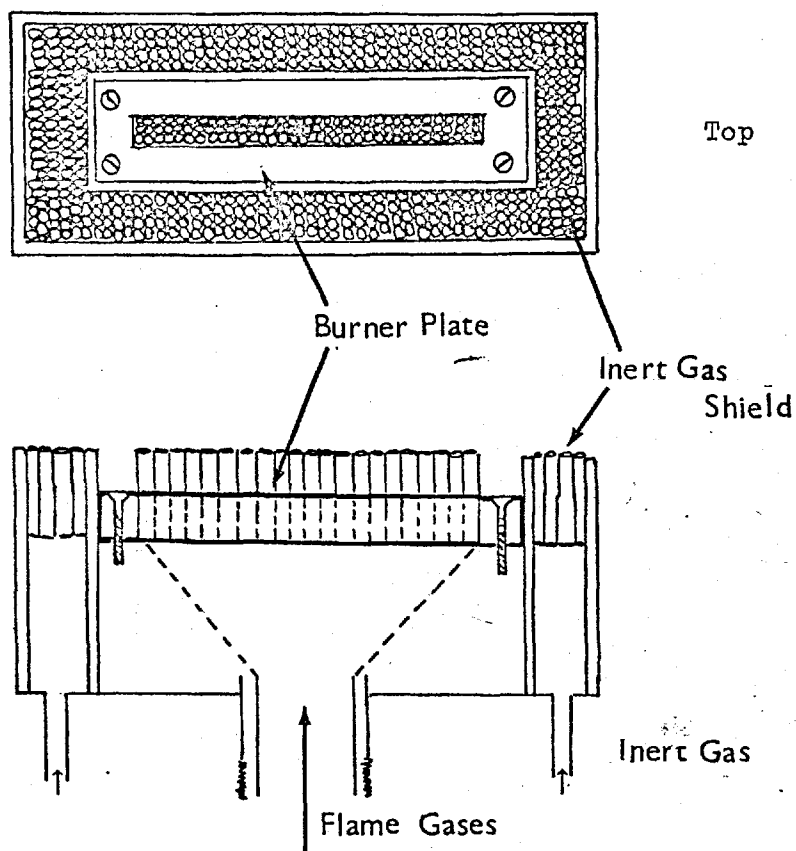
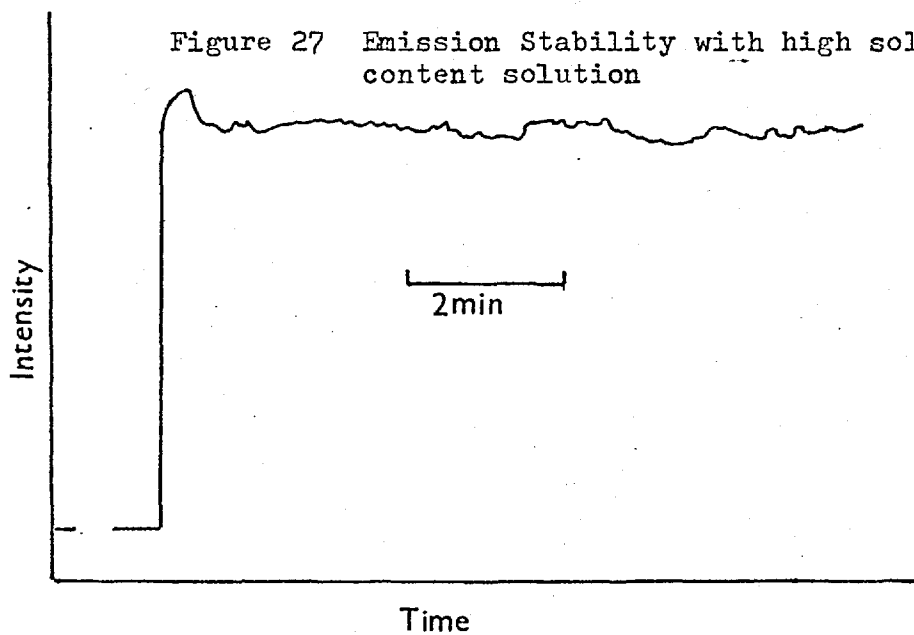


Figure 27 Emission Stability with high solid content solution



Signal from a 10 ppm Ca in 10% glucose solution at 4227Å in nitrous oxide/acetylene flame

and hexagonally close packed in the configuration required. Circular emission heads were constructed from a bundle of tubes 1 cm in diameter and the long-path heads (Figure 26) from a triple row; giving a 5 cm flame path. The epoxy resin was allowed to fill the interstitial gaps in order that the fuel and oxidant mixture flowed only inside the capillary tubes. It was soon found that if the capillaries were allowed to remain flush with the surface of the burner body over heating occurred but this was completely eliminated by allowing the tube to project 6 mm above the burner body. When the epoxy resin has hardened the tops of the individual capillaries were ground level on a grinding wheel and finally by hand with silicon carbide (wet and dry) abrasive paper.

The size and number of capillaries required for each configuration and gas mixtures is shown in Table XIV.

TABLE XIV

Gas Mixture		Typical Gas Flows		Capillary		Maximum Head Temp.
Ox.	Fuel	Ox. l/m	Fuel l/m	Size	No.	
1 air 2	C_2H_2	16	3.6	17	110	110°C
		8	1.8		40	
1 air 2	H_2	16	12	19	150	80°C
		8	6		75	
1 N_2O 2	C_2H_2	16	8	19	150	270°C
		8	4		75	
1 O_2 2	H_2	5.5	23	20	180	250°C
		3	13		100	

- 1). Absorption burner 5 cm flame length
- 2). Emission circular flame 1 cm diameter
- 3). Gauge sizes 17= 1.00mm; 18= 0.80mm; 19= 0.68mm; 20= 0.55mm internal diameter.

These configurations were designed for operation with a Perkin-Elmer nebuliser and gas control unit. Slight modification may be required for other systems in order to achieve optimal results. When burning oxy-hydrogen flames, nitrogen (about 20 per cent by volume of total gas mixture) must be added or flash back may occur on the 20 gauge capillaries quoted. This corresponds to approximately 7 l/min for the 5 cm burner or 4 l/min for the circular burner. The temperature quoted (Table XIV) is the maximum value recorded on the top surface of the burner head after the burner had reached equilibrium. The burner body does not rise above 150°C, at which temperature the bonding epoxy resin exhibits no loss of tensile strength.

b). Advantages of Capillary Burners

These burner systems offer several advantages over the standard meker or slot types ; a) the shape of the burner can be designed to suit the purpose for which it is required and to suit the fuel and oxidant flows of a particular nebuliser unit. For AA and AE the long-path flame gives the best sensitivities whilst for AF a rectangular burner configuration offering a large area for excitation and a small path length in the direction of the monochromator to prevent self absorption of the fluorescent radiation. b) Because of the number of capillaries used a very even flow pattern is established over the entire area of the head because each tube achieves a similar poiseuille distribution of velocities. This leads to a very stable laminar flame not prone to disturbance by draughts.

c) By a suitable choice of capillary diameter all gas mixtures commonly used in flame spectrometry can be burned safely because if the diameter chosen is less than the quenching diameter for the fuel/oxidant mixture extinction will occur rather than flash back even if the burning velocity exceeds the supply velocity. d) The nitrous oxide/acetylene flame can be ignited directly without the need to change over the oxidant from air to nitrous oxide as is common practice with most other premixed burner systems. e) The burner may be made with only limited workshop facilities as the need for accurate machining of slots and hole patterns is not required. It is possible to modify existing burner heads to allow capillary burners to be fabricated.

c). Gas and Flame Sheaths

Inert gas separators for capillary burners can be constructed in a similar manner from 18 gauge tubing. Four rows of tubes around the burner head (Figure 26) have been found sufficient to cause the secondary zone of the flame to be separated when about 10 l/min of inert gas are used for the long path flame and 5 - 6 l/min for the circular burner. Too large a flow rate of inert gas will cause flame turbulence. The gas sheath provided by the capillary tubes appear to be considerably stiffer than other systems [193] and not so affected by draughts or air turbulence caused by the rising hot flame gases within the enclosed space of instrument flame housings. Qualitative studies [70] have shown using particle tracks in the sheath gas that it is laminar for about 2 cm

above the burner head even with the flame burning. This is not so with the larger separators fabricated from a matrix of steel strips [193] which tend to form a blanket of gas entrained into the flame at its base and thus the interconal gases are diluted with inert gas to a greater extent as well as being sheathed.

Flame sheaths can be made similarly by suitable choice of capillary diameter for use in kinetic work where the test flame, into which the samples are nebulised, is maintained at an even temperature and chemical environment.

d). Performance of Capillary Burners

In operation the flames may be ignited and extinguished on any fuel to oxidant ratio with little danger of flash back. The performance in emission with a high solid solution was investigated to ensure capillaries did not clog with a crust of solid (as often happens with total consumption turbulent flames). A solution of 1 ppm Ca was nebulised which contained 10 per cent glucose into a lean nitrous oxide/acetylene flame optimised for emission of the calcium atomic line at 4227A. The signal was monitored and although considerably noisier than with aqueous solutions the emission intensity only dropped by 3% after 10 minutes of continuous nebulisation (see Figure 27). Any capillaries which did momentarily block soon cleared themselves and the overall intensity was not affected.

The appearance of all flames was of a large number of well defined individual primary cones about 1 mm in height

(depending on the flame mixture) giving an overall flat reaction zone. In emission all the flames gave similar analytical results as conventional burners but the background and atomic emission signal showed a marginal improvement in stability.

A particular application of these burners is felt to be for higher temperature, higher burning velocity flames which have a tendency to be unsafe on more conventional burners. The laminar premixed nitrous oxide/acetylene is one such flame prone to flash back. On the capillary long-path burner head it shows, under slightly fuel rich conditions, a red zone above the primary zones some 1.5 cm high and 3-4 mm broad looking along the length of the flame. On inert gas separation this zone extends upward to about 25 cms in height and the width increases slightly. This flame was tested for safety in ignition and extinction under various fuel:oxidant ratios and total gas flow. Even if this total flow was reduced by a factor of three the flame could be operated safely. However, under these conditions after prolonged periods localised heating may cause damage to the burner.

In conclusion it can be seen that burners can be constructed from stainless steel capillary tubing on which very stable and laminar flames may be maintained. These burners are particularly safe in operation even with nitrous oxide/acetylene and offer the possibility of inert gas or flame sheathing facilities.

3.4 OPTICAL STUDIES AND ATOM PROFILES IN LONG PATH FLAMES

The purpose of this optical study was to investigate the degree of laminarity achieved in the burning flame gases stabilised on capillary and slot burners. Two optical methods were considered a) the shadow method and b) the schlieren method.

a). The Shadow Method

In the shadow method light from a source is rendered parallel by the use of a lens and passes through the test zone on to a screen. Any refractive index change normal to the illumination within the test zone will result in a local change of illumination on the screen. Refractive index changes parallel to the illumination beam cause no change on the screen. It is possible to illuminate the test zone with divergent light, then the position of the test zone relative to the source and screen becomes critical and will affect the image size.

b). The Schlieren Method

A similar source and condensing lens system is used as in parallel beam shadowgraphy. In addition to this a further lens focuses the beam of light after passing through the test zone on to a 'marking stop'. This may take various forms of stop, knife edge, filter and optical wedge. For the work described here a 0.3 mm stop was employed constructed from thin metal foil. This serves to prevent undeflected light reaching the screen whilst deflected light having a slightly different focus passes on to illuminate the screen with the schlieren image

of the test zone.

The intensity of the schlieren image is proportional to the refractive index gradient whilst the shadow method is proportional to the first and second derivative of the refractive index gradient.

c). Optical Arrangement

All optical components except the source were mounted on a 2 metre optical rail. The source a 500 Watt Xenon arc was rigidly fixed on a concrete area of floor and little problem was encountered with relative movement between source and optical bench. There are numerous optical arrangements possible for schlieren and shadow photography [209]. The parallel beam system using lenses rather than mirrors was chosen as it had certain experimental advantages. Firstly the image size for shadow and schlieren was the same, being restricted by the diameter of the lenses. These were 60 mm and this easily covered the flame area used for analytical measurements. Secondly, the ease with which the two methods could be compared merely by the removal of the 'marking stop' and the re-positioning of the flame, while unaffected the image size was particularly advantageous. The optical systems used in this work are shown in Figure 28 and in the shadow arrangement light from the 500 Watt Xenon arc (a) is focused by means of a 36 mm diameter 100 mm focal length achromatic doublet (b) onto a 0.3 mm pinhole stop (c). Simple lenses used in the optical set-up caused considerable chromatic aberration and thus achromats were used throughout. The focused image of the source on the

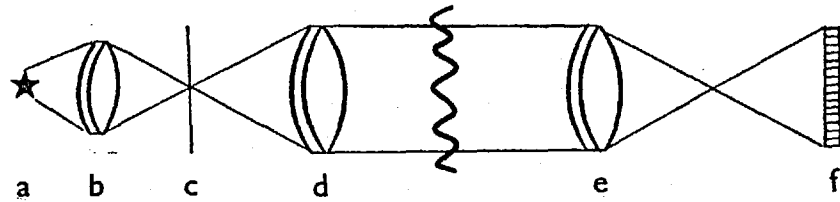
pinhole acted as effective point source the light from which was rendered parallel by the 61 mm diameter 365 mm focal length achromat (d). After passing through the flame the light was focussed by a similar achromat (e) the light finally reaching the photographic film (f). (Figure 28)

The flame position in shadowgraphy is not critical provided there is not an (in focus) image of the flame formed by lens (e) on the film (f).

For schlieren photography, the flame must be focussed by lens (e) on to the film. Also a matched pinhole (c') is placed at the focus of lens (e) to act as a 'marking stop'.

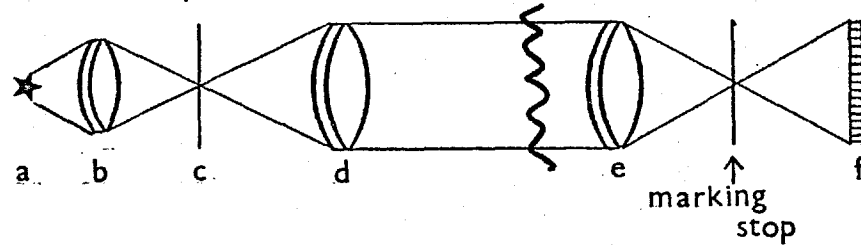
The photographic record was taken using a Pentacon Six single lens reflex camera with a 60 x 60 mm negative size. The camera lens was removed as this was not required. The exposure time of $\frac{1}{1000}$ sec on the camera was used, this was measured using a storage oscilloscope to be 1.5 m sec however, this effectively 'froze' most flame turbulence. Photographs were taken on Ilford FP4 120 Professional Roll Film, rated at 200 ASA and developed in Microphon for six minutes. The exposure value was calculated by taking light reading from the frosted glass reflex screen of the camera with a Weston Master V meter. A correction factor of 2 was applied to these readings to give the correct exposure. Because of the fixed aperture and speed of the photographic system the light intensity was raised using neutral density filters made from partly exposed film negative.

Figure 28 Optical arrangement for shadow photography



- | | |
|--------------------------------|----------------------|
| (a) Source | (d) Collimating Lens |
| (b) Condenser Lens | (e) Projection Lens |
| (c) Pinhole (effective source) | (f) Film |

Figure 28b Optical arrangement for schlieren photography



- | | |
|--------------------------------|----------------------|
| (a) Source | (d) Collimating Lens |
| (b) Condenser Lens | (e) Projection Lens |
| (c) Pinhole (effective source) | (f) Film |

The whole optical table was covered with blackout cloth supported on a framework with a chimney over the flame to allow the escape of flame gases.

Although all flames were studied only the results for long path air and nitrous oxide/acetylene burners are reported here. Nevertheless conclusions concerning laminarity and air entrainment will remain valid for circular emission burners.

Comparisons were made between the Perkin-Elmer nitrous oxide/acetylene 5 cm slot burner and the capillary burner constructed from three rows of 19 gauge capillaries. The same gas flows were used in both cases and the Perkin-Elmer expansion chamber unit used.

Plates 1 - 4 show schlieren records of the air/acetylene and nitrous oxide/acetylene flames on slot and capillary burner head. Within the field of view both types of flame appear laminar. It is interesting to note the size of the primary reaction zones and the wings clearly visible on the nitrous oxide/acetylene slot burner. Shadow photographs taken show similar gas flow patterns however because of the high emission of these flames in the ultraviolet region the records are slightly fogged because there is no 'marking stop' to prevent radiation reaching the film. For this reason alone, schlieren photographs are shown for better clarity. In general schlieren records the gradual refractive index gradients within the flame (ie turbulence) the absence of these in the two types of burner indicate the

high degree of laminarity achieved in the flame gas scellium.

The shadow technique records sensitively^{ti} rapid changes of refractive index normal to the optical path gradual changes across the flame do not register strongly. However, the technique is experimentally much simpler and for most applications quite adequate for qualitative results.

d). Atom Profiles

The flame shape recorded by the schlieren image was compared to the atom profile within the flame. To achieve a meaningful profile the atomic absorption measurements were taken using a Perkin-Elmer 290A whose entrance slit was modified to give better vertical resolution. The height of the slit was reduced until it only observed light from a 1 mm high region within the long path flame. Two elements were chosen, copper and vanadium because of their different atomisation within these flames. Copper is completely atomised in air/acetylene [86] and thus the atom profile should compare closely to the shape of the schlieren record. Vanadium, however, requires a highly reducing atmosphere and the atom profile will follow the reductive CN red zone in nitrous oxide/acetylene. This zone is dependant on the air entrainment at the edge of the flame as any atmospheric oxygen diffusing into the flame will reduce the reducing nature and size of this zone. Also the free atom population of copper will indicate the area of high temperature and absence of oxidising species. Atom profiles were measured using direct reading calipers to determine the burner traverse.

PLATES 1 - 4. Schlieren Photographs of Long-path Flames

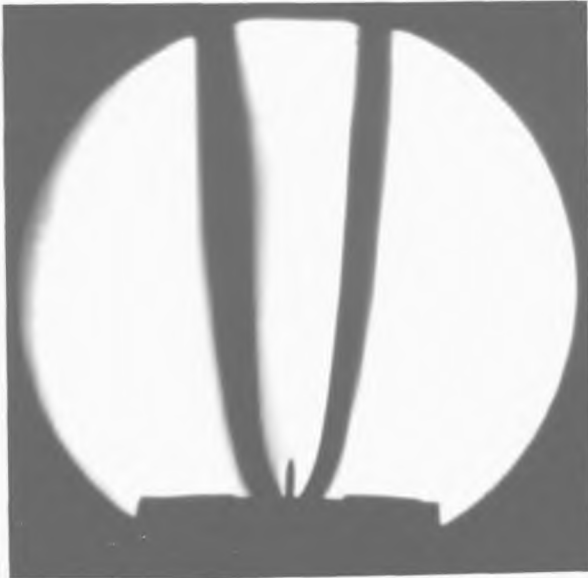


PLATE 1



PLATE 2

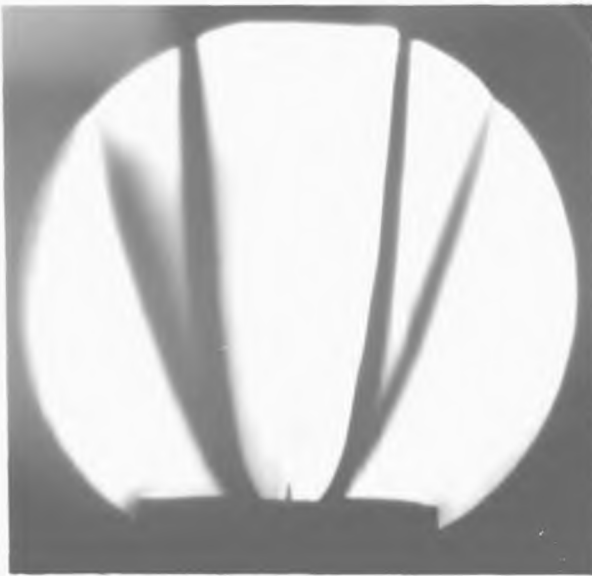


PLATE 3



PLATE 4

- | | |
|---------|--|
| Plate 1 | Air/acetylene flame on 5cm slot burner (Perkin-Elmer) |
| Plate 2 | Air/acetylene flame on 5cm triple row Capillary burner |
| Plate 3 | Nitrous oxide/acetylene on slot burner |
| Plate 4 | Nitrous oxide/acetylene on Capillary burner |

The results obtained for copper in air/acetylene and nitrous oxide/acetylene are shown in Figure 29,30. For air/acetylene the capillary burner shows a wider profile while the schlieren images are the same for slot and capillary burner. This indicates that the extra laminarity of the capillary burner over the slot burner prevents excessive air entrainment and thus the body of the inter-conal gases are more isothermal. However, the peak absorption is slightly greater in the slot type burner.

Similar results are obtained for the nitrous oxide/acetylene flame (Figure 30) however, the wings shown in the schlieren photograph contain an appreciable atomic concentration of copper. Again peak absorption is slightly higher in the slot burner over the Triple row capillary burner.

Vanadium shows a completely different profile in nitrous oxide/acetylene as may be expected. The half peak absorption width being only 1.6 mm as compared to 3.6 mm for copper in the slot burner and 2.8 mm for vanadium compared to 5.0 mm for copper in the capillary burner. The vanadium free atom population follows the reductive red zone closely and again the profile width is broader in the capillary burner probably due to less air entrainment at the base due to its superior laminarity. The effect of nitrogen separation of the capillary burner extends the free atom population from 2.4 mm for half peak width to 4.6 mm with slight increase in peak absorption.

The lack of sensitivity using the Triple row capillary burner was remedied by using a double row of 18 gauge capillaries. The profiles then obtained are shown in Figure 31 and 32. Inert gas separation again would widen and increase the profile of the capillary burner. A gas sheathing device for the slot burner was not available although it is known that a similar increase would result from gas sheathing.

To get a more complete insight into the free atom population profiles should be taken at various levels up the flame and a composite profile obtained.

This study, however, has shown that easily atomised element such as Cu have a different profile in the capillary burner to the conventional slot burner. This may be due to diffusion effects within the flame or rates of air entrainment. The free atom population of refractory elements shows a different profile more dependant on the reducing properties of the inter-conal regions. Separation has a considerable effect on the width of the atom profile.

Atom Profiles across various flames and burners

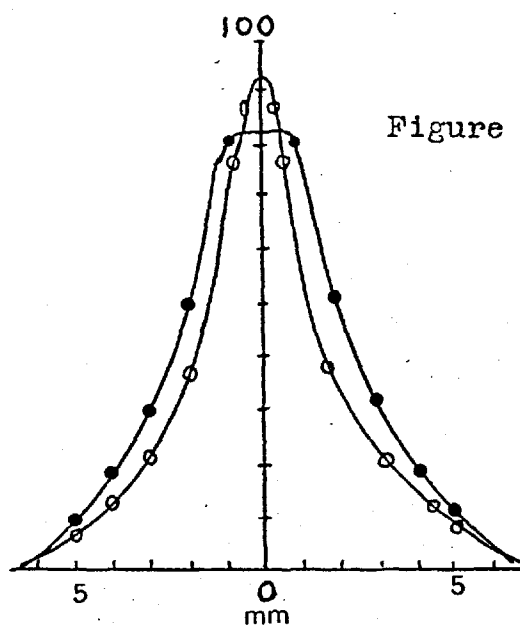


Figure 29

Copper air/acetylene

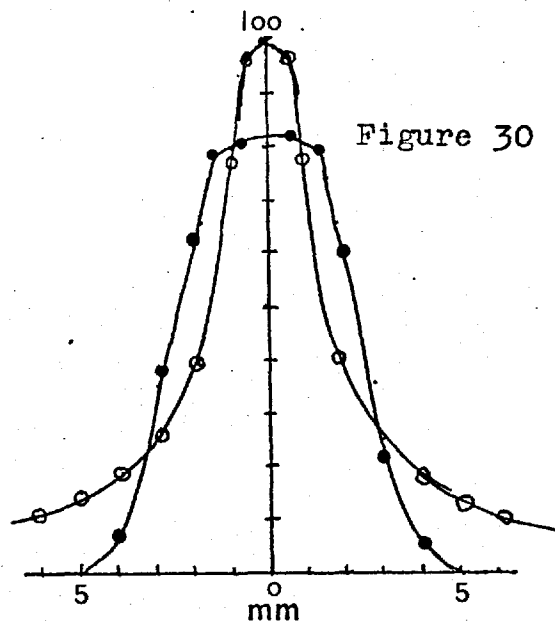


Figure 30

Copper N₂O/acetylene

- 5cm Perkin-Elmer slot burner
- 5cm Triple row capillary burner 19 gauge
- 5cm Double row capillary burner 18 gauge

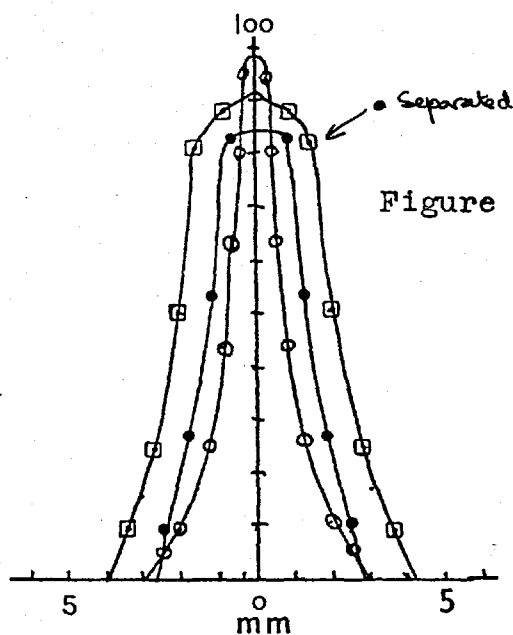


Figure 31

Vanadium

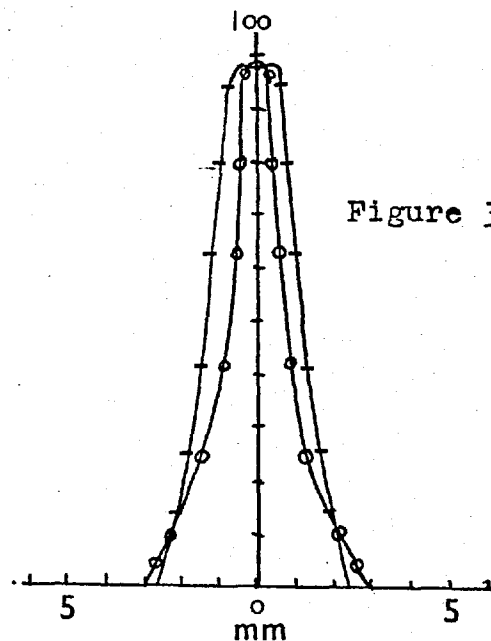


Figure 32

Nitrous oxide/acetylene

3.5 THE FLAME-SPECTROSCOPIC DETERMINATION OF SULPHUR AND PHOSPHORUS IN ORGANIC AND AQUEOUS MATRICES

Most metals can be determined by the techniques of flame photometry, atomic absorption and atomic fluorescence spectroscopy, including those that form molecular species with oxygen that do not readily dissociate except in strongly reducing flames. These techniques, however, are not suited to the determination of sulphur, phosphorus and halogens because their principal resonance lines lie in the far ultraviolet region of the spectrum, where absorption by atmospheric oxygen and flame gases is high.

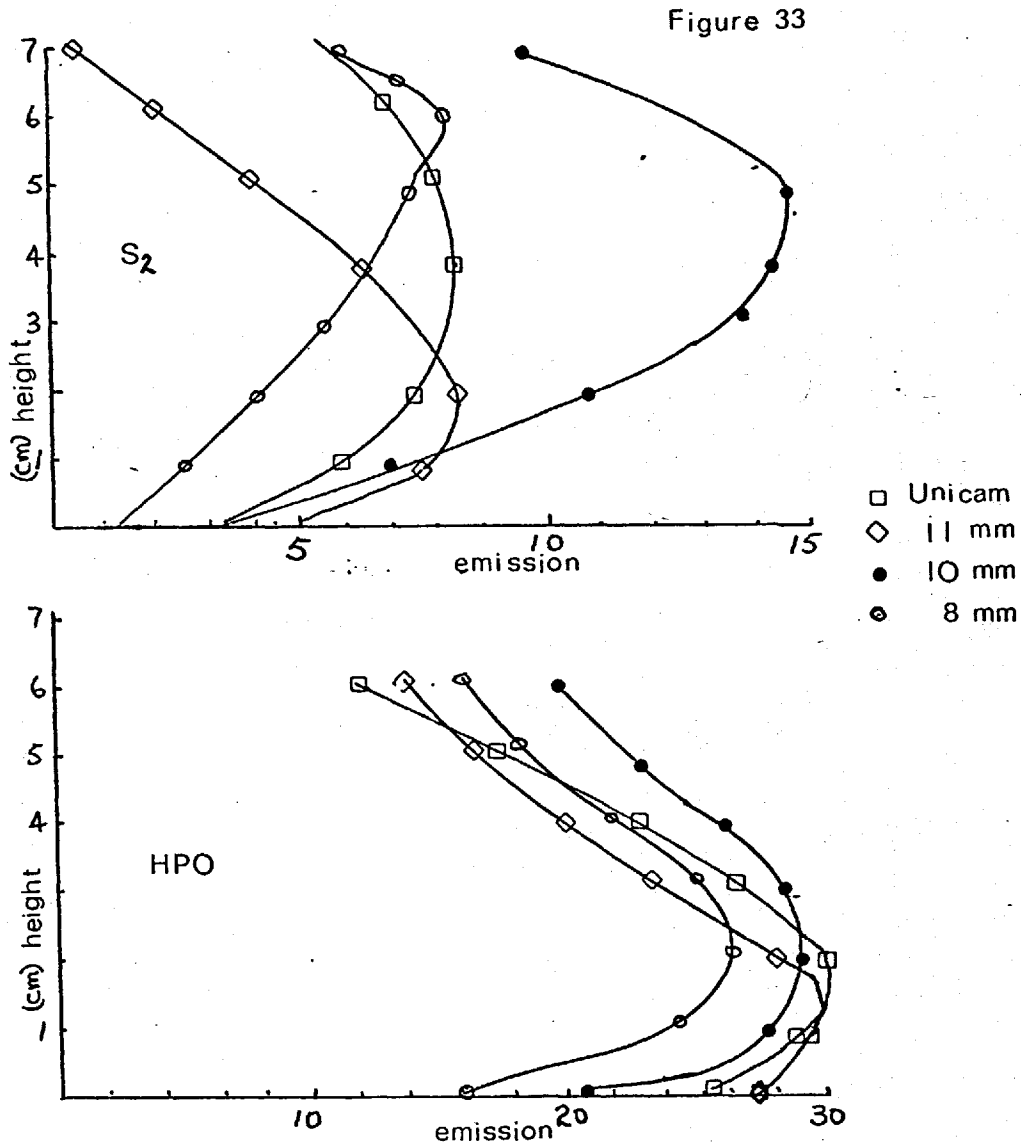
It is only recently that molecular emission in cool flames has been proposed to overcome these difficulties by using the emission of simple molecular species, such as S_2 [169], HPO [170] and $InCl$ [172]. These are formed in an excited state by chemiluminescent reactions [171] in cool flames and emit their characteristic band emission when they return to the lower electronic state. Because band emission was obtained with these species, valuable sensitivity was lost in the above studies [169] by using a monochromated instrument that only recorded radiation produced over a narrow spectral region (about $5\text{\AA}$). To increase the sensitivity of these determinations a simple filter photometer has been constructed which improves the detection limits of sulphur and phosphorus about 100 fold. This is achieved mainly by the use of broad band-pass filters and modifications to the burner design and

method of introduction of the sample into the flame.

The highly reducing nature , limiting quenching action and low incidence of molecular or atomic oxygen in the cool flame are contributing factors in the production of the intensely emitting molecular species. Atmospheric oxygen, which supports the flame combustion, diffuses only a little way toward the centre of the flame, and for this reason the molecular emission is observed only within the central region. It is important therefore, to reduce flame turbulence and prevent the available oxygen from reaching the centre, because this would tend to quench the molecular emission and also increase the temperature of the flame.

The standard Unicam circular emission burner head was initially used in these studies, but the 1 cm square pattern of thirteen holes on which the gases burned caused a considerable degree of air entrainment. The chemiluminescent signal was found to be greatly increased if an open tube Pyrex burner was used in place of the standard emission head. Hydrogen diluted with nitrogen or argon were used as the flame gases to produce the cool diffusion flame. Three sizes of burners were chosen 8, 10 and 11 mm internal diameter and these were compared with the signal obtained for the Unicam meker burner. The burner must provide a reducing area of flame gases which is not too hot otherwise the S_2 emission is reduced. The optimum temperature for emission was found to be $380^{\circ}C$. The temperature of the centre of the flame is a function of the

burner diameter for diffusion flames of this type burning on an open tube and also a function of turbulence. Figure 33 shows a profile of S_2 and HPO emission intensity against height in the flame.



It can be seen that S_2 emission is very sensitive to changes in the flame temperature resulting from reduction in physical width of the flame and increase in turbulence (8 mm burner). The HPO emission, however, seems less temperature dependant and thus measuring 4 cm above the 10 mm internal diameter

burner head gave good results for both emissions. The burner was made from a 6 cm length of 10 mm internal diameter tube of a B14 cone, fitted into the barrel of the Unicam burner with a short ring of polythene tubing over the cone, to form a gas-tight seal.

Sample introduction into this non-turbulent flame requires modification because the normal nebuliser tends to give droplets that are too large to be readily vaporised in the central cool regions of the flame. In a normal pre-mixed flame the aerosol usually passes through the hot primary reaction zone before reaching that area of flame where spectroscopic measurements are taken. However, the hottest portion of the diffusion flame is the outer thin envelope where atmospheric oxygen and the hydrogen fuel gas burn on mixing. Even this outer envelope produces only weak thermal emission of the alkali metals and the molecular emission of interest is observed only in the cooler central region. It is obvious, therefore, that an extremely fine aerosol is required because the chemical process taking place within the flame will proceed faster if the sample is in a finely divided form. Of the several commercially available nebuliser units examined the most suitable for this application was the Unicam SP 900 cyclonic expansion unit, which produces a uniformly fine mist. This system can of course, only be used if 2 ml or more of sample are available.

An injection technique was also developed for small sample volumes (1 to 5 μ l) of both aqueous and organic solvents

(containing 20 to 1000 ppm of sulphur). The organic liquids of low sulphur content (less than 10 ppm) required a pre-burning stage to oxidise the sulphur to the dioxide either by combustion in a Wickbold apparatus or in a simple oxygen flask.

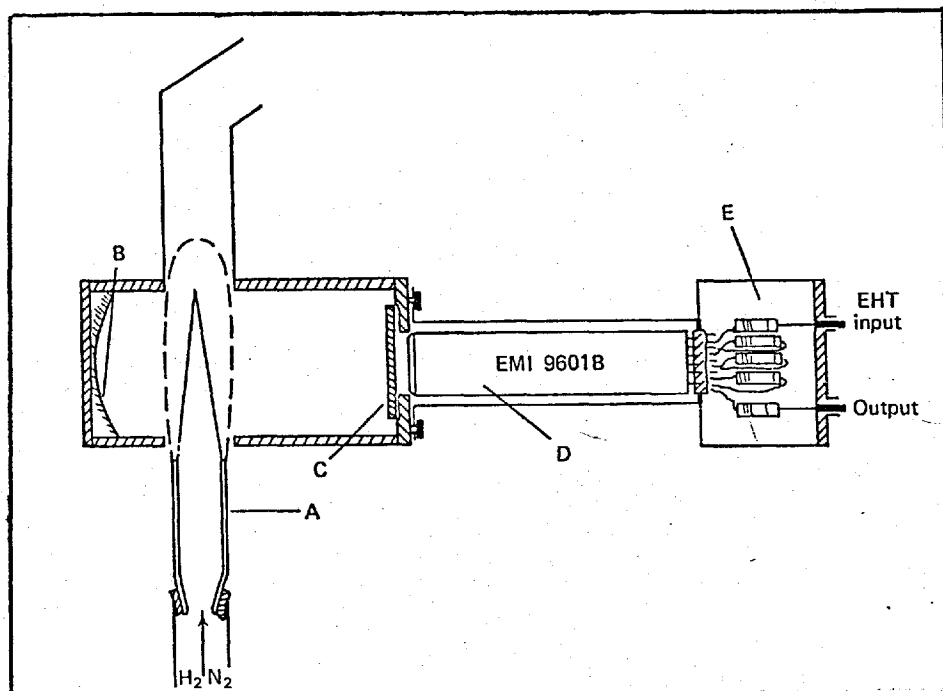


Figure 33 Filter photometer. A, Pyrex open tube burner; B, concave mirror (gives 40% signal increase); C, filter; D, photomultiplier; E, dynode resistors

a). The Filter Photometer

The basic arrangement shown in Figure 33 ; the body of the photometer (over-all dimensions 12.5x7x7 cm) was constructed from 6 mm thick sindanyo sheet with Araldite epoxy resin to joint the individual pieces. The inside of the photometer was coated with a matt black paint to minimise internal reflections. A chimney of 25 mm internal diameter translucent silica tubing

was found necessary to prevent any light from the surroundings reaching the entrance slit of the photomultiplier tube. The chimney was carefully lamp-blackened and was found to be effective provided its length was greater than 10 cm, in preventing light from entering the instrument and also in stabilising the flame.

The photomultiplier tube was held in a brass housing together with the dynode resistor chain. The two electrical connections for the EHT supply and for the photomultiplier output were made by using standard coaxial sockets mounted on a 'paxolin' panel at the extreme end of the housing.

The interchangeable band-pass filters used in this study were positioned in front of the photomultiplier slit arrangement as shown in Figure 33 . The transmission of the filters used was determined with a Hilger and Watts Ultrascan spectrophotometer and these are shown superimposed on the S_2 and HPO emission spectra in Figure 34 . The peak transmissions for these filters were at 3900 and 5200Å.

The slit width used was 2 x 20mm and was cut in brass plate that was bolted to the front of the photomultiplier housing. However, to minimise heat transfer from the flame to the photomultiplier tube, which causes a considerable increase in dark current and noise level, a piece of sindanyo sheet with the same dimensions and slit width was placed between the brass plate and the photomultiplier-tube end window.

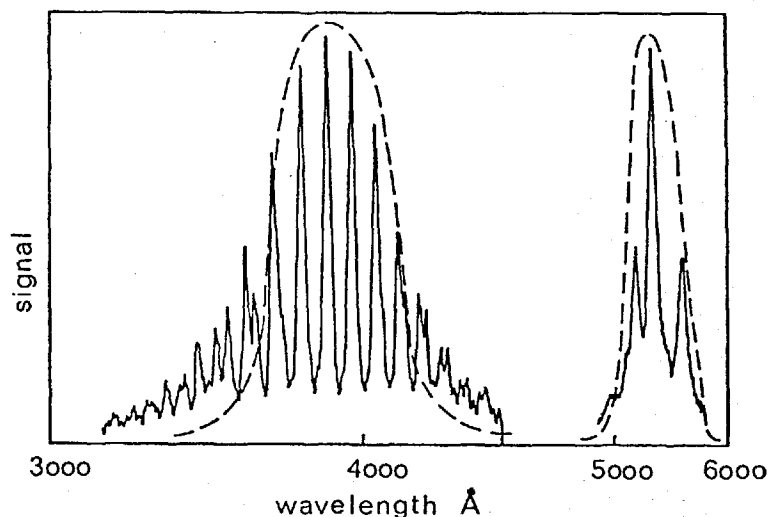


Figure 34 Spectral scan of S_2 and HPO emission on Unicam SP 900 nebulising 600 ppm of sulphur as sulphate and 100 ppm of phosphorus as phosphoric acid. Superimposed are transmission characteristics of filters used.

The photomultiplier-tube housing and slit arrangement was built as a single detachable unit to allow access to the inside of the photometer and to enable the filters and photometer housings to be interchanged easily when required.

An EMI 9601B photomultiplier tube was incorporated in the simple filter flame photometer. This was powered with a Brandenburg stabilised d.c. EHT power pack supplying 0 to 2.5 kV. The photomultiplier tube output could either be read directly in microamps by using an RCA ultra-sensitive d.c. microammeter or via a backing-off circuit (Figure 35) connected directly to a recorder (Servoscribe 0 to 10 mV full-scale deflection).

For routine aqueous determinations a standard Unicam SP 900

burner and nebulisation assembly were used with the exception that the Unicam burner head was replaced by an open borosilicate tube burner of 1 cm internal diameter as described above. For organic samples or for the detection of trace amounts of sulphur and phosphorus special modifications were used.

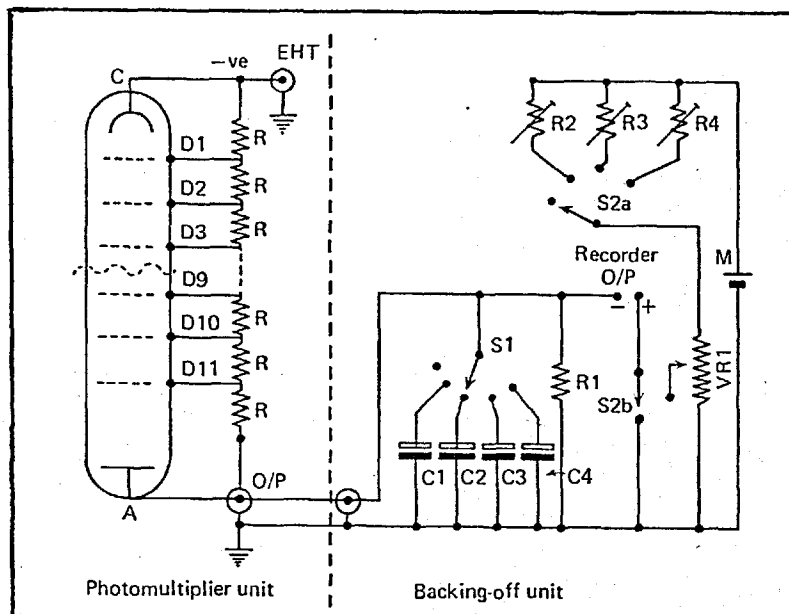


Figure 35 Photomultiplier and backing-off circuit
Photomultiplier unit: A, Anode C, photocathode
R, 100 k D₁₋₁₁ dynodes

Backing-off unit		Time constant	
R ₁	20 k to suit Servoscribe	C ₁	25 μF 0.5 s
R ₂	100 k + 50 k variable	C ₂	50 μF 1.0 s
R ₃	39 k + 10 k variable	C ₃	100 μF 2.0 s
R ₄	10 k + 5 k variable	C ₄	250 μF 5.0 s
VR ₁	1 k W/W backing-off (fine)	M	Mercury cell 1.34V
S ₁	Damping 1 pole 5 way	S ₂	Backing-off 2 pole 4 way (coarse)

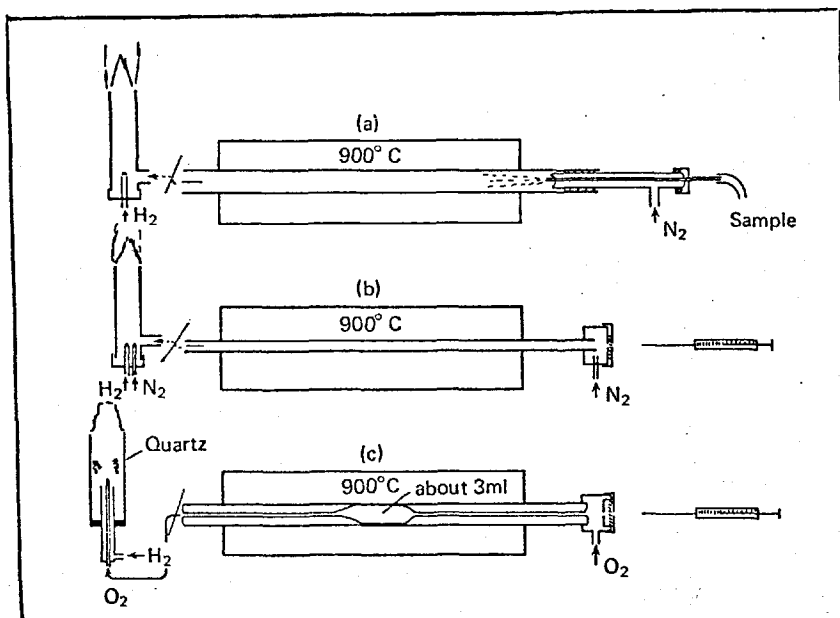


Figure 36 (a) Arrangement using heated nebulisation chamber; (b) direct aqueous injection system; (c) direct organic injection system

b). Modifications to Increase Sensitivity of Determination

Although considerable increases in sensitivity were achieved by using a filter detection system some sensitivity was still lost by inefficient introduction of sample into the flame. Most pneumatic nebuliser systems only have about 10 to 15 per cent efficiency in transporting the liquid sample into the flame and because the sulphur signal depends on the square of the concentration a 2 fold increase in sample input into the flame produces a 4 fold increase in the emission signal.

Two modifications were, therefore, developed depending on the volume of sample solution available for analysis. For

sample volumes of less than about 1 ml a heated injection manifold system was used (Figure 36b). This gave increased sensitivity when compared with the conventional system and was most suitable for sample volumes up to about 10 μ l. However, the reproducibility was poor (± 5 per cent in peak height), although the use of a recorder with a faster response time might have brought some improvement (the Servoscribe recorder used has a full-scale deflection response time of 1 s).

TABLE XV Detection Limits (Signal to Noise = 1) for Aqueous Solutions and Phosphate in Hydrogen-Nitrogen Diffusion Flame Burning on an Open Tube Burner

Detector	Detection limit ppm	
	Sulphur	Phosphorus
Unicam SP 900 spectrophotometer measuring at 5280Å for phosphorus and 3840Å for sulphur; normal nebuliser About 5Å band pass.	60	0.1
Filter photometer with glass filters with peak transmission at 6200Å and 3900Å; Unicam nebuliser	0.2	0.01
Filter photometer as above with heated chamber (Figure 36a)	0.08	0.007
Filter photometer with direct injection technique (Figure 36b)	0.1	0.01

For sample volumes greater than about 1 ml the introduction of a heated nebuliser chamber (Figure 36a) gave the lowest detection limits (Table XV). However, the increase in flame

background and noise that accompanies the increased sample input offset the expected increase in sensitivity.

The experimental arrangement for both of these modifications was similar in that an electrical resistance furnace was used to maintain the sample inlet tubes at about 900°C. In the latter system the pneumatic nebuliser unit used delivered 3 ml minute⁻¹ of solution and about 5 l minute⁻¹ of nitrogen into the heated quartz tube. The transparent silica tube was 20 cm in length and 8 mm internal diameter and was heated over a length of 15 cm to about 900°C. The sample was vaporised, passed through the side arm of the Unicam SP 900 burner, pre-mixed with hydrogen and carried into the diffusion flame. The increase in sample volume reaching the flame per unit time gave an increase in emission intensity and thus a lower detection limit.

The heated injection system was developed for those cases when the volume of sample solution available for analysis was less than about 1 ml, eg for a micro oxygen-flask combustion for the determination of sulphur in organic matrices. The quartz aspiration tube in this instance was replaced by a narrower quartz or stainless-steel tube of about 2 mm internal diameter. A standard chromatographic serum-cap injection port was used for sample injections, which were made with a 0 to 10 µl Hamilton syringe. Nitrogen was passed along this sample tube and the tube was heated as before to about 900°C by means of an electrical resistance furnace. To maintain diffusion flame

conditions auxiliary nitrogen was introduced into the base of the Unicam SP 900 burner via a double jet as shown in Figure 36b

The vaporised sample was swept along with the nitrogen and was carried into the flame where the sulphur emission was observed. Aqueous sample injections of 10 μ l gave detection limits comparable with those obtained with the heated tube and pneumatic nebuliser. Because of the poor reproducibility, connected mainly with the recorder system used, the continuous introduction of sample is to be preferred except in those instances in which only a limited volume is available.

c). Interferences

Because of the nature of the hydrogen-nitrogen diffusion flame and also the process by which the emissions (S_2 and HPO) are produced, the intensity observed is subject to many interferences. For example, organic solvents completely quench the emission by interfering with the chemiluminescent reaction process in the flame. After acetone has been nebulised on the conventional system, a period of several minutes' passage of distilled water through the nebulising system is necessary before any emission can be obtained for even concentrated solutions of sulphur and phosphorus. Matrix effects in the cool flame are also serious and all metal cations interfere to some extent, usually depressing the emission. Copper, however, gives a positive interference on phosphorus as the CuH and CuCl band emissions coincide with the HPO emission and the resulting intensity is larger than would

be expected for the phosphorus content of the solution.

Because the flame temperature is lower than with most pre-mixed flames, the interference from atomic emission of even the alkali elements is small and only really significant for sodium. In this instance the flame background is increased by the continuum emission from NaOH molecular species. The depressive effects caused by other ions were removed readily by swirling the sample solution with a few grams of cation-exchange resin (H^+ form) in a beaker for 1 to 2 minutes before nebulisation. Ten fold molar excesses of Cl^- , ClO_4^- , BCl_4^{3-} , NO_3^- , acetate, oxalate and H_2O_2 gave no interference. No interference of sulphate on phosphate or vice versa was noted at the 1000 fold molar excess level with the Unicam spectrophotometer. Slight mutual interference was, however, observed at this level when using the glass filters shown in Figure 34. Lower levels than a 1000 fold molar excess gave no interference and it is probable that narrower band-pass filters than those used above would reduce the interference at higher levels.

d). Determination of Organic Sulphur

One of the major problems associated with the analysis of sulphur is found within the petroleum and oil industry. The method at present in common use for the determination of sulphur in hydrocarbons involves the preliminary combustion of the gas or oil sample in a device such as the Wickbold apparatus. Two modifications of this apparatus are currently in use, both involving the initial burning of the hydrocarbon in oxygen at

reduced pressure with a dynamic system. The combustion products are scrubbed by passing the gases up through an absorber column containing hydrogen peroxide solution which converts the oxides of sulphur into sulphate. The sulphate produced in this manner is usually determined either turbidimetrically or by means of a Fritz titration. Neither of these finishes is considered rapid or accurate for samples containing less than about 5 ppm of sulphur.

At this level of sulphur no emission is observed when the hydrocarbon sample is introduced directly into the conventional nebuliser system of the cool flame unit. This occurs because organic fragments readily quench chemiluminescent emissions. In addition, the diffusion flame possesses only a low thermal energy, which is often insufficient to break down certain molecular structures. The combustion procedure involving the Wickbold-type burner was, therefore, examined to see if it produced a suitable sample for subsequent analysis in the nitrogen-hydrogen flame. The first type of Wickbold assembly used vaporised the sample in a stream of nitrogen passing through a Pyrex burner unit which consisted of two concentric spheres and could be heated externally. The inner sphere possessed a combined gas and sample inlet and a capillary outlet jet, while the outer sphere had a gas inlet and outlet tube coaxial with the jet. The sample is introduced at the top of the burner unit into a nitrogen stream (40 l hour^{-1}) and is vaporised in the inner sphere which is maintained at about 350°C with an

external heating mantle. Simultaneously oxygen (700 l) is passed through the space between the spheres so that as the sample issues from the jet it can be burned in an atmosphere of oxygen. The combustion products from this burner unit are drawn at a flow rate of about 800 l hour⁻¹ through a water cooled burner expansion chamber into the absorber column. The oxides of sulphur are absorbed by scrubbing the gas with an aqueous solution containing 1 to 2 per cent of hydrogen peroxide. The sulphate produced in this manner can now be nebulised directly into the filter photometer, and from the amount of sample combusted and the volume of absorber solution the total sulphur content can be calculated with reference to calibration graphs previously obtained.

This combustion technique used in conjunction with the filter flame photometer considerably reduces the time required for an analysis, mainly because the better sensitivity achieved by the detector allows a smaller sample to be burned. If a turbidimetric finish is used for a sample containing 1 ppm of sulphur a combustion of 100 ml of sample at a maximum rate of 40 ml hour⁻¹ would normally be required. This would give a final solution of sulphate after evaporation equivalent to 10 ppm of sulphur. However, with the filter photometer flame detector only one tenth of the above amounts are required. A 10 ml sample can be combusted to give an aqueous solution containing 1 ppm of sulphur which can be readily determined.

The second Wickbold-type of apparatus used combusted

samples much faster, at a rate of 120 ml hour⁻¹. This burner consisted of four concentric silica tubes and was favoured for its safety and ease of operation. The centre capillary tube carried the sample into an oxy-hydrogen flame which burned when the oxygen and hydrogen gases mixed as they issued from the annuli produced by the second and third tubes. Oxygen passed at 18 l minute⁻¹ through the outer annulus (about 1.5 cm diameter and 1 mm wide) and provided the excess of oxygen for the total combustion of the hydrocarbon sample. This unit fitted, by means of a ground-glass joint, into a water cooled silica expansion chamber where the combustion products were again scrubbed with an aqueous solution containing 2 per cent of hydrogen peroxide as before. The vacuum take-off was monitored with a simple calibrated mercury manometer. A flow rate of 20 l minute⁻¹ was required when using the above burner arrangement. By using this combustion apparatus a complete determination could be carried out in 5 minutes for samples containing more than 0.5 ppm of sulphur (see Table XVI).

TABLE XVI Results Obtained for Determination of Total Sulphur in Petroleum Hydrocarbons by using the Flame-Photometric Detector after Initial Wickbold Combustion

Sample	Sulphur, ppm	
	Quoted sulphur content*	Amount found
1	18.3 to 19.7	17.2
2	9.7	10.2
3	260 to 290	289
4	150 to 170	152
5	133	130
6	11.6	11.4

*with turbidimetric finish

If the sulphur content of hydrocarbons is relatively high, eg, greater than 20 ppm then the organic quenching effects may be reduced to a level at which the analytical utility of a direct injection technique is feasible. Conventional nebulisation is still not practicable, however, because of the low thermal energy of the flame. A method was developed that allowed the direct injection of an organic liquid sample (up to 2 μ l) into a heated combustion tube. After combustion, the products were passed on into a shielded hydrogen-rich diffusion flame. In this procedure the organic sample is initially combusted in a silica combustion tube at about 900°C in a 3 ml volume of oxygen (Figure 36c) whereby the sulphur is converted into sulphur dioxide. This gas stream then passed into the burner unit through a 2×10^{-2} inch internal diameter stainless-steel tube and burns in an excess of hydrogen supplied through $\frac{1}{8}$ inch internal diameter stainless-steel tube running concentrically. Thus the sample is again passed through a combustion zone where any unburnt organic fragments are finally combusted. Above the reaction zone, the hydrogen-rich atmosphere preserved by the silica sheath reduces the sulphur species and the characteristic chemiluminescent emission is observed.

Although this method is useful for the rapid analysis of total sulphur in organic solvents, its main disadvantage is related to the small background signal which arises from emitting organic fragments. This could be minimised to some extent

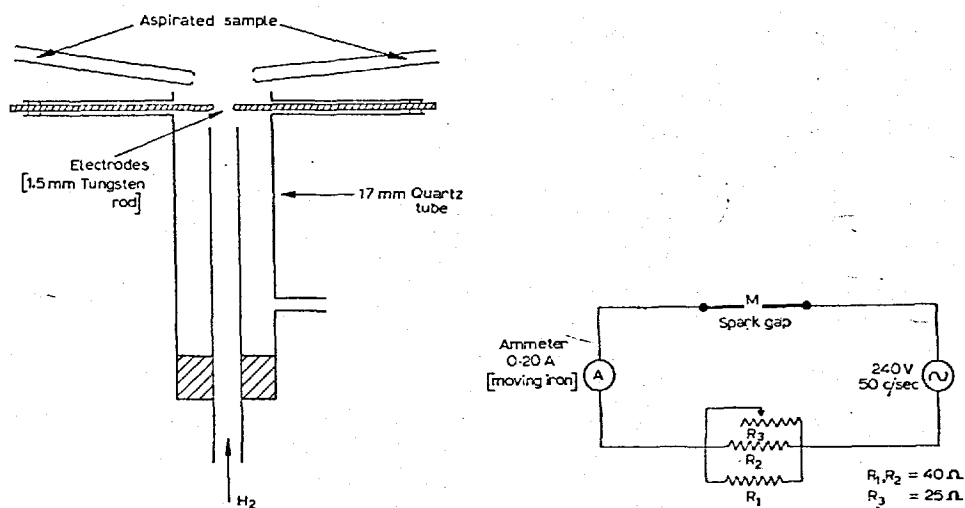
by the use of narrower band pass filters (eg interference filters) or by simple gas-liquid chromatographic separation of the sulphur species from the other carbonaceous materials which result in increased flame background. For 2 μ l injections the limit of the working range was found to be 20 ppm for samples containing carbon disulphide and dimethyl sulphoxide in light distillates.

For solid organic sulphur compounds the oxygen-flask combustion technique is a rapid method of converting the sulphur in the sample into sulphate in aqueous solution. A combination of oxygen-flask combustion and use of the filter photometer described above enables a rapid accurate determination to be made.

A convenient arrangement consisted of a 250 ml flask and an aqueous absorbing solution containing 2 per cent of hydrogen peroxide. About 3 mg of material were combusted and the resulting solution (after dilution if necessary) was sprayed directly into the conventional nebuliser of the filter photometer. This method was tested with benzene disulphide as standard and the agreement in sulphur content was within 2 per cent of the theoretical value in all instances.

3.6 SOME EXPERIMENTS WITH ELECTRICALLY AUGMENTED FLAMES OF HYDROGEN

Some initial studies [210] using a hydrogen plasma as an atom reservoir indicated that very high temperatures could be reached by augmenting hydrogen flames with electrical power. The torch design used in initial experiments is shown in Figure 37



A 14 ampere arc struck between two tungsten electrodes 2 mm in diameter in hydrogen has been reported to give a flame plasma temperature in excess of 3500°K [211]. We observed emission for several elements but found difficulty in sample introduction and emission stability.

The possibility of producing a hydrogen plasma with radio frequency was investigated. Essentially the plasma production involves the coupling of a hydrogen diffusion flame to an rf field generated inside the tank coil of an rf oscillator valve. Once the rf power is coupled to the flame gases an

increase in bulk enthalpy takes place and the effective temperature increases considerably.

The plasma cell design (Figure 38) consists of a standard Unicam burner stem and circular acetylene emission head. This arrangement was used in conjunction with conventional nebuliser units utilising argon (about 15 psi) as nebulising gas and a hydrogen flow rate sufficient to give a steady diffusion flame. The Radyne SC15 plasma generator unit was used to provide rf power (at 36 MHz) up to 2.5 kW. Various flames were studied initially and all were found to be capable of coupling the rf power when seeded with a 0.1 M solution of potassium chloride which provided sufficient ions to initiate and carry the discharge. It was found that a quartz sheath was necessary to shield the rf copper coil from the resulting plasma to prevent the rf current from shorting between the turns of the coil. It was also found necessary to use a stabilising electrode which was best attached to the burner head and held at ground potential (Figure 38). With this arrangement a stable plume of plasma some 8 cm in length and 1 cm in diameter was observed emanating from the tip of the 1 mm diameter tungsten electrode stabiliser. Rf power inputs as low as 0.5 kW were capable of producing a stable plasma.

The stability of a number of stabilising electrode materials was investigated, but most fused, melted in the plasma and

yielded an emission spectrum characteristic of the electrode material. Carbon was effective in producing a stable discharge but gave a high background radiation. Tungsten, however, showed little background emission and relatively little burn-up. Under those conditions the background radiation produced in the tail flame (about 2 cm above the copper coil) showed a region of continuum with a maximum at $5500\text{\AA}$ over the spectral range $4500 - 6500\text{\AA}$ which corresponds to the $\text{NO} + \text{O}$ reaction. The only emission observed in the ultraviolet region was due to OH band emission at about $2800\text{\AA}$ and $3100\text{\AA}$, which was some 40 times less intense than that observed in a typical premixed air/hydrogen flame; no tungsten lines were observed in this region of the plasma although strong emission was observed from the potassium resonance lines at $4040\text{\AA}$. The glare produced at the electrode tip was shielded from the view of the spectrophotometer.

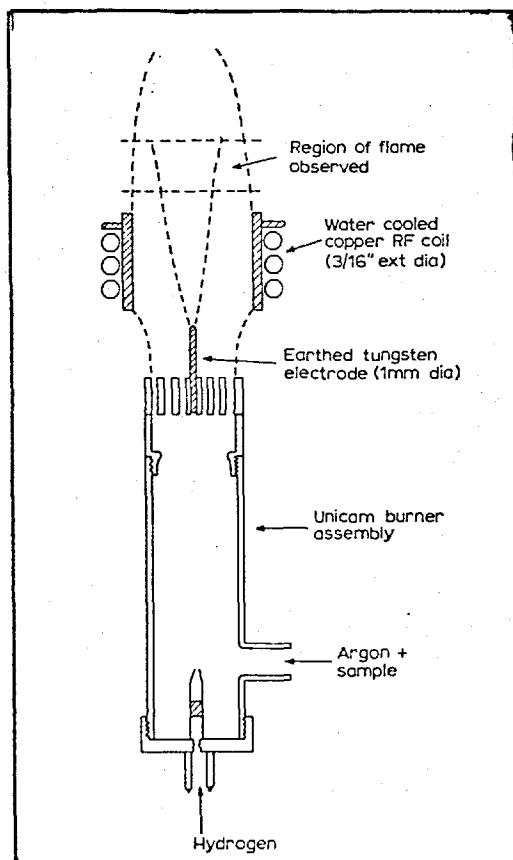


Figure 38

TABLE XVII Emission from various metal ion solutions ^a

Element (200ppm)	Wavelength Å	Emission signals (μA) ^b		
		A/H ₂	rf coupled A/H ₂	Air/H ₂
Li	6708	0.84	91.0	1.00
	6104	0.20	190	0.40
Ca	4227	0.00	16.0	0.00
Sr	4607	0.00	183	0.00
	4832	0.00	6.00	0.00
Ba	5535	0.06	42.0	0.80
Hg	5461	0.00	24.0	0.00
	2537	0.00	1.20	0.00
Zn	3345	0.00	2.30	0.01
	2139	0.00	1.20	0.00
Na ^c	5890	3.10	140	14.0
	5896			
Cs ^c	4555	0.02	5.00	1.50
	4593			

a) Measurements made with a modified Beckman DU spectrophotometer with 900 V EHT applied to an EMI 9601B photomultiplier with slit width 0.4 mm. All aqueous solutions were 200ppm in metal ion and 0.1 M in potassium chloride. All emission intensities were corrected for background radiation. An rf power of 1.5 kW was coupled to the diffusion flame.

b) The minimum measurable signal with the system used was 0.005 A.

c). Unresolved spectral lines.

In these preliminary studies, the thermal emission intensities thus obtained were compared with those observed in the non-augmented diffusion flame and a typical premixed air/hydrogen flame burning on the same burner assembly for several metal ion solutions (Table XVII).

The rf coupled diffusion flame described is relatively easy to operate and maintain and appears to exhibit little

background radiation in the ultraviolet region of the spectrum. These observations and the results in Table indicate that the augmented flame may be of some application in analytical emission spectroscopy.

The rf power coupled to the flame and the gas flow rates used may be varied over a wide range without significantly affecting the plasma obtained. In our experience these parameters are less variable with the conventional argon plasma (obtained using a Radyne SC15 generator) which requires a minimum rf power of about 2.5 kW to produce a stable discharge. Moreover, a conventional argon plasma is not always able to provide sufficient thermal energy to vaporise solid particles which then pass through the plasma region without significant excitation occurring; analyses of powdered samples can, therefore, present serious problems. A further difficulty encountered with low powered argon plasmas is continuous operation whilst nebulising aqueous solutions. All of these problems may be reduced using the augmented flame described.

CHAPTER IV



DETECTION SYSTEMS IN ATOMIC SPECTROMETRY

Little work seems to have been reported on the development of detection systems compared to the work published on sources and atom reservoirs. With the trend of research towards atom reservoir producing transient atom clouds and the use of pulsed light sources, their use with detection systems designed for steady state measurements give poor reproducibility and sensitivity. Ultra-violet recorders have been used with success for recording transient fluorescent signals [212], however, the electronic amplifier must have a comparable response time to use the recorder to its full advantage. Even then peak area must be measured to give an integrated intensity. Studies by the author using a storage oscilloscope have shown that the emission obtained from the vaporisation of cadmium solutions from a platinum loop [220] into an atmospheric argon plasma do not follow a smooth curve. The measurement of peak heights in these cases gave poor precision and electronic integration must be used to improve the precision of measurement.

The recent development of solar blind photomultiplier tubes (PMT) (available from EMI and Hamamatsu T.V. Co) which have effectively zero response characteristics at wavelength greater than $3100\text{\AA}$ have shown promise as detectors for atomic absorption and fluorescence. [213]

In the following study it was hoped to use the solar blind detectors in atomic fluorescence and compare the results obtained for dc measurements with those using photon counting.

4.2 PHOTOMULTIPLIER TUBES

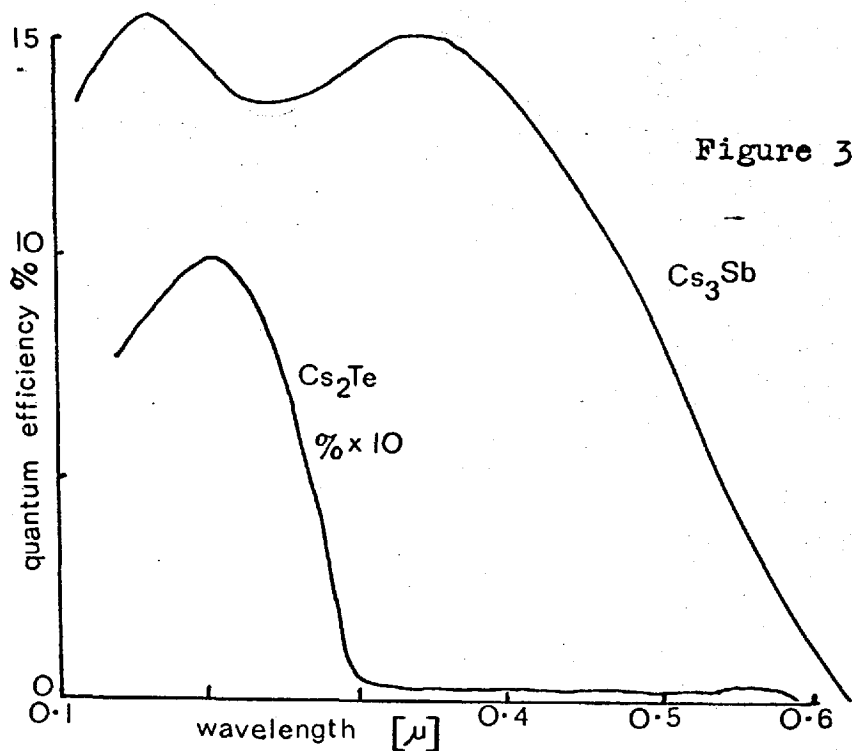
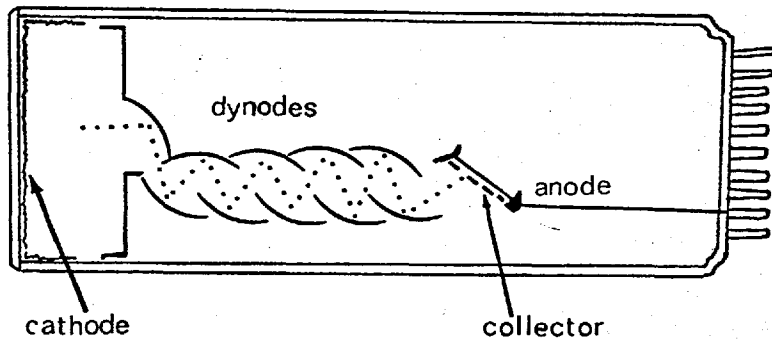
At present, one of the most sensitive devices for detecting light radiation is the photomultiplier tube. A photomultiplier may be sub-divided into a photocathode, an electron-optical input system, a secondary emission multiplier and an anode. In end-on photomultipliers, the photocathode is deposited on the inside of the tube window and is semi-transparent. An alternative system employs an opaque reflection cathode situated some distance within the glass envelope. It is found that semi-conducting compounds of metals from Groups I and V of the Periodic table have good photemissive properties. Historically, the most celebrated of these is the compound of antimony and caesium of stoichiometry Cs_3Sb . In more recent years, cathodes have been developed giving increased photoelectric efficiency and extended spectral sensitivity eg. the KNa_2CsSb trialkali cathode.

Photoelectrons from the desired area of the cathode must be guided on to the first dynode of the secondary emission multiplier with the maximum possible efficiency. This is achieved by the optimisation of the cathode to first dynode geometry, and the maximisation of the collecting field.

Photoelectrons impinging on the first dynode produce a number of secondary electrons which are accelerated on to the next dynode of the multiplier where they, in turn, produce secondaries. A potential gradient is maintained between the successive dynode stages by means of a suitable resistor chain.

In general SbCs dynodes are employed in tubes designed for use at very high temperatures and in windowless multipliers.

The last dynode is in the form of a shallow box, within which the collector mesh is stretched. Electrons from the penultimate dynode pass through the anode mesh to strike the last dynode; the low energy secondaries produced are then collected at the mesh.



4.3 THE USE OF SOLAR BLIND DETECTORS IN ATOMIC FLUORESCENCE

Two solar blind photomultiplier tubes were studied, both having Cs_2Te photocathode material.

(a) The EMI 9616 - 50 mm end-window; 13 stage, venetian blind type of dynodes .

(b) The HTV R166 - side window; 9 stage, squirrel-cage dynode type .

The 9616 having 13 Be - Cu dynodes has a fused silica (spectrosil) end window. Since Cs_2Te is itself an insulator deposition of a semi-transparent photocathode layer on the end window is preceded by the evaporation of a layer of tungsten which while it only absorbs 10 per cent of the incident light, provides sufficient conductivity for a photocurrent to be drawn [218]. The peak quantum efficiency of the PMT occurs at $2500\text{\AA}$ and is about 1 per cent. The tube gain was 2×10^7 at 1.8 kV.

The Hammanatsu R166 has a similar spectral response peaking at $2500\text{\AA}$ with virtually no response to radiation of wavelength longer than $3100\text{\AA}$. The response in the ultraviolet is limited by the window material with spectrosil to $1900\text{\AA}$. The variation of quantum efficiency with wavelength is given in Figure 39 .

a). Experimental Arrangement

The atomic fluorescence of zinc was investigated using separated and unseparated flames of air/hydrogen and air/acetylene,

a premixed capillary emission type burner was used in conjunction with a Perkin-Elmer nebulisation unit and expansion chamber. A zinc electrodeless discharge lamp was used as excitation source. Liquid organic filters were developed to give, in conjunction with the response of the solar blind photomultipliers, a transmission band of only a few tens of Angstroms. The range of filters developed is shown in Figure 40. The 50 per cent acetone in water, having a peak transmission of 30 per cent at $2110\text{\AA}$ and half width of $120\text{\AA}$ was used to isolate the $2138\text{\AA}$ zinc resonance line from flame background.

The results obtained are summarised in Table XVIII for the atomic fluorescence of zinc. The detection limits that could be obtained was limited by the tolerable amount of background detected by the photomultiplier. The air/ acetylene flame even when separated with inert gas and the aperture of the photodetector reduced was such that considerable noise resulted from the background. Thus the absolute limits of detection are quite poor but the relative values of interest.

TABLE XVIII Detection Limits for Zinc using the 9616 PMT

Flame	Relative background	Detection Limit ppm
air/acetylene	100	0.03
sep. air/acetylene	6	0.01
air/hydrogen	9	0.006
sep. air/hydrogen	4	0.005

background relative to air/ acetylene = 100

Table XVIII(continued)

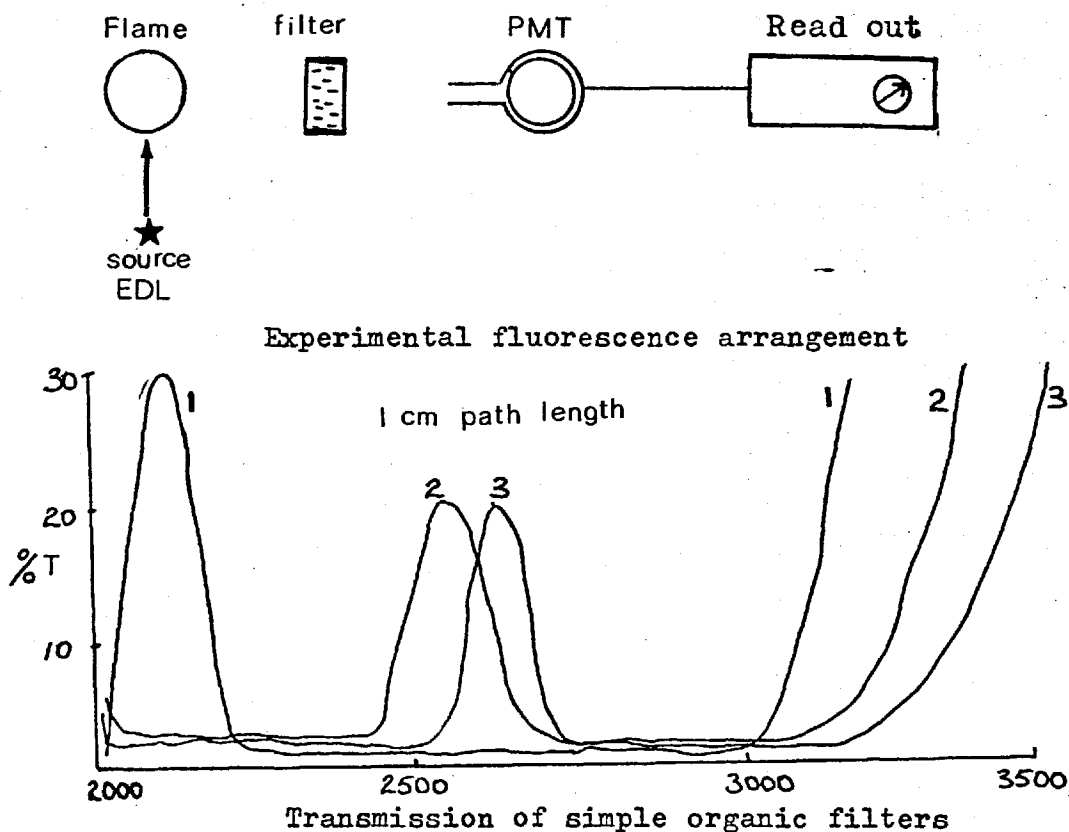
Detection limits for Zinc using 9616 PMT and Liquid
Organic filter

Flame	Relative background	Detection Limit
Air/acetylene	10	0.07
sep air/acetylene	5	0.04
air/hydrogen	4	0.002
sep air/hydrogen	2	0.001

background relative to air/acetylene without filter.
detection limits quoted for signal to noise ratio = 1

In conclusion it may be seen that solar blind PMT's
may be used for atomic fluorescence measurements provided the
radiative background of the system is not too high and show great
potential when used with simple filters.

Figure 40



1. 50% Acetone in Water
2. 12% Carbon Disulphide in Ethanol
3. 0.1g/l. Paracimethylaminobenzaldehyde in Ethanol.

The output signal of a photomultiplier tube is inherently digital as a result of the quantum nature of the photoelectric effect. Photons arrive at the photocathode and eject photoelectrons with an efficiency that depends on the quantum efficiency of the photocathode surface [214]. The rate at which the photons arrive fluctuates as a result of radiation noise (photon noise) inherent in the incoming light. This fluctuation is rigorously treated by Bose-Einstein statistics but little error results if it is assumed that photons are emitted independent of one another; that is, they occur randomly in time. Each photoelectron is amplified nearly one million times inside the photomultiplier tube by the process of secondary electron emission so that the ejection of a single photoelectron at the photocathode results in a relatively large packet of charging arriving at the anode. The statistical nature of secondary electron emission from the dynodes introduces a further fluctuation to the charge packets in the form of an amplitude distribution. The combination of these two fluctuations, the random time behaviour of the pulses as a result of the incident radiation and the amplitude distribution as a result of secondary electron emission causes the so-called shot-noise commonly associated with a photomultiplier tube. The fact that shot noise is a function of the incident light leads to important considerations in making precise spectrophotometric measurements with a photomultiplier tube.

If the rate of photomultiplier ejection and the frequency

response of the measurement system are such that individual current pulses can be resolved, then the number of pulses per unit time can be counted. Because the count rate is a measure of the rate at which photons are striking the photocathode, the measurement technique is appropriately called photon counting.

Photon counting has recently gained importance in spectrophotometric methods where the radiation is so low in intensity that it is difficult to obtain reliable measurements by conventional techniques. This is particularly true in Raman spectrometry [215]. The ability to detect low light level with a satisfactory signal-to-noise ratio is certainly one of the big assets of the photon counting method.

Another advantage is that the results are obtained in a direct digital form. It is becoming common practice to use various types of digital voltmeters at the output of spectrophotometers to facilitate readout and processing of data. Almost always the inherently discrete digital signal is converted to an analog signal (dc voltage) and then back to a digital signal for final readout and processing. This standard approach often introduces needless noise, conversion errors and instrument expense that could be eliminated by direct processing of the digital information from the transducer by the photon counting technique.

At present the signal from the PMT can be determined by

dc current measurements, lock-in amplifications, noise-voltage and photon counting.

The basic characteristics of each of these techniques in measuring the PMT output are illustrated by Figure 41.

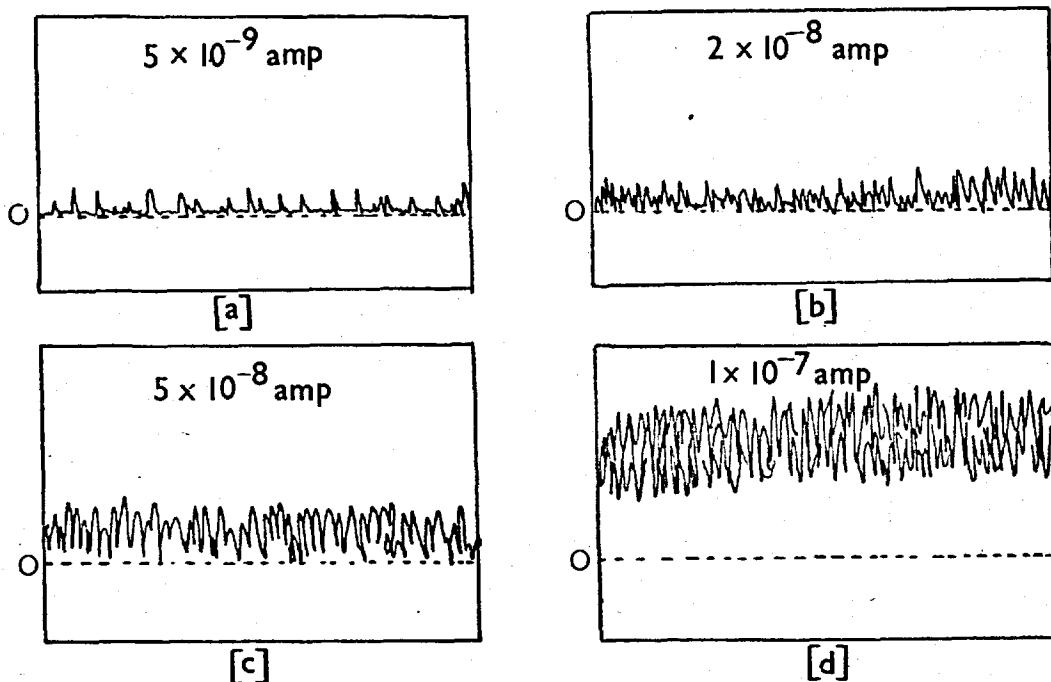


Figure 41

Oscilloscope traces showing change of dc voltage level and shot noise with increasing illumination of photocathode.

This shows the oscilloscope display of the output from a PMT for various light intensities falling on the photocathode. At low light levels the discrete current pulses are easily resolved and as the light level is increased the current pulses begin to overlap and pile up as a result of the finite frequency response of the system.

a). Direct Current Measurement

The most conventional method of detecting the photomultiplier signal is to measure the dc signal current. This can be

accomplished basically in two ways. If a large resistor is inserted as the the load, the photocurrent pulses produce a voltage across the resistor that can be measured by a potentiometric recorder or voltmeter. A better method is to employ an operational amplifier as a current measuring system which offers several advantages. Because the photomultiplier tube output is connected between virtual ground and common ground, instead of to a large load resistor, stray noise pickup is reduced. Other current sources can be connected directly to the summing point of the operational amplifier input to provide a difference or ratio measurement, and compensating current to offset photomultiplier dark current can be summed directly at the input.

The response time of a dc current measurement system is usually sufficiently long that the shot noise, as seen in Figure 41a is effectively integrated so that the average dc current is recorded with only a small ripple.

b). Lock-In Amplifier Measurements

The lock-in amplifier technique is becoming an increasingly popular measurement system for low level electrical signals. This technique involves selective modulation of the signal information, amplification with a tuned amplifier, synchronous rectification, and low pass filtering. This translates the signal information to a frequency region where the $1/f$ noise is minimised. The tuned amplifier and phase locked rectification

result in an effective bandwidth of approximately 0.1 Hz. All noise frequencies outside the bandwidth are rejected. Also synchronous rectification rejects all noise components not phase locked to the signal modulation frequency. Low pass filtering of the rectified signal produces a dc output signal. This method is effective in improving the signal-to-noise ratio by greatly reducing the bandwidth of the system.

c). Noise-Voltage Measurements

In Figure 41b the point at which the current pulses are just beginning to overlap is illustrated. At this point there is still more signal power in the ac portion of the signal than in the dc portion of the signal. It is also true for the conditions in Figure 41a where the majority of the pulses are resolved. This observation led to the development of the noise-voltage measurement technique by Pao and Griffiths [216]. The ac portion of the signal has traditionally been called noise and is usually rejected, but it is due to the presence of a signal. In this case the noise power varies linearly with the light flux. The measurement system then consists of high pass filtering of the output signal of the photomultiplier tube, amplification with a square law detector, and low pass filtering to generate a dc voltage. This method is advantageous only in the region where the RMS power in the signal induced fluctuations is greater than the dc component of the signal and would not be advantageous for the measurement conditions of Figure 41d.

d). Photon Counting Measurements

Each photon striking the photocathode has a probability κ , that it will cause the emission of a photoelectron from the photocathode. This quantum efficiency depends upon the photocathode material and also the wavelength of the incident light. Of the photoelectrons emitted by the cathode only a certain fraction η reaches the first dynode and produces output pulses of electrons. By careful PMT design η can be close to unity. The arrival rate of photons at the cathode is designated by n_p the total number of pulses appearing at the anode 'Ne' in time 't' is given by $N_e = n_p \kappa \eta t$. These pulses after appropriate electronic processing are recorded digitally on counters.

If the PMT was an ideal device, the pulses resulting from single photoelectrons would have exactly the same charge or pulse height. However, the output pulses have a spectrum of pulse heights because of the statistical process of secondary emission. In addition to these pulses due to photoelectrons there are also a certain number of spurious pulses, known as dark pulses, generated whether or not the cathode is illuminated. The pulse height distribution of these pulses in general differs from the photoelectron pulse height distribution.

These dark pulses result from thermionic emission often down the dynode chain and these low amplitude pulses can be considerably reduced by cooling the photomultiplier. A reduction

of a factor of 10 in background count rate may result on cooling a Cs_3Sb cathode from room temperature to 0°C ; a corresponding factor of 16 may be obtained under similar conditions for trialkali cathodes. The high amplitude dark pulses are unaffected by cooling and these are caused by cosmic particles and as a result of Cerenkov photons produced in the tube window by β particles from the decay of K^{40} which has a natural abundandance in the window material.

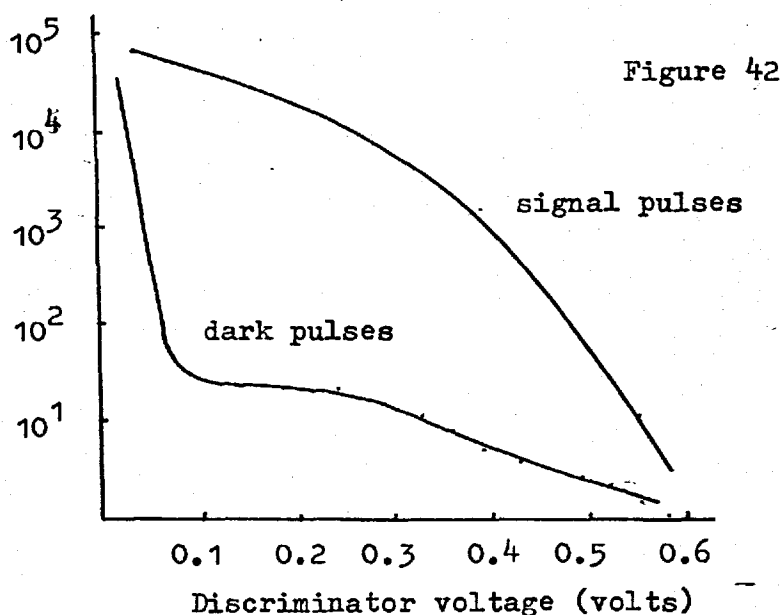


Figure-42 shows a typical plot of count rate vs integral pulse height (all the counts above a certain level being counted) for dark pulses and signal pulses. By setting the pulse height discriminator to a value around 0.15V it can be seen that about 70 percent of the total count is recorded with the rejection of a majority of dark background counts.

4.4 ASSESSMENT OF PHOTON COUNTING DETECTION IN AF

From theoretical considerations it seems that photon counting offers several distinct advantages as a method of detecting weak and transient light signals.

(a) It is easier, more precise and more logical to photon count at low pulse rates than to dc measure the low anode currents.

(b) Some distinction may be made between the signal pulses and dark pulses and other external pick-up by means of a pulse ^{im}ight discriminator set to respond above a certain pulse height. This gives improvement in signal to noise ratios obtained.

(c) The system can be used to monitor rapid and transient signals such as those arising from many non-flame atom reservoirs which frequently use small samples for analysis. In these instances rapid, integrated, digital read-out is obtained.

(d) In comparison to the other forms of detection system such as lock-in amplifiers and pico-ammeters the photon counting system described below is economically more viable.

A possible disadvantage may arise from its high sensitivity in that the system has a limited dynamic range above which pulse pile up in the PMT and electronics give erroneous results.

a). Experimental Photon Counting System

The amplifier design of Eather and Reasoner [217] Figure 43 was constructed with the omission of the diode-pump ratemeter.

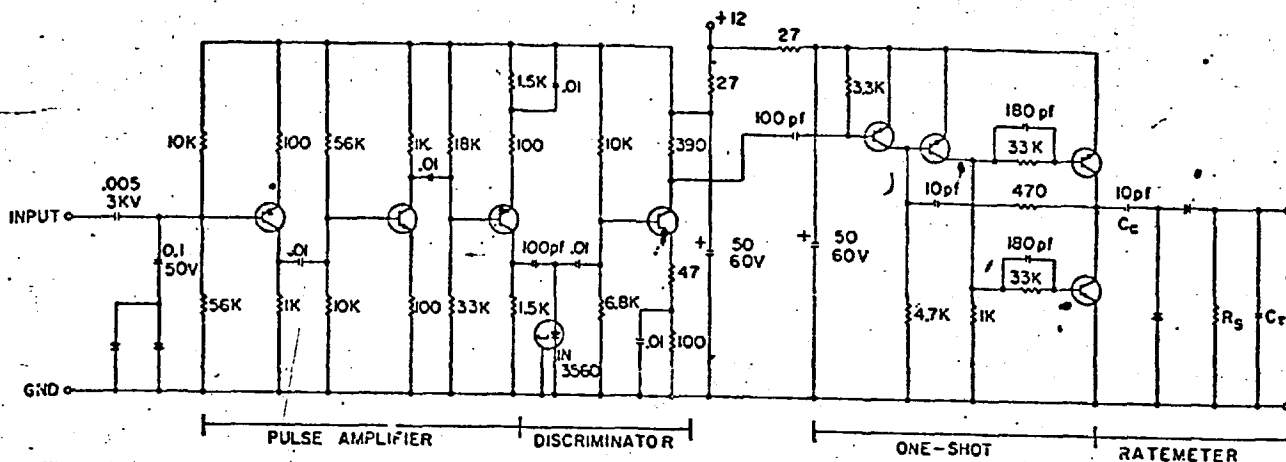


Figure 44 Circuit diagram of photon counting system.

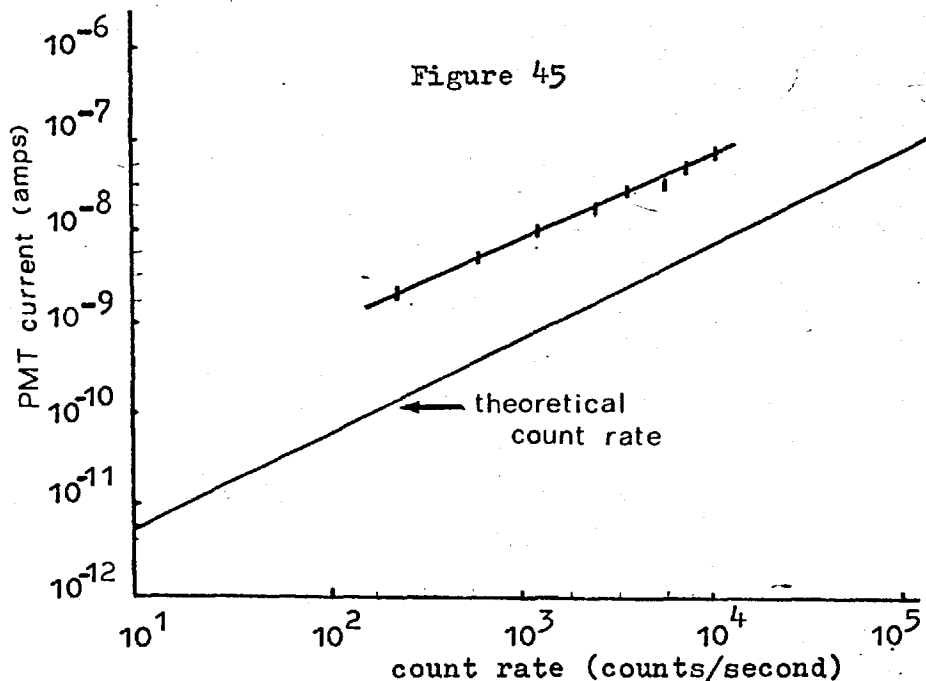
The one-shot multivibrator caused some initial constructional difficulties as it tended to free-run at about 0.5 MHz.

This was a result of feed back across the copper strips of the veroboard on which it was made. By using a printed circuit board with a minimum of copper conductors the free-running was prevented. The output pulse was found to be 10 volts in amplitude of ~ 100 n sec duration and was adequate to drive a normal digital frequency meter/counter. The system was tested when first built using a double pulse generator and showed good frequency response up to 5 MHz with no drop in the one-shot pulse amplitude.

A comparison was made of the performance of the photon counting system and normal dc current measurement using the photomultiplier (EMI type 9601B) used in the Unicam SP 900A.

An external stabilised EHT power supply was used (Brandenburg type PM 2500) the cathode of the PMT was operated at 1kV negative with respect to ground. This allows the anode and output of the PMT to run near ground potential.

By illuminating the monochromator slit with a tungsten filament lamp operated from a stabilised dc supply and detecting the emission at 4000Å a comparison of photon counting and direct dc measurement was obtained.



The voltage developed across a 20k anode load resistor was measured using a servoscribe potentiometric recorder to obtain dc measurement results. The gain of the PMT was calculated from the specification to be 3.1×10^6 . The figure 45 shows the theoretical count rate curve for comparison. This initial

experiment showed that the discriminator was effectively reducing some dark current over the dc measurement system but also, when no signal could be detected over the noise of the background, the photon counting system was still giving appreciable counts over the background. The dark current at 1 kV for the 9601B PMT was 1.5×10^{-9} amperes the equivalent dark current at the discriminator level used corresponding to 10 counts/sec was 4.9×10^{-12} amperes; this is a reduction of 3 order of magnitude in the dark current by using photon counting detection.

b). Practical Considerations

There are a number of practical considerations which must be taken into account when low level photon counting is undertaken. The following are the essential requirements of the individual components used in the experimental system.

- 1) The PMT should be selected to have a high gain and low dark current. The photocathode ideally should have a high quantum efficiency at the wavelength of measurement for maximum count rate. If high light levels are also to be studied the time constant for the dynode chain becomes a factor for consideration.
- 2) The amplifier should not introduce an excessive amount of noise onto the signal. Therefore, a low noise amplifier with a minimum capacitance input, to respond to fast photomultiplier pulses, should be used. The output impedance of the amplifier should be low enough to drive the load at high frequency without producing voltage drops in the amplifier itself. Given a large enough gain PMT and sensitive pulse height discriminator

it may be possible to eliminate the need for an amplifier and to interface the detector directly with the pulse height discriminator.

3) The readout counter must have a counting speed and adequate number of digits to display the fastest expected count rate without overflow. A Venner digital frequency meter was used having a frequency response up to 20 MHz. The crystal oscillator in this meter was accurate to better than 1 in 10^6 and this was used as the preset time base control for the integration period.

c) Counting Technique

The photon counting system measures the number of pulses from the PMT during the counting interval. This count includes both the signal count N_s and the dark count N_d , the difference between the total count and N_d gives the signal count. The rms error in the number $N_s + N_d$ counted by the system is given by $(N_s + N_d)^{\frac{1}{2}}$. The signal to noise ratio is thus given by $N_s / (N_s + N_d)^{\frac{1}{2}}$. If the system is used to measure signal over a background level where the signal count rate is R_s and the background rate R_b then the error is then given by $(R_s + 2R_b)^{\frac{1}{2}} T^{\frac{1}{2}}$ where T is the time of observation. The signal to noise ratio now becomes

$$s/n = \frac{R_s^{\frac{1}{2}} T^{\frac{1}{2}}}{(1 + 2R_b/R_s)^{\frac{1}{2}}} \quad (54)$$

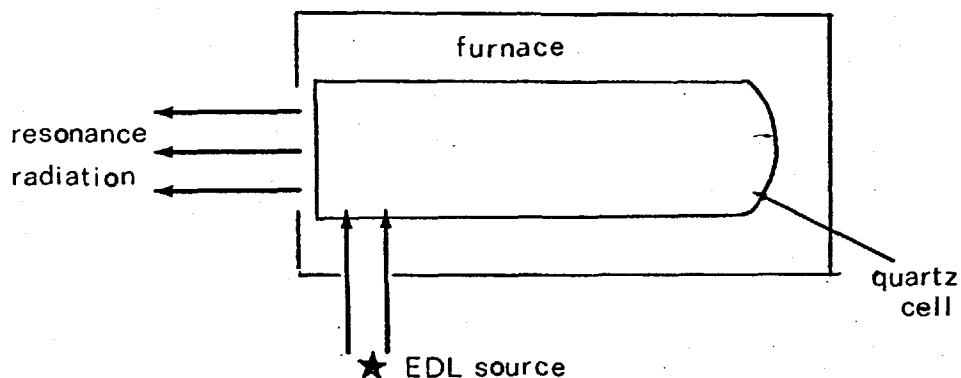
It was hoped to be able to make a direct comparison of photon counting and dc current measurement for the determination of zinc using the solar blind filter arrangement described earlier in section 4.3. However, the main difficulty was the background count that resulted from the flame radiation even using the lowest background system ie. liquid organic filter and separated air/hydrogen flame. This results in poor signal to noise ratios for the photon counting because R_b in equation 54 was of the order of 10^4 . The detection limit obtained by photon counting was 0.040 ppm which is forty times higher than by dc measurement.

However, it has been shown that in a case of a low background system photon counting has several advantages in its ability to integrate the light pulses from a transient atom cloud and also the improvement in signal to noise for steady state measurements.

SELECTIVE MODULATION

Lowe [162] described a technique whereby the resonance lines were selectively modulated inside a standard HCL without using extra electrodes. This was done by operating the HCL at a steady dc current and superimposing upon this a series of short high current pulses. By adjusting the pulse height the vapour cloud characteristic of the cathode material was modulated producing alternate 100 per cent transmission and nearly 0 per cent transmission of the resonance lines. The source described by Van Gelder is also capable of giving this effect [103].

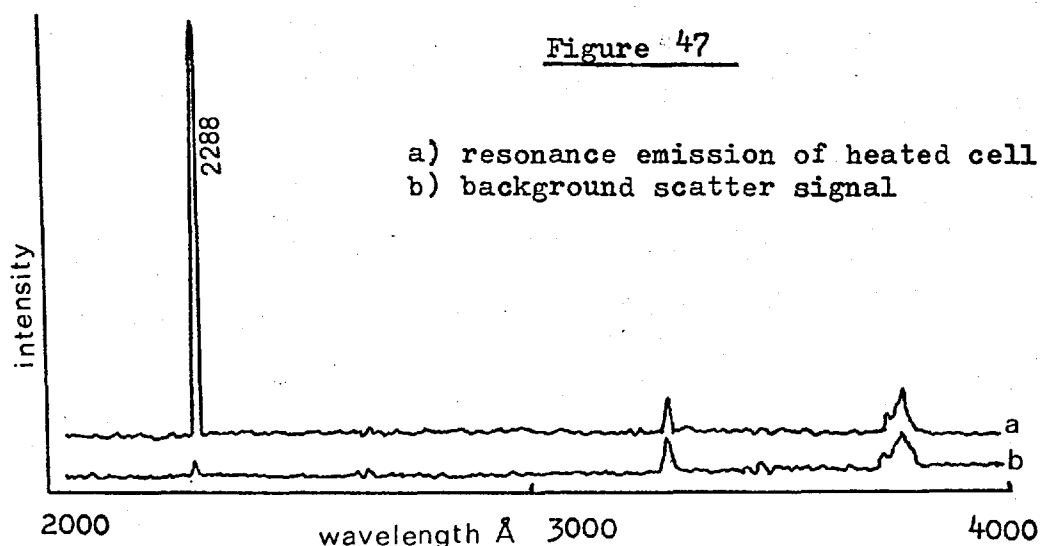
Although this effect has not been observed with electrodeless discharge lamps it is possible to obtain modulated resonance emission for certain volatile elements using the arrangement shown in Figure 46 .



Resonance radiation has been observed for Hg, Cd and Zn from this thermal atom reservoir made from quartz. The optimum shape of resonance atom cells has been discussed by Mitchell and Zamansky [4]. If the EDL source is modulated the resonance

radiation is also selectively modulated. The line profile obtained from a resonance cell should be very narrow because they only contain the metal at a low pressure of inert gas (1 torr). By careful control of the temperature of the furnace the lines should not be much broader than the Doppler width. This arrangement is very attractive for AA without a dispersive monochromator. The source radiation is all capable of absorption by analyte atoms in the flame only a photodetector is required to measure the reduction in transmission. This would be an application where solar blind PMT's in conjunction with simple filters could be used as detectors provided flame background transmitted by the filter did not cause too large a photoanodic signal.

Figure 47 shows a spectral output of a cadmium resonance cell at room temperature and when heated to about 150°C the $2288\text{\AA}$ resonance line is emitted strongly when the cell is heated. another possible use of this system is as a resonance monochromator using again a solar blind PMT as detector of the resonance.



CHAPTER V



CONCLUSIONS AND SUGGESTIONS FOR FUTURE STUDIES

On a theoretical basis expressions have been derived indicating the parameters that affect the sensitivity of determinations of trace metals by the techniques of atomic emission, atomic absorption and atomic fluorescence. With these parameters in mind each unit in the experimental systems used have been studied and developments in each reported. The brightest atomic sources used for excitation in atomic fluorescence have shown to be electrodeless discharge lamps [66] and a preparative scheme has been described to enable sources for most elements to be made. The microwave power generator units and cavities have been critically examined and suggestions and designs have been put forward and shown to give improved spectral stability and warm-up characteristics. A versatile design of capillary burner using epoxy resin to bond the individual tubes is reported. This shows aspects of safety and produces a laminar gas flow not achieved with conventional slot or meker burners.

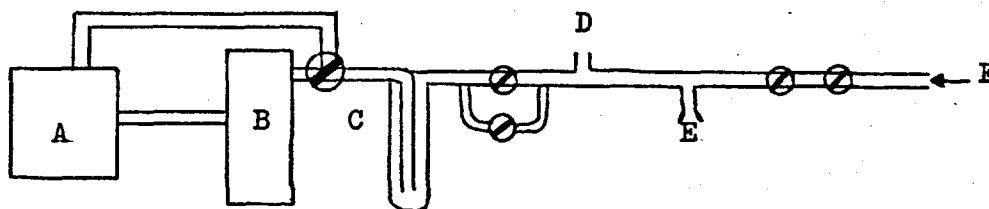
A method is proposed for the trace determination of sulphur in fuel oils and petrol hydrocarbon utilising the molecular emission band due to S_2 in the cool hydrogen diffusion flame.

Photon counting has been shown to provide a sensitive and versatile method for detecting low level and transient light signals, and should prove very useful in conjunction

with non-flame atom reservoirs. The ability to integrate the light pulse and give digital read-out will greatly assist research in this field.

A considerable amount of useful data concerning atomisation processes and interference effects in flame could be derived from the device described by Malmstadt ^{/59/}. This is capable of introducing isolated droplets of a known size into flames and with careful spacial detection systems atomisation processes could be studied and insight given into the interference effects which occur in flames.

Further research into factors affecting the stability and spectral quality of atomic emission from EDL's will require that the lamps be made under more rigorous conditions. To ensure this a good vacuum system must be used (Figure 48) which is capable of pumping to at least 10^{-4} - 10^{-5} torr. Non-mercury containing vacuum gauges should be used such as a thermistor gauge for the region atmospheric to 10^{-1} torr and an ion gauge for low pressures down to 10^{-5} torr.



- A Two-stage rotary pump
- B Silicone oil diffusion pump
- C Cold trap
- D Thermistor and Ion gauge
- E B10 adaptor
- F Inert gas from cylinder

Figure 48

The effect of pressure on an atomic line intensity and profile

could then be studied more accurately and a comparison made of intensity with charge weight at the optimum pressure examined.

There is a considerable amount of work which could be done on modulating and pulsing sources for use in atomic fluorescence. The modulation of microwave power until recently had always been with sinewaves mainly because modulation transformers were used. However, initial studies by the author show that square and pulse operation of EDL's is possible.

Non-flame atom reservoirs have shown considerable promise because of their lack of background noise. Unfortunately the cells depending on thermal atomisation of samples suffer from the problem that many compounds will vaporise rather than atomise and since there is very little thermal energy away from the heated device atomisation is not very efficient. A combination of thermal vaporisation followed by atmospheric argon plasma excitation for atomic emission may be a possible way of overcoming these disadvantages and still maintain the advantage of small sample handling.

For multielement analysis the ideal system would be a combination of atomic emission and atomic fluorescence using a continuum source and flame atom reservoir. If a brighter continuum source could be developed this would provide a very versatile and powerful tool for trace element analysis.

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