SOME PRACTICAL STUDIES WITH FLAMES USED IN ANALYTICAL ATOMIC SPECTROSCOPY.

by

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ABSTRACT.

The modification of the Beckman Laminar Flow Burner to facilitate separation of both the air-acetylene and the nitrous oxide-acetylene flame by inert gas shielding is described. The modified burners were employed for the determination of arsenic, selenium, lead, tellurium, zinc, vanadium, molybdenum and titanium.

The stability of separated flames is discussed and methods of flame stabilisation are described. A burner was designed and constructed which enables the sample to be aspirated into the flame without passing through the primary reaction cones.

The use of the nitrous oxide-acetylene flame for the determination of arsenic and selenium by atomic absorption spectrophotometry was investigated. The use of both single pass and triple pass optics was evaluated.

Boron was determined by flame emission spectroscopy employing an oxygen sheathed nitrogen-hydrogen flame. The Technicon A.F.S.6 spectrophotometer and the Technicon Autoanalyser were used in this investigation. They were also employed in the simultaneous determination of six elements by atomic fluorescence spectroscopy, after an automatic solvent extraction procedure.

ACKNOWLEDGEMENTS.

The work presented in this thesis is entirely original except where due reference is made and no part has been previously submitted for any other degree. The work was carried out in the Chemistry Department of Imperial College of Science and Technology, between October, 1969 and September, 1971.

I wish to thank my supervisor, Dr. G. F. Kirkbright and the Head of the Analytical Chemistry Department, Professor T. S. West, for their assistance and encouragement throughout this project.

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L. Ranson.

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CHAPTER 1.

INTRODUCTION

1.1 ATOMIC ABSORPTION SPECTROSCOPY.

Atomic absorption spectroscopy was not widely used as a general analytical technique for inorganic trace analysis until the description of a laboratory apparatus by Walsh [1] and Alkemade and Milatz[2]. Previously, flame emission spectroscopy had been used by analytical chemists as the principal flame spectroscopic method of analysis. During the past sixteen years there has been an almost exponential increase in the application of atomic absorption spectroscopy to analysis, and at the time of writing there are more than twenty major instrument manufacturers throughout the world who offer instrumentation for this purpose.

The essential features of such instruments are a stable light source, an atom cell to produce and contain atoms of the element to be determined, a prism or grating monochromator and a detection and readout system.

An atom has a discrete set of electronic energy levels and electrons within the atom may be excited by heat or radiation from a lower to a higher energy level. If radiation is used as the excitation source then one has the basis of atomic absorption spectroscopy. When a monochromatic beam of light passes through an absorbing medium

$$I_\nu = I_0 e^{-k_\nu l}$$

where Io is the intensity of the incident light, I_ν is the intensity of the transmitted light, k_ν is the absorption coefficient and l is the path length of the absorbing species. Now k_ν can be obtained as a function of ν . A plot of k_ν against ν is shown in Figure 1.1.

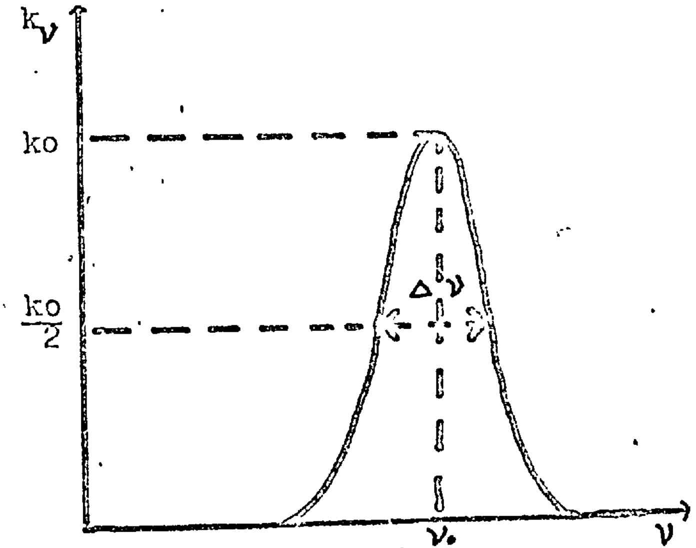


Figure 1.1.

The term $\Delta\nu$ is used to denote the distance between the two points at which the value of k_ν has fallen to half the maximum value ko and is termed the half-width of the absorption line. There are three main reasons for the fact that the line profile has a finite width. These are: natural broadening, Doppler broadening and Lorentz broadening. Natural broadening is a consequence of the

Heisenberg Uncertainty Principle. Doppler broadening is associated with the random thermal motion of atoms relative to the observer; and Lorentz broadening is due to the collision of the absorbing atoms with atoms or molecules of a different type.

It can be shown[3] that the integral of the absorption coefficient, called the integrated absorption, is proportional to the number of absorbing atomic species per unit volume, N. Thus

$$\int k_{\nu}\, d_{\nu} = \mathcal{K} N$$

where $\mathcal{K}$ is a constant independent of N. Therefore, if the integrated absorption could be measured, then N might be determined. Unfortunately this is difficult to achieve in practice. Walsh[1], however, suggested the measurement of the absorption coefficient at the line centre ko, as a method of determining N. Again, it can be shown that

$$ko = b\frac{2}{\Delta\nu}\int k_{\nu}\, d\nu$$

Therefore $ko = b\,\frac{2}{\Delta\nu}\,K\,N$, where b is a numerical factor. As $\log \frac{Io}{I_{\nu_0}} = k_{\nu_0} l$

then a plot of $\log \frac{Io}{I_{\nu_0}}$ against N should produce a straight line. This is the basis of analytical atomic absorption spectroscopy. To measure ko a beam of radiation is passed through the absorbing medium such that its frequency is centred on the absorption frequency ν_0. Also the emission half-width, $\Delta\nu_e$, should be small compared to $\Delta\nu$. Figure 1.2 shows the comparison of the absorption and emission line profiles.

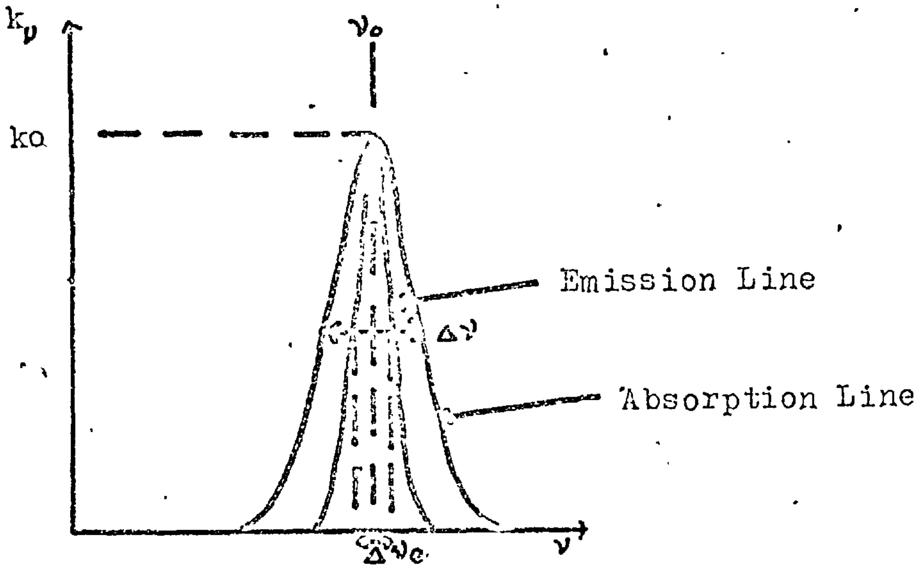


Figure 1.2.

Therefore, by measuring the power of the incident radiation that has been absorbed for known concentrations of the element to be determined, a calibration graph can be plotted and unknown concentrations determined. Absorption is greatest in lines resulting from transitions from the ground state (resonance lines). It must also be stated that if N becomes too large, then $\Delta\nu$ is not completely independent of N. Therefore, ko is not directly proportional to N, and a plot of log $\frac{I_0}{I_{\nu_0}}$ against N is no longer a straight line.

Electrons excited to higher energy levels by absorbing light may return to some lower level, losing energy in the form of radiation in the process. The emission of this radiation is termed fluorescence and is the basis of atomic fluorescence spectroscopy. This technique has recently been reviewed by West[4], Mansfield and Winefordner[5], and Windefordner and Elser[6]. When the excitation is by thermal means the measurement of the emitted light is the basis of flame emission spectroscopy.

In atomic absorption spectroscopy the source of radiation, atom cell and monochromator are in line on the same optical axis. To avoid detection of radiation emitted by the atom cell, which is usually a flame, the source radiation is chopped or modulated, and an A.C. amplifier tuned to the modulation frequency is employed. Each of the above components will now be discussed with greater emphasis on the atom cell.

Spectral Sources.

To-day the most common spectral source used for atomic absorption spectroscopy is the hollow cathode discharge lamp. These were first described for use in analytical atomic absorption spectroscopy by Walsh[7,8]. Hollow cathode lamps are normally filled with an inert gas such as helium or argon at a pressure of a few torr.

The cathode consists of the element to be determined. The vapour from the cathode enters the emitting plasma by cathode spluttering caused by the positive ions of the filler gas striking the cathodic surface, or by thermal evaporation due to cathodic heating during the discharge.

Although hollow cathode lamps can be prepared and operated satisfactorily for a wide range of relatively involatile elements, for highly volatile elements such as mercury, arsenic and selenium they are not satisfactory from the viewpoint of life-time and atomic line to background intensity ratio. For such elements microwave-excited electrodeless discharge lamps have been found most useful. These sources have been used previously as spectroscopic standards,[9,10]. Several workers have investigated these sources, including Winefordner[11] and Dagnall and West[12] for both atomic fluorescence and atomic absorption spectroscopy. An electrodeless discharge lamp consists of a small bulb of silica which contains a small quantity of the element whose atomic spectrum is required and an inert filler gas at a low pressure. The lamp is placed in a resonant cavity and the discharge is maintained by coupling with a micro-wave power generator; the discharge is generally initiated by a Tesla coil.

Other possible sources are vapour discharge lamps and continuum sources. Vapour discharge lamps are usually operated at low power for use in analytical atomic absorption spectroscopy work, in order to avoid self-reversal of the excited atomic resonance lines of the element contained in the lamp envelope. A monochromator of high resolution is required when continuum sources are employed for atomic absorption spectroscopy; this requirement results from the need to make the spectral band-pass of the source radiation transmitted by the monochromator comparable to the spectral half-width in absorption of the resonance line of the analyte atom.

Monochromators.

As just mentioned, if a continuum source is used a high resolution monochromator is required to isolate the particular resonance line of interest; these devices usually have low light transmission factors and are expensive. However, if a hollow cathode lamp or an electrodeless discharge lamp is used as a sharp line source, a less expensive monochromator of moderate resolution can be successfully employed for atomic absorption spectroscopy.

There are two principal types of monochromator; one employs a prism to disperse the incident radiation, the other uses a diffraction grating. By varying the angle of incidence of the incident radiation at the prism or grating, a particular wavelength of radiation can be detected at the exit slit. The resolving power of a monochromator is the capability to distinguish two separate spectral lines. In order to achieve the highest resolution permitted by the particular prism or grating employed, the exit slit width is usually made as narrow as possible. A narrow slit, though, allows less total radiant energy from the beam to reach the detector, hence the magnitude of the signal is decreased. A point is thus reached where the signal cannot be distinguished from the background noise. Thus an optimum slit-width must be used which gives the best compromise between signal-to-noise intensity ratio and spectral band-pass.

Detector-Readout Systems.

The radiant energy associated with the required spectral line isolated by the monochromator is most frequently detected by a photomultiplier. The incident radiation passes into the photomultiplier onto a photosensitive cathode. This results in the production of photo-electrons. The photoelectrons produced at the cathode are directed to a dynode chain, which results in multiplication of the electrons. The current which results can be measured directly or applied across a load resistor so that a voltage is measurable at a potentiometric recorder. As mentioned earlier, in atomic absorption spectroscopy the spectral source is modulated; therefore, before the signal is measured it is amplified by a tuned amplifier so that only the modulated signal is detected.

1.2 NON-FLAME ATOM CELLS.

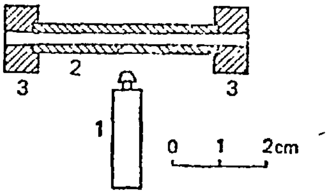
The work in this thesis has been concerned with the use of a flame as an atom cell. In recent years, however, there has been considerable interest in non-flame atom cells. A brief survey of the most important types of non-flame cells, as they are often termed, is given below:

Electrical Methods.

In such methods the sample, in solution form, is vaporised by electrical resistance heating. One of the first methods to be developed was the L'vov furnace[13]. A diagram of this furnace is shown in Figure 1.3a. This consists of a small cylindrical graphite furnace normally 3.0 to 5.0 cm. in length, and of 0.25 cm. to 0.3 cm. internal diameter. In earlier forms of the furnace the inside wall of the tube was lined with tantalum or tungsten foil to eliminate diffusion of vapour through the porous walls. More recently L'vov and his co-workers have lined the inside and outside of the tube with pyrographite, which prevents diffusion of vapour through the walls and ensures uniform heating of the tube and a longer life-time. The sample is evaporated on a graphite electrode which is introduced into the furnace. This electrode is placed in position below the tube, which is purged with argon and then heated for about 25 sec. to the required temperature. The sample, in solution or powder form, is then vaporised and the atomic absorption signal is recorded.

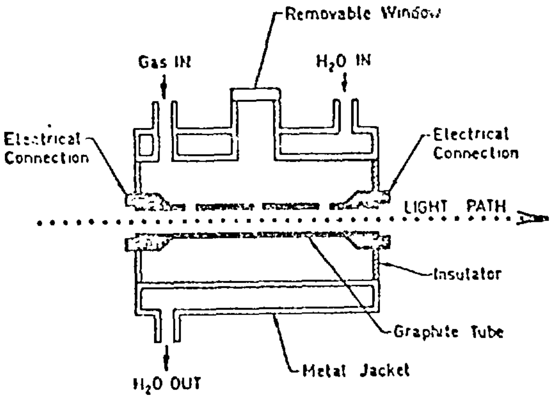
Another method is due to Massman[14], who developed an electrically heated graphite cell which is again purged with argon. A diagram of this device is shown in Figure 1.3b , and, as shown, can be used for both atomic absorption spectroscopy and atomic fluorescence spectroscopy. The sample is placed into the cell via a microsyringe and vaporised by the heat generated in the cell, the temperature of which can rise to 2,600°C. in a few seconds. Sample solution volumes of between 5 and 200 µl. were used for atomic absorption spectroscopy work and 5 and 50 µl. for atomic fluorescence studies. Solid samples up to 1 mg. in weight can also be used. Massman[14] determined several elements such as antimony, iron, thallium, lead, magnesium, silver and copper by atomic absorption spectroscopy using this device. Recently, Manning and Fernandez[15] have used a Massman cell to determine copper and strontium in milk. A non-flame technique has been developed by West[16,17,18,19] and co-workers; this technique utilises an electrically heated carbon filament, which is shown diagramatically in Figure 1.3c . The graphite filament is 0.2 cm. in diameter and about 2.0 cm. long, supported by water-cooled stainless steel electrodes. The sample, in solution form, is placed on a small depression in the filament via a microsyringe, 5 µl. being the volume usually taken. A heating cycle of drying, ashing and vaporising is then performed. The temperature of the filament can reach between 2,000 and 2,500°C. within 5 sec. by passing a current of about 100 Amp. at 5 volts through it. Several reports of this technique for practical application work have been reported, including the determination of lead in blood[20] .

Several other methods of producing an atomic vapour have been suggested, e.g. using a laser for pulse vaporisation of metal samples[21, 22] . The laser is used to evaporate the material from a preselected area of the specimen into the optical path of the atomic absorption spectrophotometer.



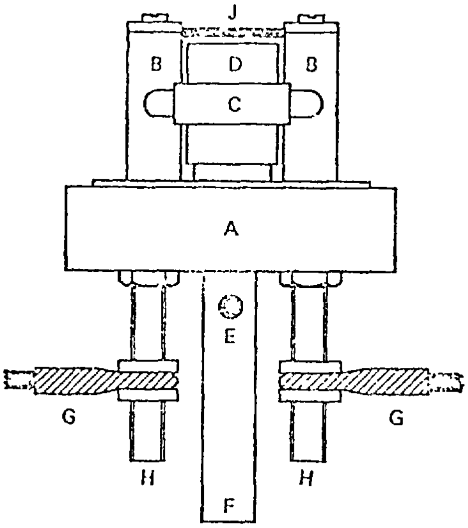
Graphite tube assembly of L'vov furnace (from L'vov): 1, electrode with sample; 2, crucible; and 3, graphite contacts placed inside coolers

a.



CROSS SECTION OF HEATED GRAPHITE ATOMIZER

b.



Filament atom reservoir (from Alder and West). A, base, B, water-cooled electrodes, C, water link between electrodes; D, laminar-flow box, E, inlet for shield gas; F, support stem for reservoir; G, transformer terminals; H, water inlet and outlet; and J, filament

c.

Figure 1.3.

It has been shown by Greenfield [23] and Wendt and Fassel [24,25], that an induction coupled plasma can be used as an atom cell. This type of plasma torch was developed in order to overcome the problem of electrode memory effects and electrode material contamination which is observed in the direct current plasma jet.

Wendt and Fassel have shown that by using triple pass optics elements such as aluminium, titanium and vanadium can be determined with a sensitivity (that concentration which gives 1% absorption) in atomic absorption spectroscopy similar to that obtained with a nitrous oxide-acetylene flame. One advantage of their system was that only 0.12 ml. per minute of sample solution was used; this compared with about 2.0 ml./min. for a flame. Veillon and Morgoshes , however, found that the detection limits of many elements determined by atomic absorption spectroscopy using the induction-coupled radiofrequency plasma torch were poor compared to flames. This illustrates one of the disadvantages of plasmas, the fact that they themselves emit radiation which can result in noise at the detector.

The main advantages of non-flame cells are:-

(a) They provide a very good micro-technique for small samples. Often the volume of sample available may be too small to be of use with an indirect nebuliser system.

(b) Ideally they do not exhibit emission or absorption background, which some flames do exhibit at the wavelength of the resonance line of the analyte element, giving rise to signal noise.

The following are some of the disadvantages of non-flame cells:-

(a) The absorption signal could be so transient that a rapid response system is needed to monitor it.

(b) They often exhibit greater interference effects[15].

(c) A continuum background occurs in the presence of matrix elements.

(d) Non-flame cells have poorer reproducibility than flames due to the manual sampling.

1.3 THE FLAME AS AN ATOM RESERVOIR.

The development of flameless atom cells is still in the early stages and they at present supplement, but do not replace, the flame in atomic absorption spectroscopy. The vast majority of all atomic absorption spectroscopy work is still undertaken using flame cells; this situation will probably persist except where only small liquid samples are available.

The most common type of flame used in atomic absorption spectroscopy is the premixed laminar flame. Such flames have a primary reaction zone from which the reaction products move into what is known as the interconal zone. The products in this zone then burn with the surrounding atmosphere, forming the secondary reaction zone.

In the primary reaction zone there are species such as C_2 and CH. These species give the intense blue radiation from this zone. Depending upon the flame other species that could be present are OH, NH, CN and NO. This zone is not in thermodynamic equilibrium, and one cannot, therefore, use the word "temperature" in connection with it.

The fuel is only partially oxidised in the primary reaction zone, so that the interconal zone immediately above the primary reaction zone contains species such as CO, H_2, CO_2, H_2O, O_2, N_2 and radicals such as H, OH, C_2 , CH and NO. This zone is frequently in approximate thermal equilibrium and experimentally determined flame temperatures are in good agreement with those which have been calculated. The flame temperature of a hydrocarbon flame varies with the fuel:oxidant ratio before the primary reaction zone. This is because as this ratio varies so does the concentration of the various species in the interconal zone. The highest flame temperatures normally occur when the gas mixture is stoichiometric. Thus, for an air-acetylene flame the stoichiometric reaction may be written as:

$$C_2H_2 + O_2 + 4N_2 \longrightarrow 2CO + H_2 + 4N_2$$

- and for the nitrous oxide-acetylene flame one may write:

$$C_2H_2 + 2N_2O \longrightarrow 2CO + H_2 + 2N_2$$

Species such as CO and OH react with atmospheric oxygen which is entrained or diffuses into the flame. This produces the secondary reaction zone. This zone emits a continuum which results from the chemiluminescence of the reaction of CO and atmospheric oxygen:

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2$$

In this zone intense radiation from OH produced on the oxidation of the hydrogen in the interconal zone is also observed. The secondary reaction zone is an outer mantle around the interconal zone and helps to maintain the high temperature in this zone. The mechanism and stability of such flames will be described in Section 1.8.

In a laminar flame the gas velocity has a parabolic distribution across the burner. When this is not the case a turbulent flame can be produced. A dimensionless quantity known as the Reynolds number, Re, is used to give an indication of whether a flame is turbulent or laminar. This number is defined by the following equation:

$$Re = \frac{vd}{\nu}$$

Where v = gas velocity
d = diameter of the burner
ν = viscosity/density

When Re is less than 2,300 the gas flow in the burner is always laminar; when the value is greater than 3,200 then the flame is generally turbulent.

For a flame to be used in atomic absorption spectroscopy care has to be taken into the design of the burner and nebulisation system. Several factors must be taken into consideration, such as safety, nebulisation and atomisation efficiencies and the noise produced by the flame.

Turbulent flow burners have been used successfully in flame photometry by several workers, including Gilbert[26] and Robinson[27]. These flames are safe. They cannot flash back because the fuel and support gases are only mixed at the point at which they enter the flame. The sample solution also enters the flame at this point. Although this burner appears to be very efficient, because all the sample solution enters the flame, several workers including Winefordner, Mansfield and Vickers[28], have shown that some of the aerosol vapour passes completely unaffected through the flame. Another disadvantage of this type of burner is that there is a great deal of flame fluctuation which results in noise at the detection system.

In a premixed laminar flow burner system the sample solution is aspirated from a capillary usually by the support gas. The aerosol produced then passes into an expansion chamber in which the larger droplets in the spray are collected. Thus only the smaller droplets enter the flame. The fuel is added either before or after this chamber. Willis[29] has made a study of the operation of a typical nebuliser, spray-chamber burner system. The burner heads usually have single slots between 7 and 10 cms. long for the air-acetylene flame and 5 and 7 cms. long for the nitrous oxide-acetylene flame. In the case of the air-acetylene flame a line of small holes is sometimes drilled through the steel burner head plate. Multiple slot burners have also been developed[30].

One of the disadvantages of the pneumatic nebuliser system is that only a small percentage of the total solution reaches the flame. Therefore, research has been carried out to develop different types of nebulisation techniques. One such technique is the ultrasonic nebuliser[31, 32]. In this type of system a fine spray is produced by using sound waves generated by a vibrating crystal. In order to obtain efficiencies better than those obtained with the pneumatic nebuliser, frequencies greater than 500 kHz and a high power must be used. Thus the simplicity, reliability and cheapness which are gained by using the pneumatic nebuliser is lost.

The function of the flame is to convert the sample solution droplets to an atomic vapour. The efficiency at which this occurs depends upon many factors and the type of flame. The process may be generalised as follows: The solution droplets are evaporated to produce solid particles which are then converted to a gaseous state. The molecules in this state are further dissociated to give a free atomic population.

1.4 THE TYPES OF FLAME USED IN ATOMIC ABSORPTION SPECTROSCOPY.

At the present time the two main types of flame used are the air-acetylene and the nitrous oxide-acetylene flames. In early work in analytical atomic absorption spectroscopy the flames used as atom cells were the relatively cool air-propane and the air-acetylene flame, the latter being used to a greater extent. These relatively cool flames do not permit the determination of several groups of important elements. These include elements such as beryllium, zirconium, aluminium, molybdenum, vanadium and titanium that form thermally stable (or refractory) oxides.

In the late 1950's Fuwa and Vallee[33,34,35] had investigated the use of the oxy-cyanogen flame as an atom reservoir for use in flame photometry. This flame has a burning velocity (see Section 1.8) of 140 cm.sec.$^{-1}$ and a temperature of about 4,500 °C. Robinson[36,27] investigated this flame further for use in both flame photometry and atomic absorption spectroscopy. Because of the high temperature of this flame, it was hoped that the oxides of the refractory metals would be dissociated. Somewhat surprisingly, at the time vanadium absorbed only slightly when determined by atomic absorption spectroscopy, and no absorption from aluminium or tungsten was observed. The flame temperature decreases appreciably when solutions are nebulised, however, and this prevents efficient and reproducible atomisation in this flame. The toxic nature of the fuel has also restrained extensive attempts to utilise the flame for atomic absorption spectroscopy.

In 1965, Willis[37] suggested the use of the premixed nitrous oxide-acetylene flame in atomic absorption spectroscopy. Amos and Willis[38] demonstrated that, using this flame, twenty-five more elements could be determined by atomic absorption spectroscopy, including the refractory oxide-forming elements which are only poorly atomised in the cooler flames. The temperature of the nitrous oxide-acetylene flame is about 2,900 °C. and it has a burning velocity of 180 cm.sec.$^{-1}$.

Fassel[39] has shown that the sensitivities obtained with the nitrous oxide-acetylene flame and the oxy-acetylene flame are comparable. Now, the nitrous oxide-acetylene flame has a temperature which is about 1,500°C. lower than the oxy-cyanogen flame. It seems, therefore, that the temperature of a flame is not the sole criteria for producing more atoms of the refractory elements. This topic will be discussed further in Chapter 2 .

Several other more exotic flames have also been investigated. One such flame is that of nitrous oxide-hydrogen. Dagnall, Thompson and West[40] suggested that this flame may be useful for the determination of the refractory elements as it has a burning velocity of 390 $cm.sec.^{-1}$ and has a temperature of 2,920°K. However, Willis, Fassel and Fiorino[41] undertook some further investigations with this flame and found that such elements as aluminium, vanadium and titanium are almost undetectable in absorption. A further paper by Dagnall[42] attempts to explain these discrepancies on theoretical grounds.

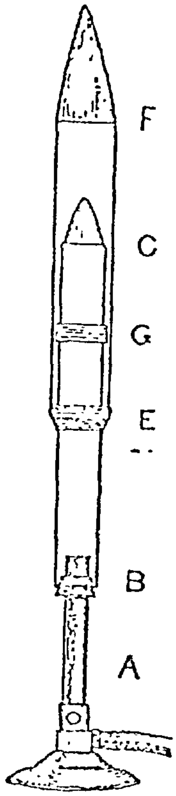
Another flame that has been considered for atomic absorption spectroscopy is the nitric oxide-acetylene flame,[43,44]. This flame has a temperature of about 3,100°C. and a burning velocity of 90 $cm.sec.^{-1}$. It has been found to give sensitivities for aluminium, tantalum and tungsten similar to those obtained with the nitrous oxide-acetylene flame.

The choice of flame for the determination of a particular element is very critical. Many considerations such as the sensitivity required, noise from the flame and interferences must be taken into account. This will be elucidated later in the thesis.

1.5 SEPARATED FLAMES USING MECHANICAL SEPARATORS.

The performance of premixed flames in analytical spectroscopy can be improved by separating the flame. A premixed flame as mentioned in section 1.3 has three main zones. They are the primary reaction zone, the interconal zone and the secondary combustion zone. Owing to the fact that the two different sets of reactions occurring in the primary and secondary zones have different burning velocities, it is possible to support each reaction at a different burner, i.e. to lift the secondary reaction away from the primary reaction zone.

Such a 'separated' flame was first reported by Teclu[45] and Smithells and Ingle[46]. These workers found that when a glass tube was placed over the top of a bunsen burner and the flame burnt on this tube, then by decreasing the fuel the flame flashed back and burned on the bunsen. The primary cone was then supported at the top of the bunsen and the secondary cone on the top of the glass tube, as shown in Figure 1.4 . The bunsen flame had been 'separated' and the interconal zone was visible through the glass tube without having to view through the secondary diffusion flame. The separated flame was used by Smithells and Ingle to study the composition of the interconal gases of the flame.



A = Bunsen burner
BC = Inner glass tube
EF = Outer glass tube
B: Joint is cork
E: Joint is a rubber ring
G: Asbestos ring

Figure 1.4.

As the interconal zone of a separated flame could be viewed without interference from the secondary zone, species in this zone may now be more easily examined spectroscopically. This fact was first used analytically for the determination of nitrogen in organic compounds [47]. A natural gas-air flame was used and the CN band emission at 388.3 nm. was monitored. Phosphorus and sulphur have also been determined by emission spectroscopy using a separated flame [48,49].

The use of separated flames for the determination of trace metals in analytical spectroscopy was first investigated by workers at Imperial College, although the possibility had been suggested by Mavrodinineau[50]. The first paper on this subject was by Kirkbright, Semb and West[51]. A fused silica tube was fitted to a Unicam meker type air-acetylene burner. A stable separated flame was obtained over a relatively narrow range of fuel-oxidant concentrations. It was found, as expected, that the flame background emission was considerably reduced. However, on separating a flame there is a decrease in the flame temperature. Under conditions of thermal equilibrium by the Boltzmann equation:

$$N = No\ e^{\frac{-E}{kT}}$$

where N is the number of atoms in a particular higher energy level, No is the number of ground state atoms, E is the energy required, k is the Boltzmann constant and T is the absolute temperature. Thus in flame emission spectroscopy

$$I \propto e^{\frac{-E}{kT}}$$

where I is the intensity of the emitted light.

Therefore, a reduction of flame temperature will cause a reduction in the emitted light intensity. This was in fact found when metal solutions were sprayed into the separated flame. Nevertheless, improved detection limits were obtained for bismuth and magnesium. These elements have their main emission lines in the highest flame background region which causes noise at the detector and prevents the use of a wide spectral band-pass. On separation of the flame this is greatly reduced and provides for improved detection limits.

The nitrous oxide-acetylene flame has also been separated with a quartz tube device, and elements which form refractory oxides, such as alumunium, beryllium, molybdenum, titanium, vanadium and tungsten have been determined by flame emission spectroscopy[52]. The quartz separator used for this flame was fitted with a short side arm, at the end of which a silica window was fixed. A Unicam cylindrical air-acetylene burner barrel was used, but the Meker type burner head used for air-acetylene was replaced with a circular slot. On separation, the slightly fuel rich nitrous oxide-acetylene flame had a greatly extended reducing interconal zone compared to the unseparated flame. Although the emission due to OH and CO was reduced on separation, that due to CN and C_2 was enhanced by the protective effect of the tube device in shielding the reducing interconal zone from oxidation by the surrounding atmosphere.

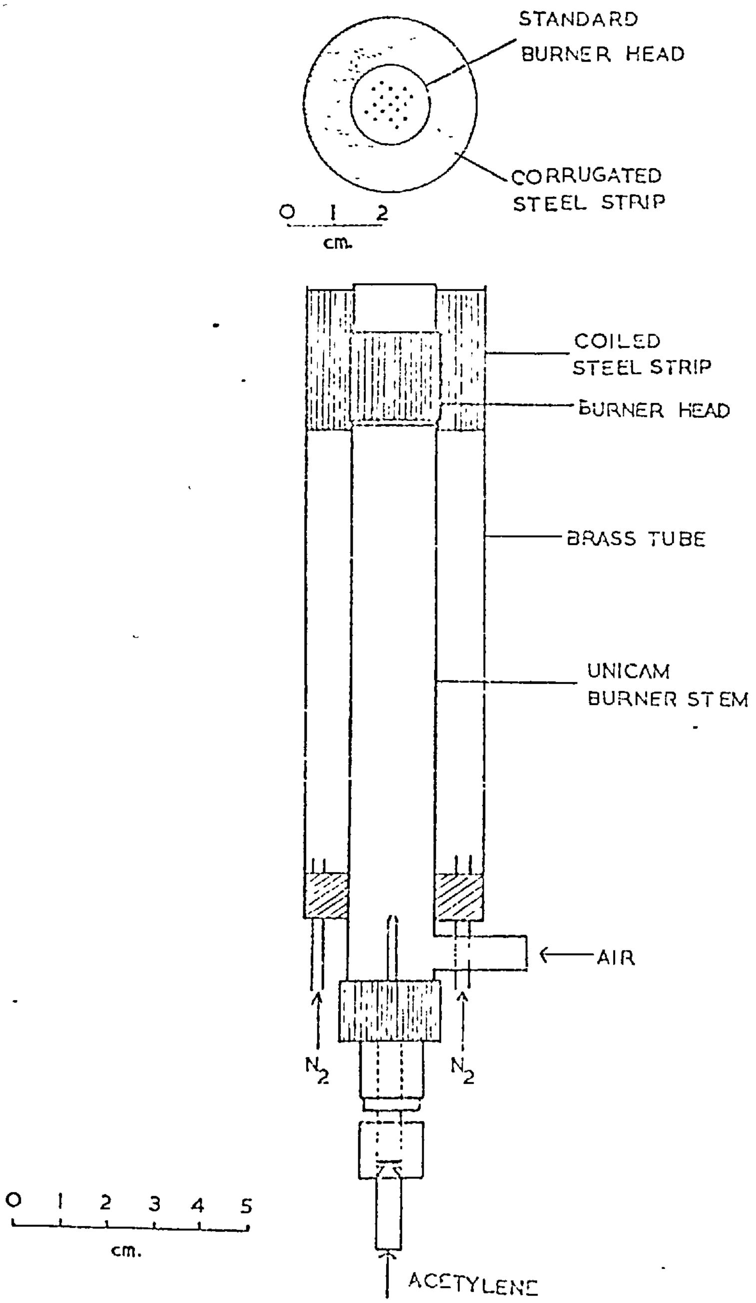
The first use of a separated flame in atomic absorption spectroscopy was described by Hingle, Kirkbright and West[53]. A Unicam air-acetylene burner was used, over which a pyrex separator was placed. A long tube was placed in the side of the separator, thus enabling the interconal zone flame gases to be drawn along it by suction to produce a long absorption path. A small side arm was also placed in the silica separator which enabled hydrogen to be introduced to the base of the secondary diffusion zone and hence stabilise it in fuel lean conditions. Again the flame background was considerably reduced and a stable flame was obtained along with good sensitivity for zinc, iron, copper, mercury and magnesium.

The long path nitrous oxide-acetylene flame has been mechanically separated by Ure[54], this was accomplished using silica plates. Ure reported the determination of molybdenum with this burner.

1.6 SEPARATED FLAMES USING INERT GAS SHIELDING.

One of the problems in using the quartz type separator tubes described earlier is their liability to devitrification carbon deposition when organic solvents are nebulised. In addition, stable separated flames can only be achieved over a relatively limited range of flame gas compositions. These disadvantages may be overcome by using an inert gas to effect the separation of the zones. Much of the work in this thesis is devoted to the use of such flames. In this section, therefore, the history of such separated flames will be traced, the results obtained being more fully discussed in later chapters.

The first paper to describe the use of an inert gas separated flame for analytical determinations was by Hobbs, Kirkbright, Sargent and West [55]. The shielding of a premixed air-acetylene flame using nitrogen, however, had previously been described by Alkemade and Zeegers[56,57]. These workers used such flames for the study of the formation, recombination and electronic excitation of flame radicals. Kirkbright et al [58] passed nitrogen upwards in a laminar flow around a premixed laminar flame. Figure 1.5 shows the burner type and the gas shielding arrangement.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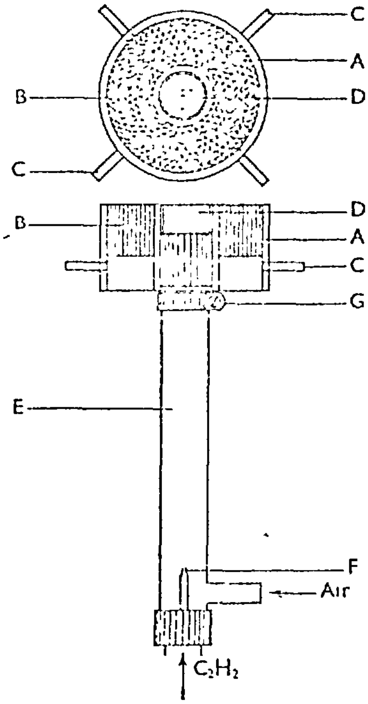
ACETYLENE

Figure 1.5.

A cylindrical Unicam air-acetylene emission burner was used. A brass tube was placed over the burner and held in place with a rubber bung. The end of the brass tube, which was in the same horizontal plane as the burner-head, was packed tightly with alternate corrugated and flat stainless steel strips (0.1 mm. in thickness and 2 cm. wide). The nitrogen flow rate was about 10 litres/min. and a stable flame could be supported over a wide range of acetylene:air concentration ratios. Improved detection limits were reported for the determination of bismuth by flame emission spectroscopy and for cadmium and zinc by atomic fluorescence spectroscopy. These improvements were a direct result of reduction in the flame background noise on separation. An inert gas separated flame does not have the disadvantages associated with quartz tube separators. Hobbs, Kirkbright and West[55] reported improved detection limits for fifteen elements for the separated air-acetylene flame compared to the conventional air-acetylene flame.

Figure 1.6 shows the burner arrangement used:



A = Brass shielding jacket
B = Coil of alternate layers of corrugated and flat cupro-nickel strip
C = Nitrogen inlet pipes
D = Stainless-steel burner head
E = Stainless-steel burner stem
F = Acetylene jet
G = Adjustable clip to retain shielding jacket at desired height

Figure 1.6.

Comparing Figure 1.5 with Figure 1.6 , it can be seen that the separator chamber is reduced in length.

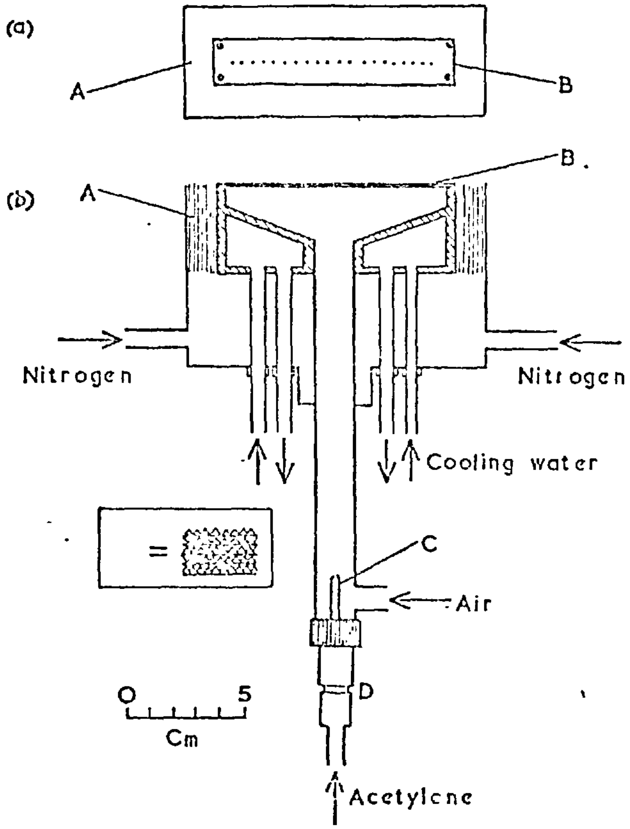
The arrangement shown in Figure 1.6 was used for the separation of the nitrous-oxide acetylene flame.

The air-acetylene head was replaced by a stainless steel head with a circular slot 0.75 mm. wide, with an internal diameter of 11 mm. . On separating the nitrous-oxide-acetylene flame, the secondary zone was 'lifted' ca 7.0 cm. above the burner head. The CO and OH emission from the flame was suppressed and that of the CN increased. This increase was greater when argon rather than nitrogen was used as the shielding gas. This may be due to the fact that nitrogen cools the flame more than argon. Improved detection limits for the determination, by flame emission spectroscopy, of Al, Be, Mo, Mb, Si, Ti, V, W, and Zn were obtained using the separated flame.

The use of an inert gas separated flame for atomic absorption spectroscopy was first described by Kirkbright, Sargent and West 59 . Figure 1.7 shows the burner arrangement used. It consisted of a standard premixed Unicam Meker-type long path air-acetylene burner, around which a shielding tank was fitted and packed with the previously described metal strip. The burner was water-cooled.

Nitrogen separation of the air-acetylene flame for the determination of Arsenic and Selenium by atomic absorption spectroscopy resulted in improved detection limits, compared to the conventional flame. This is because the separated flame has lower flame background and hence lower noise levels are experienced. Kirkbright, Sargent and West[60] described the separation of the nitrous oxide-acetylene flame by nitrogen or argon and its use in atomic absorption spectroscopy. The burner arrangement used was essentially the same as that shown in Figure 1.7, except that the burner-head consisted of two stainless steel blocks screwed to the top of the burner to give a slot 5.0 cm. long and 0.038 cm. wide. Significant improvements in detection limits and sensitivities were obtained for the elements Al, Be, Ge, Mo, Si, Ti, V and Zr; using the separated flame. Amos, Bennett and Brodie[61] have reported similar improvements. The improvements obtained by using a separated flame in atomic absorption spectroscopy will be discussed in much more detail in Chapter 2.

Separated flames using an inert gas have been used successfully in atomic fluorescence spectroscopy. Browner, Dagnall and West[62] used a separated Argon/Oxygen/Hydrogen flame for the determination of lead.



Long path nitrogen-shielded burner.
a) Top view.
b) Side view.
A = Laminar flow packing
B = Removable burner plate
C = Acetylene jet
D = Anti flashback valve

Figure 1.7.

Sychra and Matousek[63] have also determined lead, by atomic fluorescence spectroscopy, using a separated air-acetylene flame. The air-acetylene flame was burned on a Techtron FE-1 emission burner. A chamber with five concentric rows of holes and a tangential nitrogen inlet was fitted round this burner head. A diagram of this arrangement is shown in Figure 1.8:

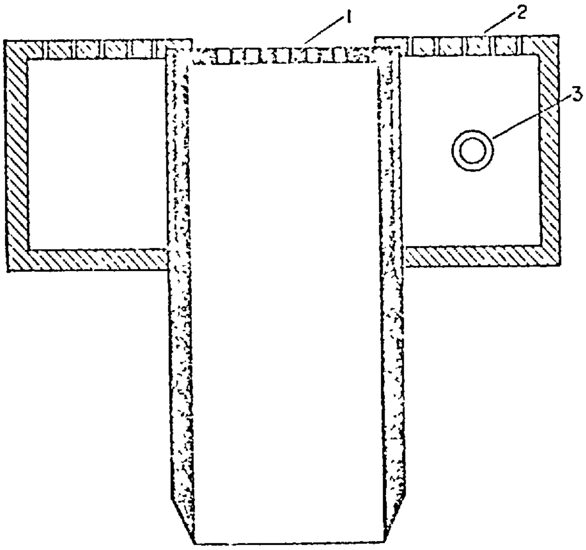


Figure 1.8.

These workers[64] have also determined gold by atomic fluorescence spectroscopy and using a nitrogen separated air-acetylene flame.

Dagnall, Kirkbright, West and Wood[65] have used the separated nitrous oxide-acetylene flame for the determination of germainium by atomic fluorescence spectroscopy. Flame separation gave an improvement in the detection limit compared to the conventional flame. The improvement with argon as the sheathing gas being greater than when with nitrogen. These workers have also used the separated nitrous oxide-acetylene flame to determine the atomic fluorescence characteristics of aluminium, molybdenum, titanium. vanadium and zirconium[66].

More recently Larkin and Wills[67,68] have used the separated air-acetylene, nitrous oxide-acetylene and the nitrous oxide-hydrogen flames in a non-dispersive system for atomic fluorescence spectroscopy. Excellent detection limits for several elements with resonance lines below 300 nm. were obtained with this system[67]. A separated air-acetylene flame is incorporated in the Technicon A.F.S.6 multielement atomic fluorescence instrument[69]. Cresser and Keliher[70] have recently studied the separated nitrous oxide-hydrogen flame and the separated air-MAPP and nitrous oxide-MAPP flames for flame emission spectroscopy. MAPP gas is a mixture of methylacetylene and propadiene with propylene and other hydrocarbons as stabilisers.

1.7 THE STABILITY OF FLAMES.

One of the problems involved with the practical uses of separated flames is their instability at high fuel and support gas flow rates. This is the case for both mechanically and inert gas separated flames. Before discussing the stability of such flames it is necessary to consider the stability of normal premixed laminar flames.

Until 1967 the principal theory for the stability of flames, especially their blow-off limit, was that of Lewis and von Elbe, the boundary velocity gradient theory [71, 72, 73, 74]. In 1967, Reed [75, 76] suggested a new theory, the flame stretch theory of blow-off, which questions some of Lewis and von Elbe's concepts.

There are two limits to the stability of a flame at a burner port, the flash-back and the blow-off limits. For a given composition of premixed combustible gas (oxidant and hydrocarbon) passing in laminar flow through a burner tube, a critical gas flow is reached at which the flame no longer sits on the burner rim, but travels back down the tube. This condition is known as flash-back. There is also a critical gas flow at which the flame will rise from the burner rim. Such a condition is known as blow-off. Each of the two theories of flame stability will now be discussed.

The Boundary Velocity Gradient Theory.

A combustion wave which propagates through a mixture of oxidant and fuel is in fact a zone of burning. In this zone, heat and chain carriers flow to an adjacent layer in the gas mixture, so initiating heat and chain carriers in this layer, which itself becomes a source for the next layer. The rate at which this propagation occurs is called the burning velocity, Su, and is the velocity of the unburned gas with respect to the wave.

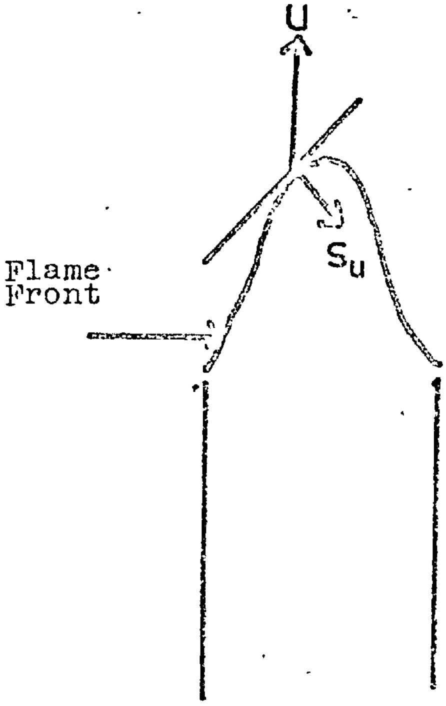
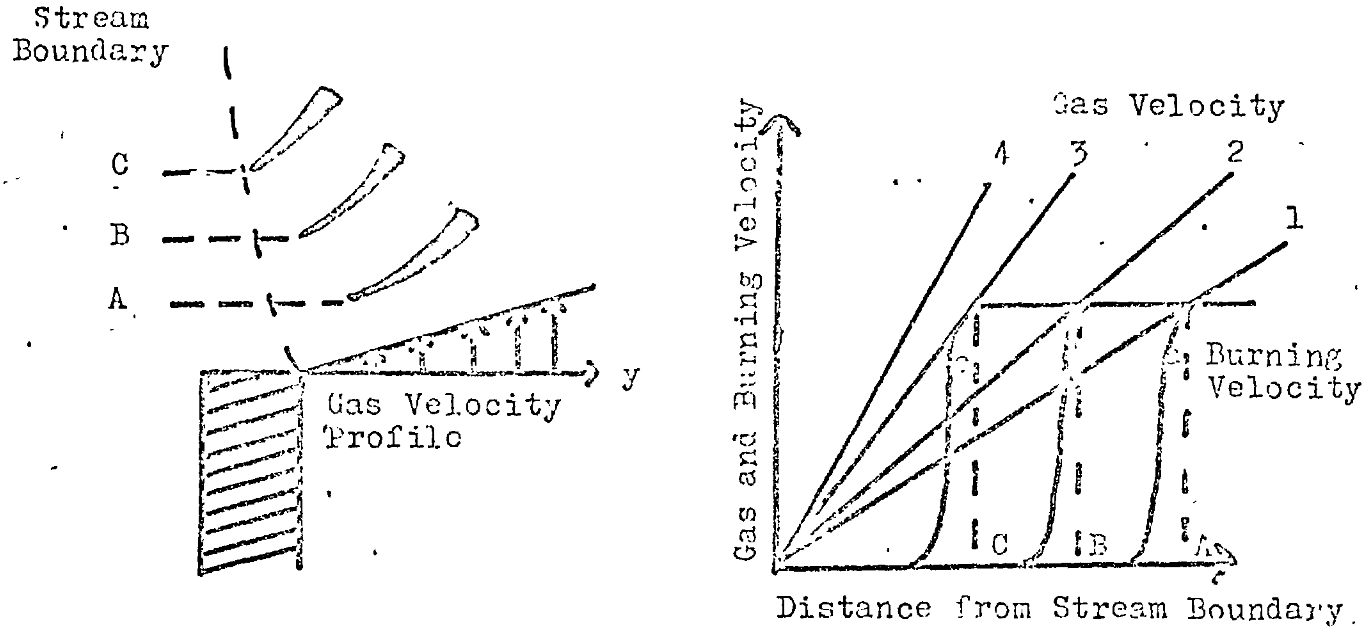


Figure 1.9.

If one considers a flame stabilised on a burner, the burning velocity varies from the normal value, Su, to zero at the burner rim. The value falls to zero because the burner port is a heat sink, so lowering the temperature which reduces the concentration of chain carriers and causes the flame reactions to be quenched. The burner rim also adsorbs some of the chain carriers. Assuming that the fringe of the combustion wave approaches the burner rim, then the gas velocity, U , will be greater than the burning velocity, Su, and so the wave will be driven back from the rim by the gas flow. As the wave is now at a larger distance from the heat sink, the loss of heat and chain carriers is reduced and hence the burning velocity is increased. A position is eventually reached at which at some point on the combustion wave the burning velocity, Su, equals the gas flow velocity, . Then the flame is stabilised with respect to the rim. The distance between the flame base and the burner rim is termed the "dead space."

If the diameter of the burner port is large, the gas velocity profile is considered to be linear, i.e. the flow lines are assumed to travel parallel to the burner wall. In fact, due to thermal expansion, the flow lines are bent outwards. This is shown in Figure 1.10(I), which also serves to explain Lewis and von Elbe's boundary velocity gradient theory.



I.

II.

Figure 1.10.

For a given flow rate of the combustible mixture, the flame is stabilised at some point a distance A from the stream boundary. That point being where the local gas flow velocity is equal to the burning velocity. Figure 1.10(II) shows that this point is where the gas velocity line 1 is a tangent to the burning velocity, curve a. As the gas velocity is increased the flame base moves further away from the burner port and the dead space increases as shown in Figure 1.10(a) . As there is less quenching of the flame reactions by the burner rim, the burning velocity consequently increases and a new equilibrium position is reached at a distance B from the stream boundary. This position is where the gas velocity line 2 is a tangent to the new burning velocity, curve b. Further increases in the gas flow rate result in the flame being stabilised at position C. As the dead space increases so the combustible mixture becomes more and more diluted by interdiffusion with the surrounding gases. This gives rise to a decrease in the burning velocity. A point is then reached at which the increased burning velocity due to increased distance from the burner rim is compensated for by the decreased burning velocity due to interdiffusion. A gas flow velocity is then reached which exceeds the burning velocity everywhere, and the flame blows off. This is indicated by the gas velocity line 4.

Flash-back can be described in a similar way with reference to Figure 1.11.

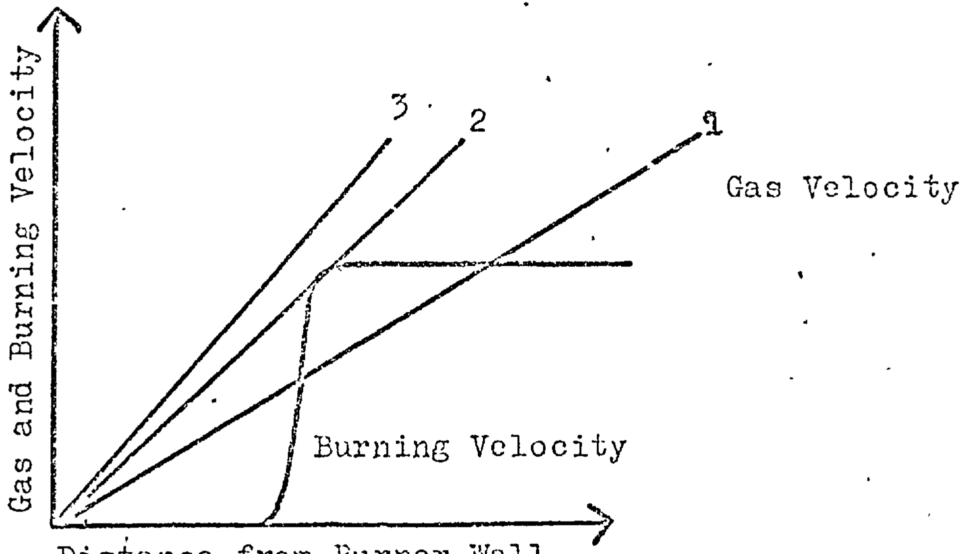


Figure 1.11.

If the gas velocity described by line 1 cuts the burning velocity curve, then the combustion wave moves down the burner tube against the gas flow. The flame is then said to have 'flashed back.' Line 2, which is a tangent to the burning velocity, indicates the gas flow at which flash-back does not occur. Line 3, which is outside the burning velocity curve, indicates the gas flow at which the combustion wave moves out of the tube.

Lewis and von Elbe state that the conditions of flash-back and blow-off can be described by a term called the '<u>boundary velocity gradient</u>,' g. This value is defined by the following equation:-

$$U = gy$$

where 'U' is the gas velocity, 'y' is the distance from the stream boundary, and 'g' is a constant. When the gas flow is reduced, g decreases and at the point of flashback the value of g is denoted by g_F. Similarly, when the gas velocity is increased, g increases until a value g_B is reached, the value at the blow-off condition.

Since the development of this theory many workers have used the concepts of the boundary velocity gradient theory to interpret their results on flame stability. Maccallum and Grumer,[77] Harris and Schultz[78] have studied stabilisation and blow-off limits at non-circular ports. It is found that if the critical boundary velocity at blow-off is plotted against the percentage of fuel gas in the mixture, then no matter what the burner size or shape is, the data lie close to a single curve. This is shown by Figure 1.12-

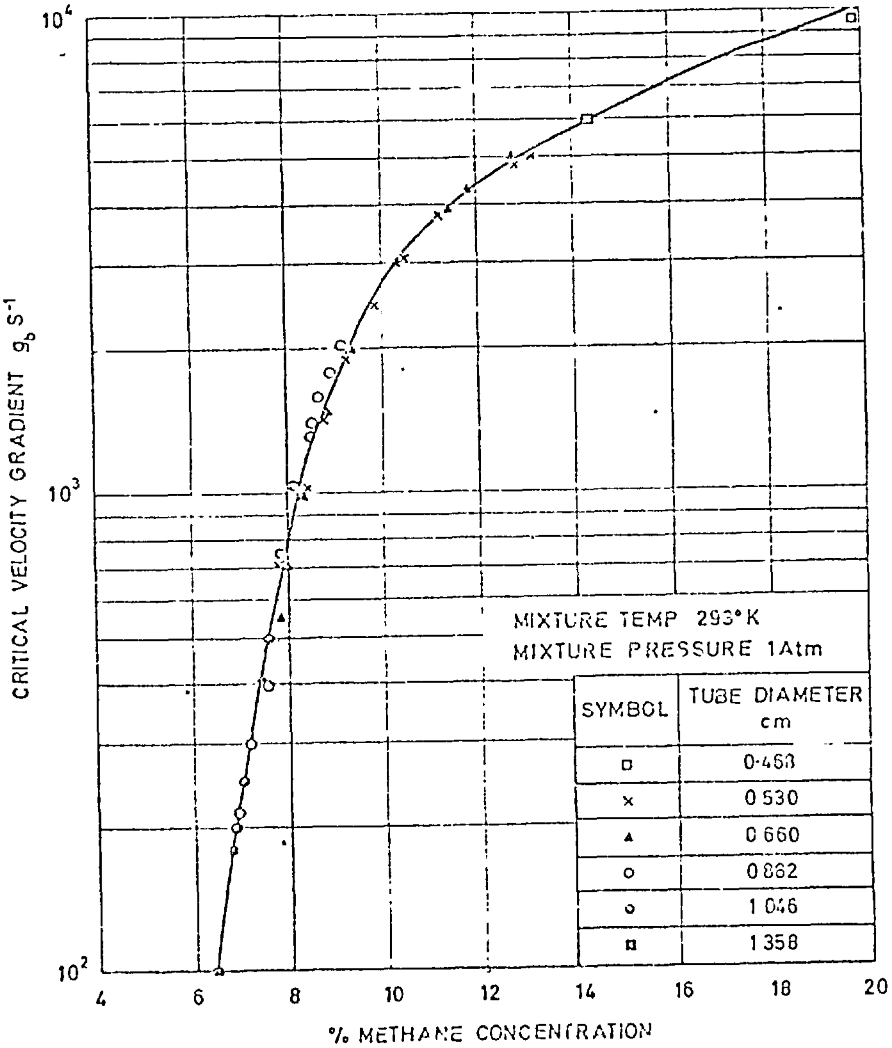


Figure 1.12.

The Aerodynamic Quenching or Flame Stretch Theory.

Reed 75, 76 has suggested a new theory to explain the phenomena of 'blow-off.' His reason for proposing a new theory is because certain experimental observations do not agree with Lewis and von Elbe's theory. As stated in the previous section, according to the boundary velocity gradient theory an increase in the gas mixture flow rate results in an increase in the dead space, eventually leading to blow-off. Reed[76] states that in certain cases such an increase in the dead space with increased gas flow is not seen to occur. Another example[79] is that when the burner diameter decreases the dead space increases. One would, therefore, expect there to be changes in the boundary velocity gradient, because there is more time available for the atmosphere to diffuse into the stabilising region. In fact no significant changes are observed to occur, except when the burner diameter becomes very small.

If the gas velocity distribution of the unburned gas approaching the flame is uniform, then an amount of energy will be transferred to this unburned gas equal to that convected back into the flame when the preheated gas moves on into the reaction zone. On the other hand, if there is a gas velocity gradient as at the burner wall, then some of the energy transferred to the preheated gas will return to a different part of the flame front from which it came.

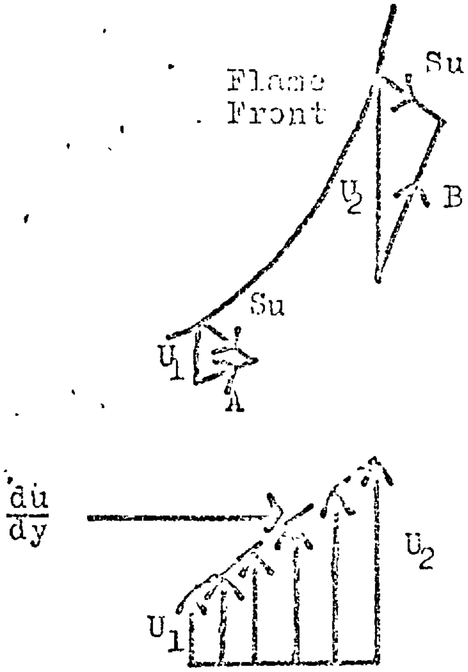


Figure 1.13.

Consider Figure 1.13, which shows a flame front propagating against a gas mixture in which the gas velocity increases from U_1 to U_2 . The flame front takes up a shape such that the component of the gas velocity normal to the flame front equals the burning velocity, which is assumed to be constant.

From Figure 1.13 it can be seen that the component of the gas velocity U_1 parallel to the flame front is smaller than that due to the gas velocity U_2. This change in the flow component parallel to the flame front represents an energy flux. Thus energy is transferred from the low gas velocity region to the high velocity region in the preheat zone. Therefore, the greater the velocity gradient $\frac{du}{dy}$, the greater the cooling of the flame and hence the greater the quenching.

The amount of quenching can be measured by the dimensionless quantity k, called the Karlovitz[80,81,76] factor. It can be shown that this factor

$$k = \frac{du}{dy} \cdot \frac{\eta_o}{U}$$

, where $\frac{du}{dy}$ is the gas velocity gradient, η_o is the thickness of the preheat zone, and U is the local gas velocity. The term k was introduced by Karlovitz as a measure of the stretch in a combustion wave. As shown in Figure 1.13 when a combustion wave propagates in a velocity gradient, the flame becomes curved. Since the flame presents a convex surface to the unburned gas, the area is greater on this side than on the burned-gas side. One can say, therefore, that the flame has stretched. Because of this, the volume of gas per unit area to be heated to the reaction temperature is greater than in plane wave propagation. This results in the lowering of the flame temperature and can, therefore, lead to flame extinction.

Reed suggested that as the gas flow velocity is increased there will be a critical value of k at which the flame will be extinguished, i.e. blows off. Furthermore, this value of k should be constant for all gases and all conditions of mixture composition, temperature and pressure.

The equation $k = \frac{du}{dy} \cdot \frac{l_o}{U}$ can be rewritten as follows; $k = \frac{l_o}{Su} g_B$ This is because the area of interest is the stabilising region,

$\frac{du}{dy} = g_B$ the boundary velocity gradient

and for a stable flame $U = Su$ the normal burning velocity. Reed collected data from the literature and plotted $g_B \cdot \eta_0$ against Su on a logarithmic scale. This was done first for flames with no secondary diffusion zone, i.e. fuel lean flames or flames surrounded with an inert atmosphere. The graph obtained is shown in Figure1.14:-

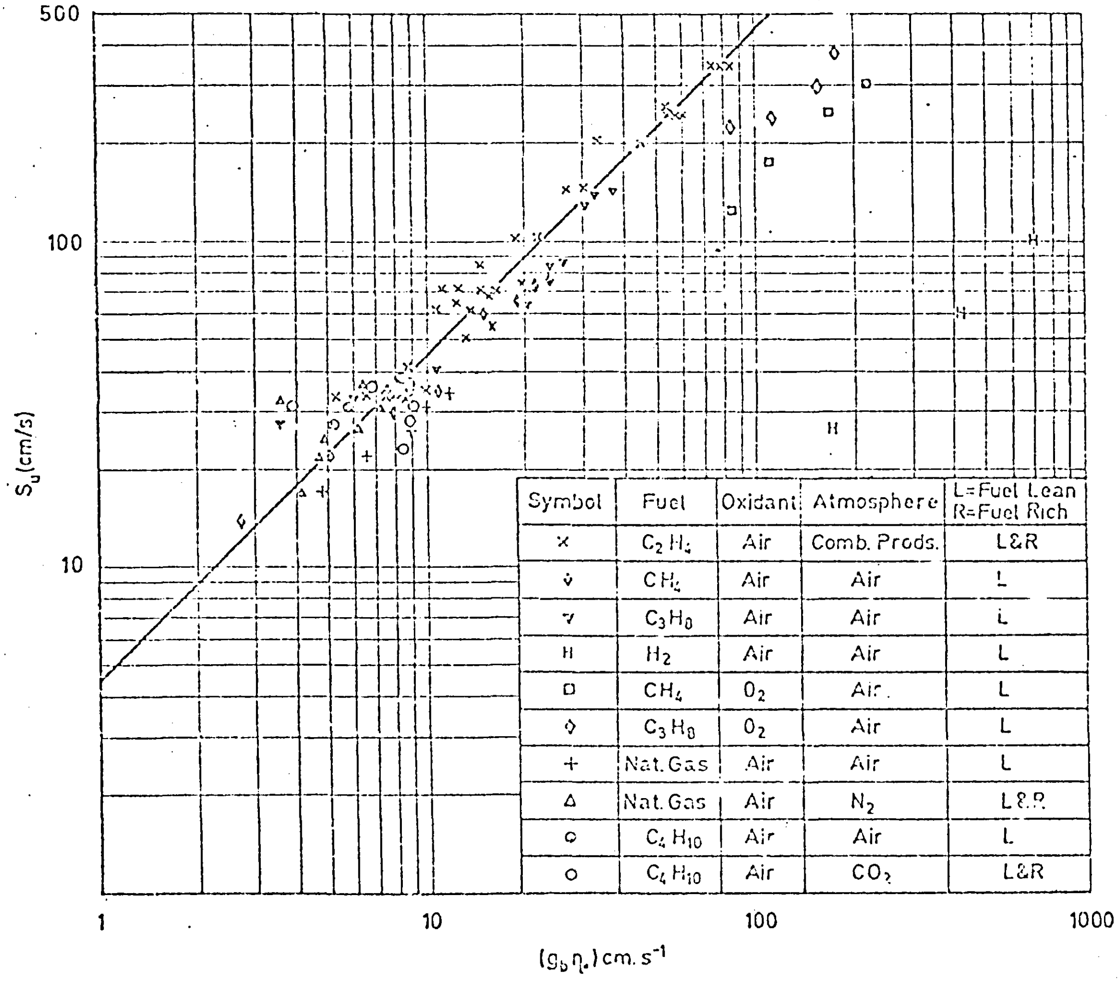


Figure 1.14.

It can be seen from the figure that correlation with a straight line is good, except for the hydrogen-air and the methane-oxygen flames. In the case of flames with a secondary diffusion zone, it is found that the value of k is greater than that for the flames with a primary reaction zone only. This greater resistance to quenching can be attributed to the outer mantle acting as an energy source or pilot light which can transfer heat to the stabilising region of the inner cone.

1.8 THE STABILITY OF SEPARATED FLAMES.

The two theories of flame stability previously described come to different conclusions. Lewis and von Elbe state that the main physical effect leading to blow-off at a burner rim is the diffusion of the surrounding atmosphere into the combustible mixture. This lowers the burning velocity due to dilution of the gas mixture and negates the increased burning velocity caused by the flame base being further from the burner rim. Thus a point is reached where $U > Su$ and the flame blows off.

The flame stretch theory of blow-off, by Reed, states that the diffusion of the surrounding atmosphere is only a secondary effect and that the main reason is that the flame stretch in the stabilising region reaches a critical value.

In a separated flame where the flame is surrounded by an inert gas such as argon or nitrogen the effect of the surrounding atmosphere on flame stability is of utmost importance. Studies by Lewis and von Elbe[72] show a flame is less stable if it is surrounded by an inert gas such as helium, carbon dioxide and nitrogen. This can be seen from Figure 1.15 :

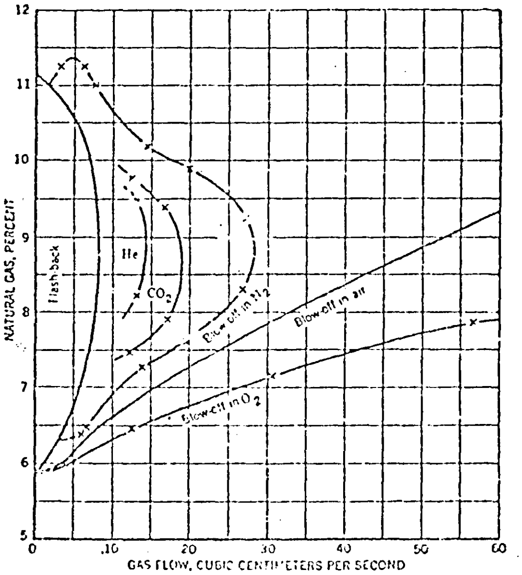


Figure 1.15.

The flame is more stable if the surrounding atmosphere is air or oxygen.

The instability of the flame increases in the order nitrogen, carbon dioxide, helium. This fact lends weight to the theory of Lewis and von Elbe, which emphasises the effect of interdiffusion on the burning velocity in the boundary layer of the gas stream; Helium having the greatest diffusion effect.

The greater effect of carbon dioxide as compared with nitrogen suggests the influence of the higher heat capacity of this gas on the temperature in the combustion zone at the boundary.

For nitrogen Cp = 6.898 cals./deg./mole..

whereas for Carbon Dioxide Cp = 8.993 cals./deg./mole.

Reed states that the removal of the secondary zone from the flame by an inert gas removes a source of energy which helps stabilise the flame. Thus the value of k, which is a measure of the flame stability decreases. The practical studies of flame stability will be discussed in later chapters.

CHAPTER 2.

THE USE OF A COMMERCIAL ATOMIC ABSORPTION SPECTROPHOTOMETER WITH A LAMINAR FLOW BURNER MODIFIED TO PERMIT FLAME SEPARATION.

2.1 INTRODUCTION:

Most atomic absorption spectrophotometers are fitted with an indirect pneumatic nebuliser, a spray (or expansion) chamber and a burner to support the flame used as the atom cell. The two most common types of indirect pneumatic nebulisers are shown in Figure 2.1 . In the 'right-angle' nebuliser the gaseous stream duct is placed at right angles to the duct for the sample solution. The second type of nebuliser has the two ducts arranged concentrically. In both types the stream of gas emerges from its nozzle with high velocity, entrains some liquid from the outlet of the liquid duct and tears from the liquid surface fragments which then disperse into a cloud of fine droplets.

There are several important requirements for the nebuliser used to supply a premixed flame with sample. These may be summarised as follows:-

(a) The rate of sample aspiration should be stable and reproducible.

(b) The mean drop-size in the mist should be reproducible and as small as possible. It has been shown[82]

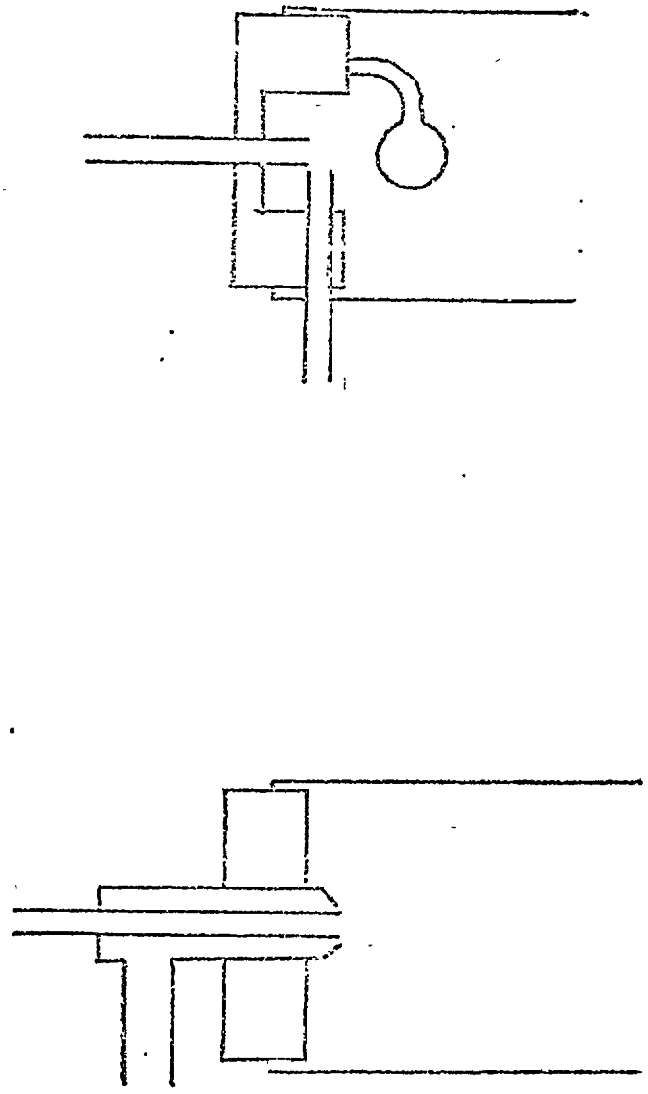


Figure 2.1.

that the smaller the drop-size, the less are the interferences in flame emission and absorption spectroscopy.

(c) The flow-rate of oxidant gas producing the optimum spray-rate should be as close as possible to that needed to support the required flame.

(d) The highest possible sample concentration per unit volume of nebulising gas should reach the base of the burner after the larger drops have fallen out of the stream in the spray chamber. Such a constant concentration of analyte should be attained in the flame as rapidly as possible after the commencement of nebulisation. The nebuliser and spray-chamber should be easily and quickly washed free of the residue of one sample before the introduction of the next.

(e) The nebuliser and spray-chamber should not be prone to clogging after long periods of use. It should also be constructed of material which resists corrosion. Modern flame spectrophotometers have nebulisers made of platinum-iridium alloy (90%:10%), while the spray chamber is constructed out of glass or inert plastic.

The main requirement of an indirect spray chamber unit is that the fraction of the original solid content of analytical samples nebulised reaching the flame be as large as possible. Many of the larger droplets collect on the walls of the spray chamber and leave the chamber via a drain tube. Several commercial spray chambers have baffles incorporated in them which help fragment the larger droplets. The efficiency of the nebulisation system is defined as the fraction of the nebulised analyte which passes into the flame, and is usually ca 5%, and rarely never more than 10%. When organic solvents are used, however, the efficiency may be as high as 20%. This organic solvent effect results from the effect of the surface tension, viscosity and vapour pressure of the organic solvent in decreasing the mean drop size and increasing the rate of evaporation of solvent from the droplets. Therefore, there is an increase in the amount of sample reaching the flame.

The main criteria in burner design is that it be safe. The danger of 'flash-back' must be reduced to a minimum. Usually, the gas flow velocity must be at least three times the burning velocity of the gas mixture. The following points illustrate further requirements for the design of efficient, safe burners:-

(a) The burner head plate should have sufficient thickness to quench any flash-back, should it occur, and it should provide as near a laminar flow as possible.

(b) The burner should be constructed of material of good thermal conductivity, in order to dissipate heat efficiently.

(c) The burner slot should be wide enough to ensure that there is no clogging by solutions containing a high dissolved solid content. A compromise in the required width must be reached so that the flame is safe when 'flash-back' occurs.

(d) The burner must be free from tendency to corrosion by acid solutions nebulised into the flame. Normally burners have been constructed from stainless steel, although titanium is being increasingly used for the burner top-plate.

2.2 The Beckman Laminar Flow Burner.

The Beckman Laminar Flow Burner was first described by Hell in 1965[83]; a further review of its properties appeared in 1968[84]. Hell designed a burner for both nitrous oxide-acetylene and air-acetylene flames after first questioning the concepts of burner design. As well as designing the burner, he devised a spray chamber. This chamber was infra-red heated to assist desolvation and had a condensing system incorporated to remove excess solvent.

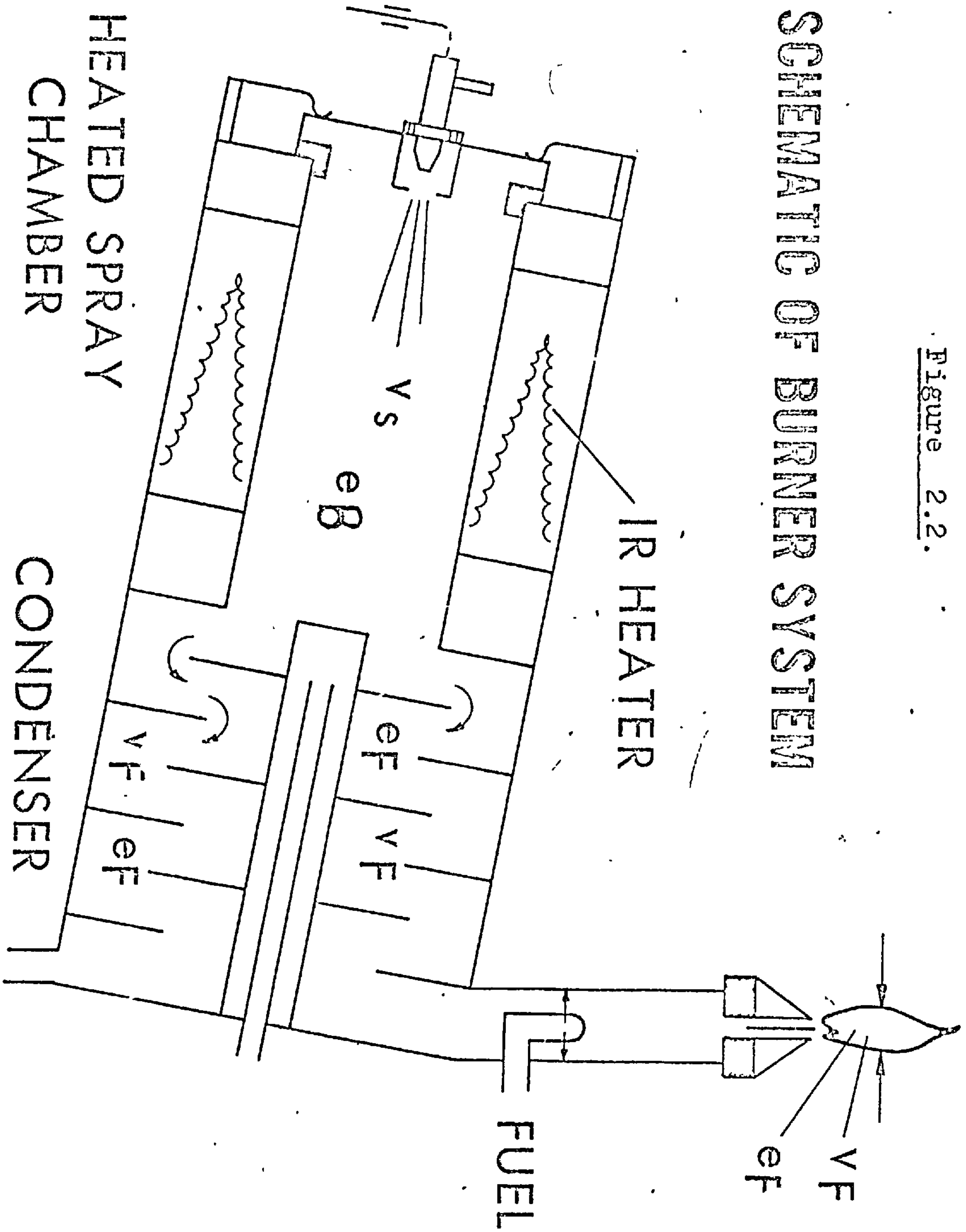


Figure 2.2.

SCHEMATIC OF BURNER SYSTEM

Figure 2.2 shows a schematic diagram of the burner system.

The spray chamber can be used in both hot and cold modes of operation. As mentioned earlier, a cold spray chamber is only about 5% efficient, because the larger droplets fall out of the gas stream and are lost to waste. Some of the droplets which do fall to waste may still be too large, so that they do not desolvate rapidly and pass through the flame without producing an atomic vapour. All these factors result in a potential loss of sensitivity. The only way to overcome the above problems is to ensure that the mean droplet diameter is as small as possible so that a greater fraction of the droplets will be carried by the gas stream to the burner. Hell[83] concluded that the best means of providing such a fine mist was to pre-evaporate the spray issuing from the nebuliser. A solid aerosol would then be obtained with a weight 5-7 times smaller than the normal spray mist.

The principal problem with heated spray chambers which rely on conduction for the heat transfer is that once spraying has commenced cooling of the spray chamber walls occurs and results in excessive drift. To overcome this problem, infra-red radiative heat may be utilised. Thus the sample mist is heated so that the solvent is evaporated before the droplets reach the spray chamber walls.

A Pyrex glass, rather than a metal, spray chamber is used, a heater is placed outside the cylindrical chamber. A 400 watt heater is used and freely suspended so that conductive heat transfer is reduced. Behind the heater there is an outer cylindrical metal radiation reflector. This system enables the solvent to be evaporated by radiative heat.

The use of a heated spray chamber, however, gives rise to a new problem. It was observed[83] that as soon as spraying started the flame became unstable. On the introduction of the sample the flame tended to 'lift off' and after adjustment of fuel and oxidant flow rates if spraying was stopped it tended to 'flash back.' The solvent increases the velocity of the gas mixture on evaporation sufficiently to tend to cause lift off. A further disadvantage is that the resultant increase in gas velocity also decreases the residence time of the analyte atoms in the path of the light beam. This, therefore, partially offsets any enhancement in sensitivity obtained. Therefore, a condenser is placed after the infrared heated spray chamber. The water-cooled condenser removes more solvent from the gas stream than the analyte and hence effectively increases the analyte concentration in the flame. The condenser is constructed so that the gas stream must follow an extended irregular path. This produces better heat exchange because of the larger surface area, and also suppresses any turbulence initially caused by the nebuliser.

Hell found, however, that even with this type of condenser, the flame still tended to 'lift-off' and 'flash-back,' when spraying was started and stopped. The reason for this is that as soon as spraying starts, when the hot mode of operation is used, vapour is immediately produced which replaces some of the air in the chamber. A pressure wave is, therefore, produced which increases the gas velocity and results in a tendency to 'lift off.' To overcome this problem the sprayer section of the burner was fitted with a circular vent, which, in the case of the air-acetylene flame, is open when a plastic cap is released.

Because the support gas leaves the sprayer (nebuliser) at a high velocity, in its immediate vicinity a slight under-pressure is produced. It is in this area that the sprayer vent is situated. Thus, air from the outside atmosphere is sucked into the spray chamber, and the pressure fluctuations which occur at the onset and finish of nebulising are equalised. The nitrous oxide-acetylene flame is 'stiff' enough to absorb any pressure fluctuations which may occur in the spray chamber and hence a sprayer vent is not required.

Both the air-acetylene and the nitrous oxide-acetylene burner heads were designed by Hell[83] to meet theoretical requirements. He derived the following expression for absorbance:-

$$A = \frac{k \; eF \; eB \; Cm \; Vs}{\sqrt{T} \; VF \; W}$$

where

A = Absorbance
k = absorption coefficient
eF = Flame efficiency (fraction of analyte reaching the flame which is atomised)
e_B = nebuliser efficiency
Cm = mole. concentration
Vs = spray rate (mls./min.)
T = Temperature of flame
VF = gas mixture streaming velocity
W = Flame width

These parameters are shown in Figures 2.2 and 2.3.

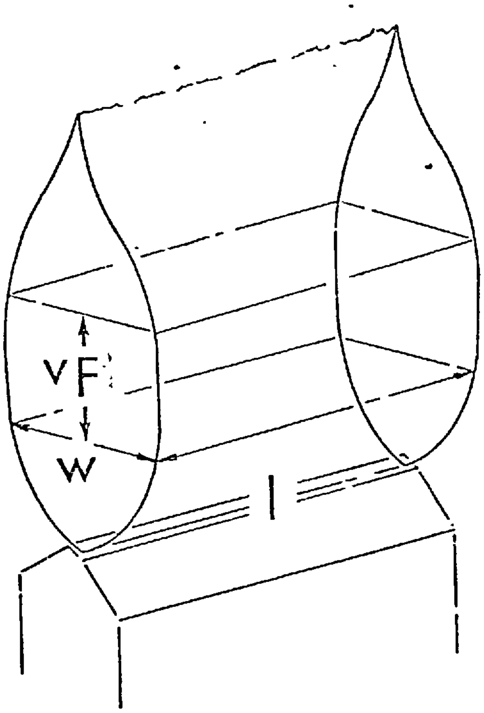


Figure 2.3.

It can be seen from the formula that a narrow flame appears to be required, but that the flame length does not appear to be important. Now sensitivity (or the percentual concentration limit) is defined as that concentration which produces an absorption of 1% (or an absorbance of 0.0044). Thus, if one substitutes $A = 0.0044$ into the above equation, the percentual concentration limit may be obtained.

$$C_{PCL} = \frac{0.0044\sqrt{T}\;\; VF \;\; W}{k \;\; cF \;\; e_B \;\; Vs}$$

Again, it can be seen that it appears that by increasing the spray rate, V_s the value of C_{PCL} would correspondingly be reduced. This is not plausible because the gas mixture would contain too much solvent and reduce e_F and e_B as well as increasing V_F . Hell, therefore, postulated that there would be an optimum value of V_s per unit length of the flame, which he termed V_s^{u} .

Thus $V_s = V_s^{u} l$ and C_{PCL} $\simeq \frac{0.0044\sqrt{T}\;\; VF \;\; W}{k \; e_F \;\; e_B \;\; V_s^{u} l}$

The flame, in order to obtain good sensitivity, should, therefore, be as long and narrow as possible. If, however, the flame does not totally envelop the light beam from the source used for atomic absorption spectroscopy, then a loss of the linear relationship between absorbance and concentration may result. Therefore, the relatively broad air-acetylene flame is obtained at Beckman Laminar Flow burners by using two slots. This is made by clamping a stainless steel plate between two symmetrical side pieces. It was found 84 that the use of multiple slots for the nitrous oxide-acetylene flame was not very successful and, therefore, a single slot burner was used.

In the Beckman Laminar flow burner system the fuel gas, normally acetylene, is introduced after the condenser, just below the burner head. The reason for this is mainly one of safety, as it ensures that there is no combustible gas mixture in the heated spray chamber. This reduces the risk of explosion in the spray chamber if flash-back was to occur. A safety valve is incorporated in the burner to cut off the fuel supply if the support gas pressure drops below a certain value.

The slot for the nitrous oxide-acetylene burner has the cross-section shown in Figure 2.4:-

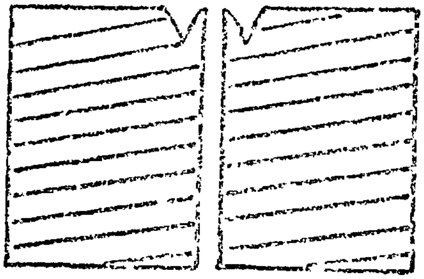


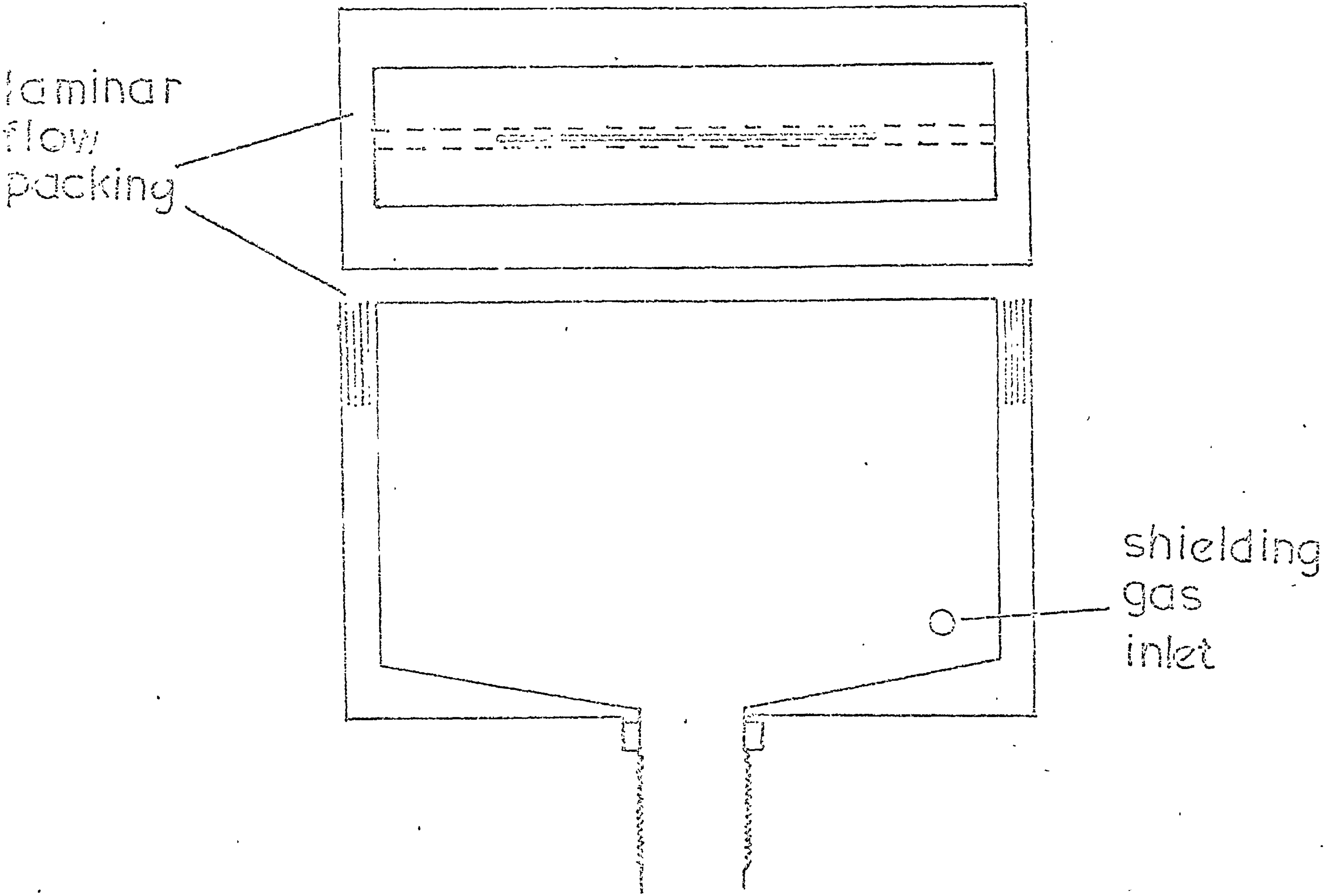
Figure 2.4.

When a fuel-rich nitrous oxide-acetylene flame has been burning on the flat-topped burner plates used with most commercial atomic absorption spectrometers for about 15 minutes carbon deposition occurs. This leads to increased flame noise, and can be dangerous. Once carbon deposition has occurred it is usual practice to scrape it from the burner plate manually, while the flame is still burning. Although the nitrous oxide-acetylene flame is very hot, the edges of the slot remain relatively cool. This results in only partial degradation of the acetylene fuel, and hence carbon deposition occurs. Beckman[84], therefore, machined grooves in the burner head plate to produce sharp slot edges, as shown in Figure 2.4. These edges cannot dissipate heat as readily, and the increase in temperature enables more complete combustion to occur. The burner is safe and retains its quenching ability.

2.3 MODIFICATION OF THE BECKMAN LAMINAR FLOW BURNER, TO FACILITATE SEPARATION OF THE PRIMARY AND SECONDARY ZONES OF THE FLAME.

It was decided to investigate the effect of inert gas shielding on both the nitrous oxide-acetylene and air-acetylene flames used in atomic absorption spectroscopy. The inert gas shielding device constructed for the laminar flow burner head with the nitrous oxide-acetylene flame is illustrated diagrammatically in Figure 2.5. This was fabricated from sheet aluminium (1.4 mm. thickness) cemented into a box-shaped structure with an epoxy resin adhesive. Alternate layers of plain and crimped cupro-nickel alloy strips (19.0 mm. width, 0.06 mm. thickness crimped at 1.2 mm. intervals) were packed tightly between the laminar flow burner head and the walls of the aluminium shielding box. The inert gas was passed into the shield through two 0.25 inch diameter copper inlet tubes at the base of the box. Although similar devices reported previously 60 have employed water cooling, no water cooling facility was found to be necessary with the apparatus employed in this study. A similar modification was made to the air-acetylene laminar flow burner head.

figure 2.5.



Before finally deciding to use the above design, it was decided to investigate the possibility of using a different method of producing a laminar inert gas flow. As mentioned in Chapter 1, Sychra and Matousek[63,64] have used a separated air-acetylene flame to study the atomic fluorescence characteristics of lead and gold. As shown in Figure 1.8, the inert shielding gas emerged from rows of holes in a metal plate. This method was investigated for use with the laminar flow air-acetylene burner.

A plate made out of aluminium was shaped, such that it would fit round the laminar flow burner. The plate had a thickness of $\frac{1}{8}$ inch. Sets of holes of 0.04 inch diameter were then drilled in this plate, as shown in Figure 2.6.

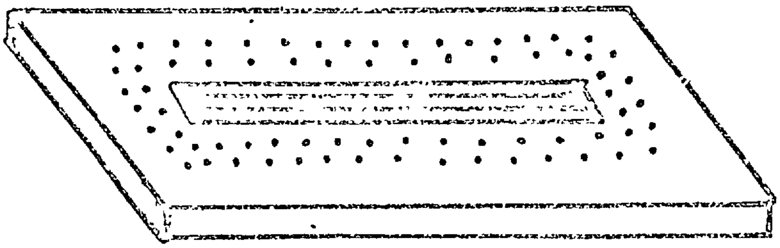


Figure 2.6.

After a set of holes had been drilled, the plate was placed in position, the air-acetylene flame ignited and nitrogen passed into the shield. With only one set of holes there was no separation of the air-acetylene flame. After drilling a second set of holes and passing nitrogen there was an observable lifting of the secondary zone of the flame. This lifting was very uneven and only about 2.00 mm. in height. Five sets of holes were found to be required with a minimum flow rate of about 15 litres/min. of nitrogen in order to lift the secondary zone by a distance of 10 to 15 mm. The distance between each set of holes was 1.0 mm. A minimum effective thickness of the wall of inert shielding gas is required before good separation occurs, as this only occurred after the fourth set of holes had been drilled.

To investigate whether there was a laminar flow of nitrogen when using the plate, the nitrogen was passed over concentrated hydrochloric acid and then over ammonium hydroxide. This resulted in ammonium chloride 'smoke ' being produced, which then passed out of the shielding device. When there was no air passing through the air-acetylene burner, the nitrogen could be seen to be issuing out of the holes in the plate in a laminar flow. As soon as the air is passed through the burner, then the 'smoke' is drawn in to form an arch shape, as shown in Figure 2.7:-

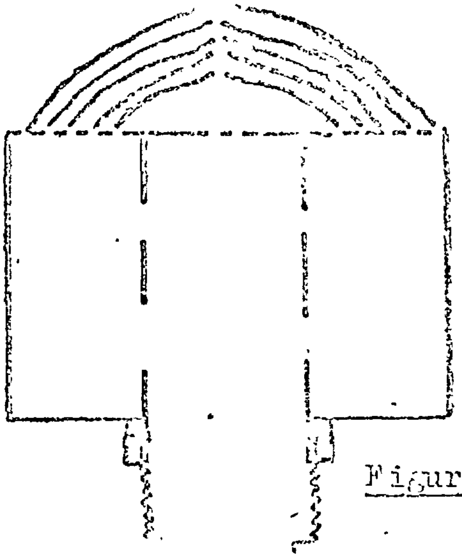


Figure 2.7.

The maximum height of this arch being 15 mm.

When the experiment was repeated, but with the crimped strip in position, the maximum height was about 25 mm. It was, therefore, decided in any further studies to use the crimped strip as a means of providing laminar flow in the shielding devices.

The Laminar Flow Burner system was used in conjunction with the Beckman 440 Atomic Absorption Spectrophotometer. This is a single beam instrument, with a grating monochromator of 30-cm. focal length and f /10 aperture. The wavelength range is 190 to 770 nm. with a standard photomultiplier and there are 2, 8, 16 or 32 second response times for 98% response to full scale change in signal. One important feature of this instrument is that it has a triple pass optical system. Two concave mirrors are arranged in such a way that the light beam from the source passes through the flame three times before reaching the detector. This is shown diagrammatically in Figure 2.8 :-

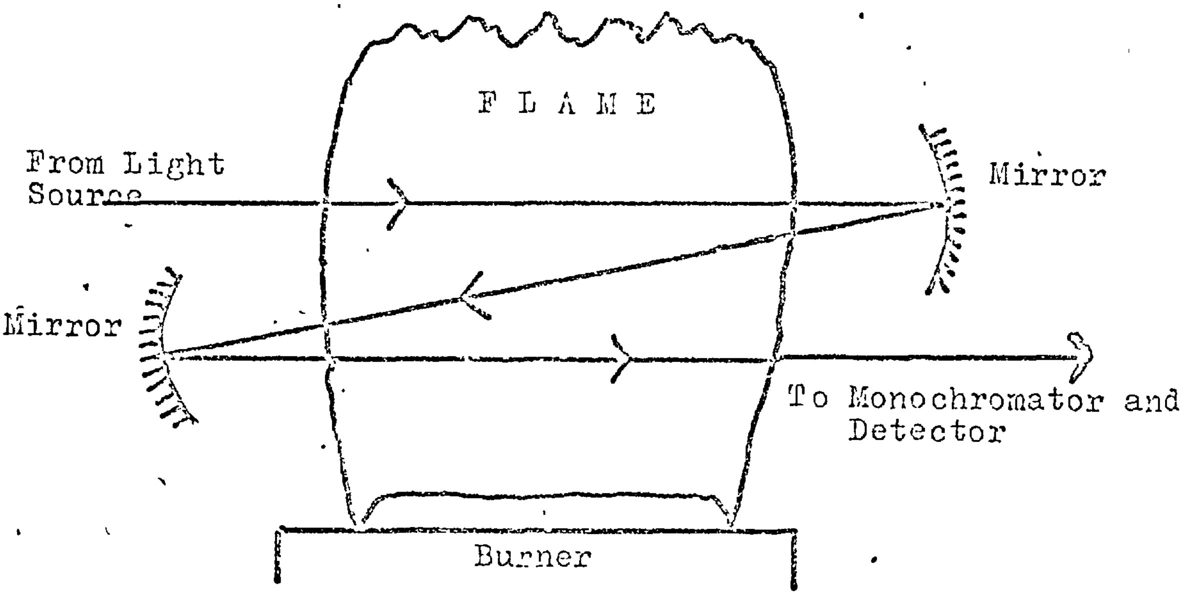


Figure 2.8.

As the light beam traverses the flame three times, more light is absorbed by the atoms present in the flame cell and an increase of sensitivity is obtained.

It has been shown by Tabeling and Devancy[85] that if a light beam passes through the flame more than five times, the light losses become so large that an unacceptable increase in detector noise is observed.

2.4 THE USE OF AN ARGON SHIELDED NITROUS-OXIDE ACETYLENE FLAME WITH THE LAMINAR FLOW BURNER.

The separation of the premixed nitrous-oxide acetylene flame has been described previously [86]. Initial attempts to separate this flame on the laminar flow burner were made by using nitrogen as the shielding gas. A stable flame could only be obtained when the flame was fuel lean. On making the flame slightly fuel rich such that there was a red feather of about 1 inch in height, the flame became very unstable and lifted off, for reasons described in Chapters 1 and 3 . It was, therefore, necessary to use argon as the shielding gas: this enabled a very stable flame to be obtained over a wide range of fuel flow rates. On separation, with argon, the 'red feather' zone increased in height by approximately four-fold.

When the nitrous oxide-acetylene flame is separated with nitrogen or argon, improved sensitivities and detection limits can be obtained in flame emission spectroscopy [58]. Similar, but less pronounced, advantages are observed when the inert gas shielded flame is employed for analytical atomic absorption spectroscopy, [60]. A study was made on the effect of shielding the L.F.B. flame on the atomic absorption spectroscopy sensitivities and detection limits for Molybdenum, Titanium and Vanadium in the hot and cold operational modes, and using both single and triple pass optics.

EXPERIMENTAL:

The data presented were obtained using the Beckman Model 440 Atomic Absorption Spectrophotometer equipped with a Laminar Flow Burner (L.F.B.) operated in hot and cold modes. A Beckman 5 inch strip-chart recorder (Model No. 93507) was employed. The absorption light sources were hollow-cathode lamps (Atomic Spectral Lamps Pty., Ltd., Australia) for Molybdenum, Titanium and Vanadium. The results were obtained with no scale expansion and at optimum source current, gain, slit-width, burner elevation and flame conditions for both shielded and conventional flames for each element.

Solutions of Molybdenum (vi) and Vanadium (iv) used in this study were prepared by dilution of stock 1,000 ppm. solutions prepared by dissolution of ammonium molybdate, $(NH_4)_6 Mo_7 O_{24} 4H_2O$ in distilled water and ammonium metavanadate in dilute HCl (0.2M) followed by reduction with hydroxylamine hydrochloride.

A stock 1,000 p.p.m. solution of titanium (iV) was prepared by dissolution of pure titanium sponge in 40% HF and dilution with distilled water. This stock solution then contained ca. 2% HF.

RESULTS:

The attainable values for the percentual concentration limits P.C.L. (that concentration which gives an 1% absorption), were derived from analytical calibration graphs prepared for each element studied using both hot and cold modes of the L.F.B. and for single and triple pass operation. The fluctuational concentration limit (F.C.L.) was defined as that concentration of analyte giving a signal corresponding to the magnitude of the peak-to-peak noise measured at 0% absorption (blank or solvent adjusted to 0% absorption) under given operating conditions. The

Table 2.1: Sensitivities and Detection Limits Obtained with Conventional and Argon Shielded Flames

Element	Wavelength nm	Conditions	PCl Values (ppm)		*FCl values (ppm)	
			Conventional Flame	Argon Shielded Flame	Conventional Flame	Argon Shielded Flame
Vanadium	318.4	Single Pass – Cold Mode	5.3	4.3	1.6	1.3
		Triple Pass – Cold Mode	3.0	2.1	6.2	2.2
		Single Pass – Hot Mode	0.63	0.54	0.33	0.29
		Triple Pass – Hot Mode	0.40	0.24	0.88	0.29
Molybdenum	313.3	Single Pass – Cold Mode	1.8	1.5	0.54	0.46
		Triple Pass – Cold Mode	0.96	0.70	2.0	0.74
		Single Pass – Hot Mode	0.23	0.20	0.27	0.25
		Triple Pass – Hot Mode	0.13	0.09	0.17	0.15
Titanium	364.3	Single Pass – Cold Mode	4.8	3.8	2.3	1.9
		Triple Pass – Cold Mode	3.3	1.9	6.6	2.0
		Single Pass – Hot Mode	1.0	0.9	0.48	0.43
		Triple Pass – Hot Mode	0.73	0.45	1.4	0.45

*Values obtained using a response time of 2 secs (i.e. time constant of ca 0.5 secs).

F.C.L. is comparable to "detection limits" expressed in the literature, if they are obtained at the same time constant. Typical calibration graphs obtained for Vanadium are shown in Figure 2.9 . The performance in atomic absorption spectroscopy for each of the three elements was studied only at those resonance lines which permit the highest sensitivities to be obtained. The results obtained are shown in Table 2.1 .

Legend to Figure 2.9 :

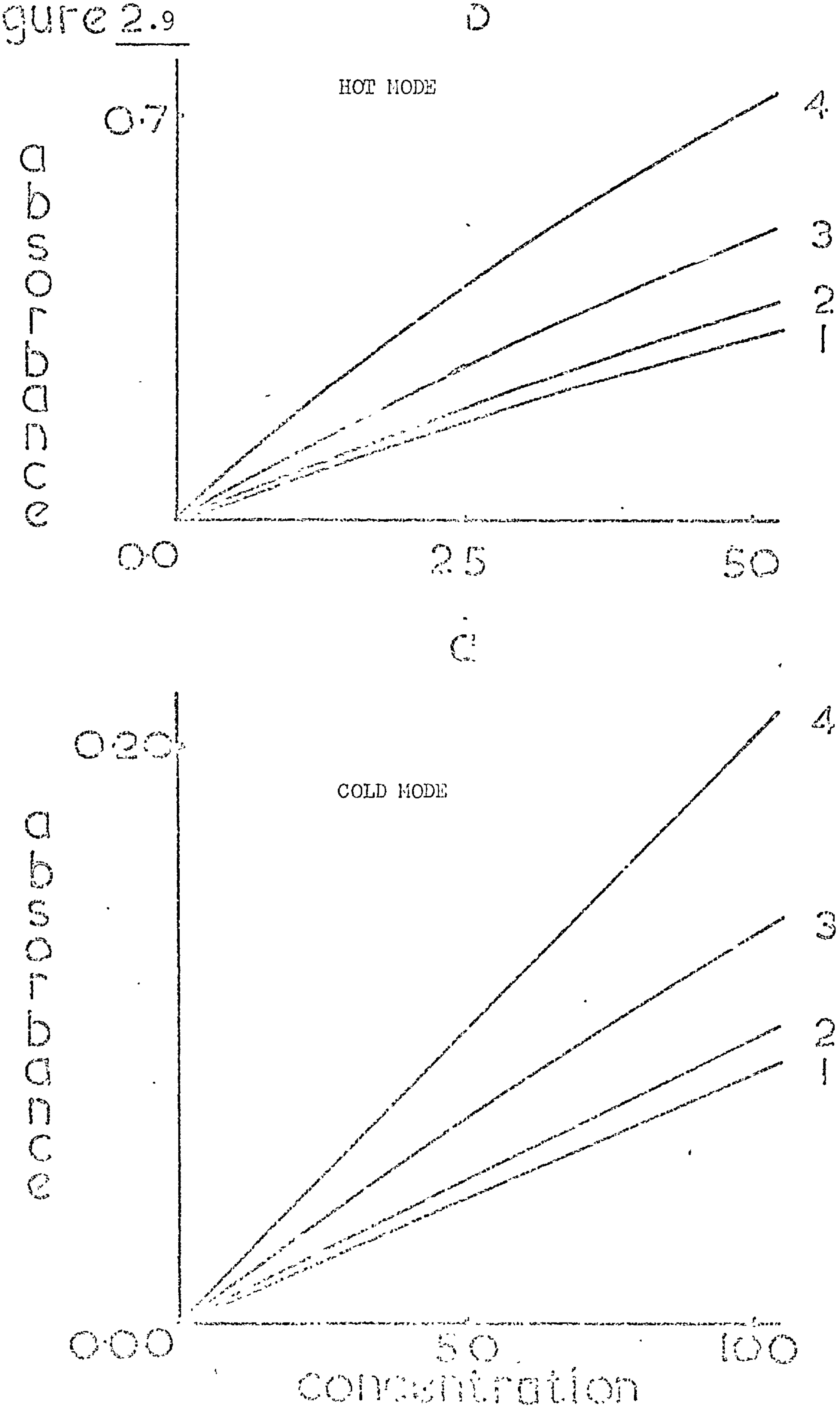
Calibration graphs for Vanadium

(a) Cold mode 1. Single pass, conventional flame
2. Single pass, shielded flame
3. Triple pass, conventional flame
4. Triple pass, shielded flame.

(b) Hot mode 1. Single pass, conventional flame
2. Single pass, shielded flame
3. Triple pass, conventional flame
4. Triple pass, shielded flame.

These results were obtained without the addition of potassium chloride to the solution to suppress any ionisation of the atoms of the elements in the nitrous-oxide acetylene flame. The results for the conventional unshielded flame at the L.F.B. compare favourably with

Figure 2.9


D
HOT MODE
0.7
absorbance
4
3
2
1
0.0
2.5
50
C
0.20
COLD MODE
absorbance
4
3
2
1
0.00
50
100
concentration

those reported by Ramirez-Munoz and Roth[87] under similar conditions. In the single pass mode of operation the argon shielding of the flame produces small improvements (percentual sensitivity in terms of the original sensitivity) up to 25%. In the triple pass mode of operation the sensitivities are improved by factors ranging up to 40%.

DISCUSSION:

Improvements in the sensitivity and detection limits for atomic absorption determination of refractory-oxide forming elements, by separation of a long-path nitrous oxide-acetylene flame has previously been described[60,61]. This study has shown that in both the hot and cold modes of operation using single path optics the L.F.B. gives similar improvements when the nitrous-oxide acetylene flame is shielded with argon. The possible reason for this improvement will now be discussed.

As previously mentioned, the slightly fuel rich nitrous oxide-acetylene flame consists of a primary reaction zone above which is a 'red feather zone,' surrounded by the blue secondary reaction zone. It has been shown by Kirkbright, Peters and West[94] that the species which predominate in the 'red feather' zone are CN and NH. These long lived species form a very reducing atmosphere. The refractory metal oxides formed in the primary reaction zone of the flame can be broken down to give the free metal atom by several processes. They are - dissociation of the metal oxides by the high nitrous oxide-acetylene flame temperature and by the reaction of the metal oxide with 'free' carbon, i.e. $MO + C \rightarrow M + CO$. Kirkbright et al[94] suggested that the metal oxide may also react with the CN and NH species in the 'red feather' zone. They postulated the following reactions:

$$MO + NH \longrightarrow M + NO + H \quad \text{or} \quad M + OH + N$$

$$MO + CN \longrightarrow M + CO + N.$$

Further evidence for the existence of high CN species concentration in the 'red feather zone' was given by Kirkbright, Peters, Sargent and West[88]. They showed, by looking at the absorption by CN at the (0,0) sequence of the CN violet band system at 3,883 A against a continuum source that the CN concentration in this increases steadily as the flame becomes more fuel rich.

Kirkbright and Vetter 89 have recently shown that the shielded fuel-rich flames are cooler than the unshielded flames by between 40 to 180 K, in the flame region used for atomic absorption spectrometry. The temperature difference is dependent on the height of observation and the shielding gas used. These facts add further to the theory, that in hot flames the existence of a reducing atmosphere in the interconal zone of the flame is a more important factor for the maintenance of high atomic populations of the refractory oxide forming elements than the high temperature of the flame. Therefore, on argon shielding the slightly fuel rich nitrous oxide-acetylene flame, oxygen from the atmosphere is prevented from diffusing into the flame and hence the reducing nature of the interconal zone is enhanced.

When the nitrous oxide-acetylene flame is shielded with argon at the Beckman Laminar Flow Burner, the 'red feather' substantially increases in height. One would, therefore, expect a greater increase in sensitivity when using the shielded flame with triple pass optics, than the unshielded flame, for the refractory-oxide forming elements. Table 2.2 shows the percentage increase in sensitivity when triple pass optics are used compared to single pass optics for the three elements studied.

Element	Mode of Operation	Unshielded %	Argon shielded %
Vanadium	Cold mode	43	51
	Hot mode	37	55
Molybdenum	Cold mode	44	55
	Hot mode	43	55
Titanium	Cold mode	31	50
	Hot mode	27	50

Table 2.2 .

2.5 THE USE OF THE NITROGEN SHIELDED AIR-ACETYLENE FLAME WITH THE LAMINAR FLOW BURNER.

The separation of the premixed air-acetylene flame has been reported to provide improved percentual and fluctuational detection limits in the determination of arsenic and selenium by atomic absorption spectroscopy, Separation of the oxidising secondary reaction zone of the air-acetylene flame results in lower flame background absorption and noise levels. The unseparated air-acetylene flame can absorb up to 80% of the source radiation at the Arsenic 193.7 nm. and the Selenium 196.0 nm. lines, the oxygen species in the flame being the most probable absorbing species.

Absorption by hot molecular oxygen extends to much longer wavelengths and even as far as 260 nm. in very hot flames [90] . It was, therefore, decided to investigate the effect of nitrogen shielding the L.F.B. air-acetylene flame on the determination of Lead, Zinc and Tellurium, which have their main resonance lines at 217.0, 213.9 and 214.3 nm., respectively, as well as Arsenic and Selenium. The study was performed for all modes of operation whereever possible.

EXPERIMENTAL:

The data presented were obtained using the Beckman Model 440 Atomic Absorption Spectrophotometer equipped with a Laminar Flow Burner (L.F.B.) operated in hot and cold modes. A Beckman 5 inch strip recorder was employed. The radiation sources employed were hollow cathode lamps for As, Se, Zn, Pb and Te.

The results were obtained with no scale expansion and at optimised source current, gain, slit-width, burner elevation and flame conditions for both shielded and conventional flames for each element. An inert gas shielding device for the L.F.B. with the air-acetylene flame was constructed in a similar fashion to that already described for the study of the separated L.F.B.

nitrous oxide-acetylene flame. It was fabricated from sheet aluminium; alternate layers of plain and crimped cupro-nickel alloy strips were packed tightly between the L.F.B. and the walls of the aluminium shielding box. The nitrogen shielding gas was passed into the shield through two inlets at the base of the box.

Arsenic solutions were prepared by dilution of a 1,000 p.p.m. stock solution, prepared by dissolution of arsenious oxide in water containing the minimum required amount of sodium hydroxide. The 1,000 p.p.m. selenium stock solution was prepared by dissolution of sodium selenite (A.R.) in water. Lead nitrate and zinc sulphate were dissolved in distilled water to prepare 1,000 p.p.m. stock solutions of Pb and Zn. Tellurium powder (Specpure, Johnson and Matthey, Ltd.) was dissolved in a mixture of nitric and hydrochloric acids, the final acidity in the 1,000 p.p.m. stock solution being ca. 1 M.

RESULTS:

The attainable values for the percentual and fluctuational concentration limits were derived from analytical calibration graphs prepared for each element studied. Both cold and hot modes of operation

TABLE 2.3.

Sensitivies and Detection Limits obtained with Conventional and Nitrogen Shielded Flames

Element	Wavelength nm	Conditions	PCl values (ppm)*		FCl values (ppm)**			
			Conventional Flame	Nitrogen Shielded Flame	Response time 2 secs		Response time 8 secs	
					Conventional Flame	Nitrogen Shielded Flame	Conventional Flame	Nitrogen Shielded Flame
Lead	217.0	Single pass – Cold Mode	0.62	0.62	0.62	0.21	0.21	0.12
		Triple pass – Cold Mode	0.24	0.22	1.25	0.29	0.62	0.08
		Single pass – Hot Mode	0.13	0.13	0.12	0.04	0.06	0.02
		Triple pass – Hot Mode	0.039	0.036	0.20	0.055	0.10	0.018
Zinc	213.9	Single pass – Cold Mode	0.038	0.038	0.04	0.02	0.013	0.008
		Triple pass – Cold Mode	0.015	0.013	0.077	0.02	0.031	0.007
		Single pass – Hot Mode	0.0065	0.0065	0.007	0.0035	0.0023	0.0014
		Triple pass – Hot Mode	0.0016	0.0014	0.008	0.0028	0.004	00007
Tellurium	214.3	Single pass – Cold Mode	1.14	1.14	1.1	0.55	0.55	0.36
		Triple pass – Cold Mode	0.60	0.53	3.0	1.14	1.5	0.28
		Single pass – Hot Mode	0.33	0.33	0.33	0.16	0.11	0.066
		Triple pass – Hot Mode	0.14	0.12	0.71	0.25	0.35	0.12

* PCl – Percentual Detection Limit

** FCl – Fluctuational Detection Limit

(contd/)

Table 2.3 (Continued)

Element	Wavelength nm	Conditions	PCl values (ppm)*		FCl values (ppm)**			
			Conventional Flame	Nitrogen Shielded Flame	Response time 2 secs		Response time 8 secs	
					Conventional Flame	Nitrogen Shielded Flame	Conventional Flame	Nitrogen Shielded Flame
Arsenic	193.7	Single pass – Cold Mode	2.00	2.00	16.00	8.00	8.00	4.00
		Triple pass – Cold Mode	–	–	–	–	–	–
		Single pass – Hot Mode	0.52	0.52	4.2	2.0	2.0	1.0
		Triple pass – Hot Mode	–	–	–	–	–	–
Selenium	196.0	Single pass – Cold Mode	2.09	2.09	12.5	6.3	6.3	2.1
		Triple pass – Cold Mode	–	1.2	–	12.0	–	4.8
		Single pass – Hot Mode	0.54	0.54	3.2	1.6	1.6	0.81
		Triple pass – Hot Mode	–	0.31	–	3.1	–	1.2

* PCl – Percentual Detection Limit

** FCl – Fluctuational Detection Limit

were employed, and where possible triple pass was investigated in addition to single pass operation. The results obtained are summarised in Table 2.3 . The results obtained for the conventional unshielded flame compare favourably with those reported by Ramirez-Munoz and Roth under similar conditions. The percentual concentration limit for each element remains unchanged on shielding the flame with nitrogen. In all modes of operation, however, improvement in the fluctuational concentration limit is obtained on nitrogen shielding for each element. This improvement, which varies between 2 and 7-fold, depending on the element and mode of operation, results from the lower flame background absorption and greater stability of the shielded flame. Figures 2.10 a, b and c demonstrate the lower noise levels and flame background absorption observed for these elements whose resonance lines occur at short wavelengths. The lower flame background facilitates the use of lower amplifier gain settings at the detector and consequently results in lower noise levels.

Legend to Figure 2.10 a, b and c :

Flame background absorption for elements studied -

(a) No Flame.

(b) Conventional Flame, optimum conditions for determination of element.

(c) Nitrogen shielded Flame, optimum conditions for determination of element.

(d) Conventional Flame, absorbance set to zero (by increasing gain).

(e) Shielded Flame, absorbance set to zero.

fig. 2.10 a.

cold mode
single pass
response time 8 sec

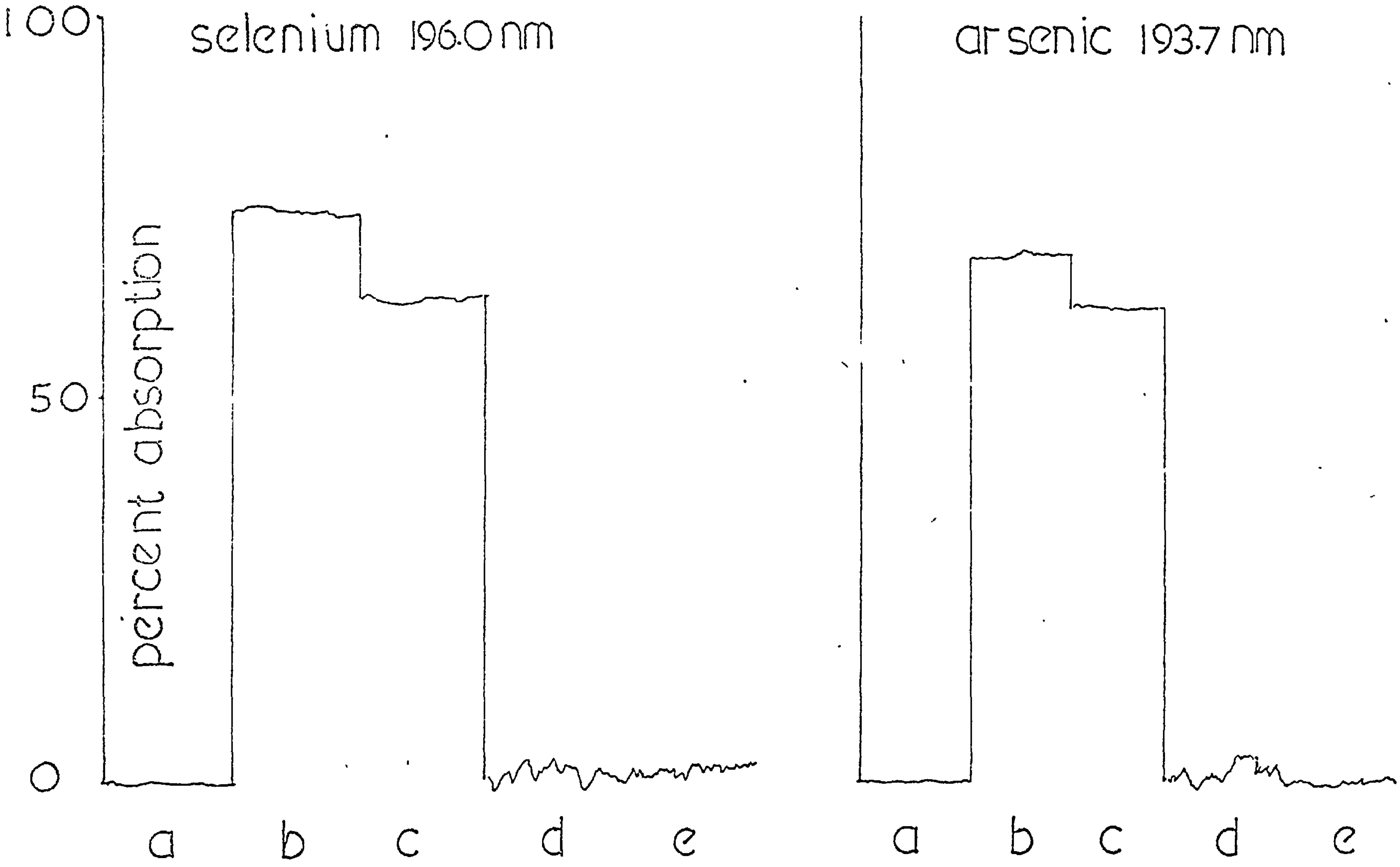


fig. 2.10 b.

hot mode
triple pass
response time 2sec

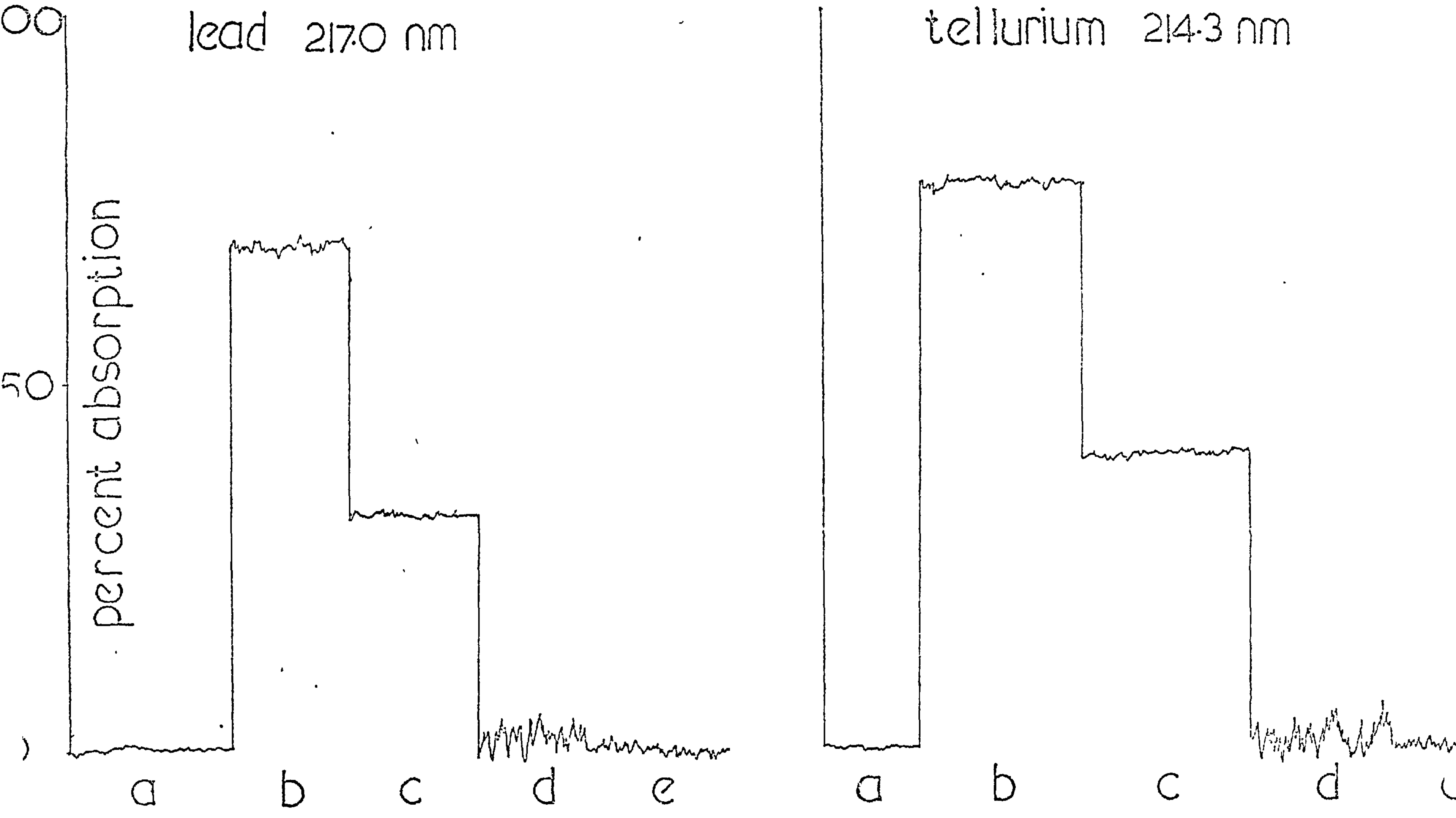
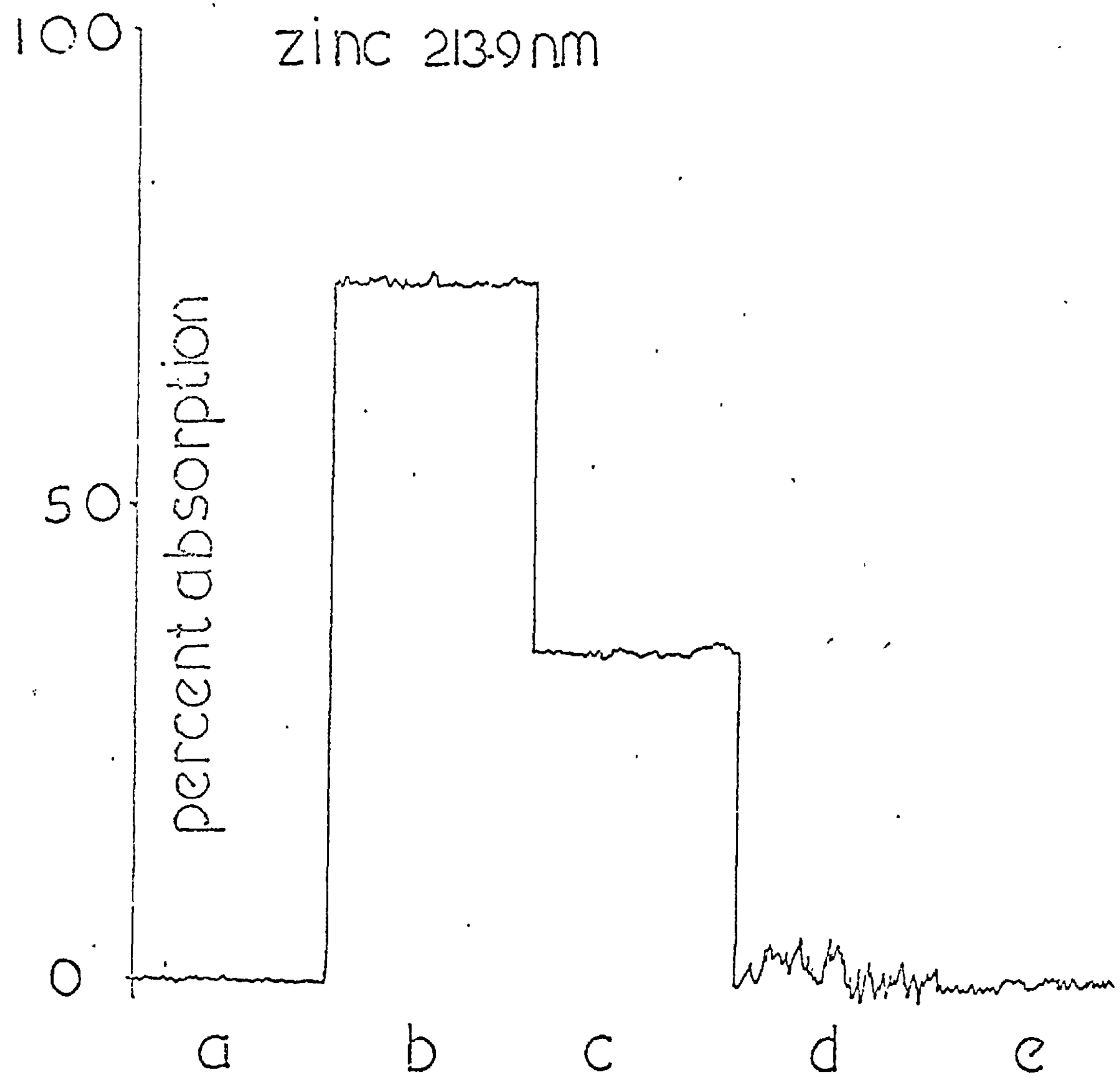


fig. 2.10 c.

hot mode
triple pass
response time 2 sec



CONCLUSION:

Separation of the air-acetylene flame results in improved F.C.L.'s for As, Se, Pb, Zn and Te.

Even with flame separation, however, Arsenic may not be determined in the triple pass mode of operation. This fact will be discussed further in Chapter 4 .

CHAPTER 3.

SOME PRACTICAL STUDIES OF BURNER DESIGN:

3.1 INTRODUCTION.

It was stated in Chapter 1, section 1.8 that a flame stabilised at a burner rim tends to become more unstable when the flame is surrounded by an inert gas such as argon or nitrogen. Lewis and von Elbe[72] postulate that the main cause of such instability is the interdiffusion of the surrounding gas into the boundary layer of the gas stream. Reed [75], however, suggests that the removal of the secondary reaction zone from the base of the flame effectively removes a heat source and hence encourages quenching of the flame.

One method of stabilising a flame is to use a pilot light placed near the flame attachment zone. Such a pilot light maintains itself because it is supplied with premixed combustible and oxidiser gases. The heat from the pilot flame reduces quenching at the burner rim and so helps stabilise the main flame. Thomas and Wilhelm 91 developed a rectangular burner with injection slots for auxiliary gas introduction at the flame attachment zone, in order to study blow-off limits. The auxiliary gas, such as oxygen or methane, was injected into the main premixed air-methane flame.

This auxiliary gas was required to mix with the other gases in the attachment zone before taking part in the combustion process. It was observed that the introduction of hydrogen or methane to the base of the air-methane flame improved the stability of the flame.

In the study reported here it was decided to investigate a method of stabilising a separated flame at a burner rim, which would take into account both the theory of Lewis and von Elbe and that of Reed. The basic proposition was to place a device on the burner rim such that it would,

a) decrease interdiffusion of the flame gases and the surrounding atmosphere; and b) help prevent the loss of heat from the base of the flame due to the absence of a secondary diffusion zone.

3.2 THE STABILISATION OF THE NITROGEN SEPARATED AIR-ACETYLENE FLAME.

The cylindrical air-acetylene flame burning at a Meker type burner is commonly used for atomic fluorescence and flame emission spectroscopy and on separation of this flame improved detection limits are obtained . These workers used a cylindrical air-acetylene burner and separated the flame with nitrogen. As the resultant separated flame has low background emission compared to the conventional air-acetylene flame, improved results were obtained for the determination of bismuth by thermal emission spectroscopy and for zinc and cadmium by atomic fluorescence spectroscopy.

The burner assembly used for the above work, however, was not capable of being used with most commercially available atomic absorption spectrophotometers as, owing to its extended length, it did not fit conveniently into the optical axis of these instruments. Hingle, Kirkbright, Sargent and West[92] have described a burner system for both air-acetylene and nitrous oxide-acetylene cylindrical shielded burners which is acceptable for most instruments. A shielded circular air-acetylene burner of this type was used in these studies. The assembly used was manufactured by Beckman-RIIC, Ltd., Worsley Bridge Road, London, S.E.26, and was fitted to the standard nebuliser system of the Techtron A.A.4 atomic absorption spectrophotometer. The burner and separator are shown in Figure 3.1 :

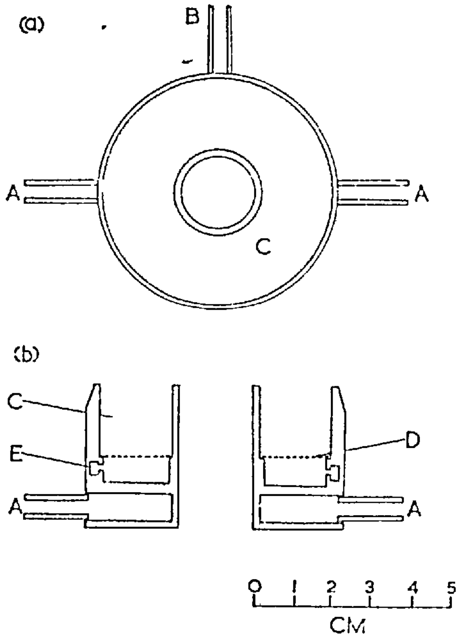


Diagram of the flame separator. (a) Top view. (b) Side view. A: Water pipes. B: Nitrogen/argon inlet. C: Laminar flow matrix. D: Support for matrix. E: Nitrogen/argon distribution channel

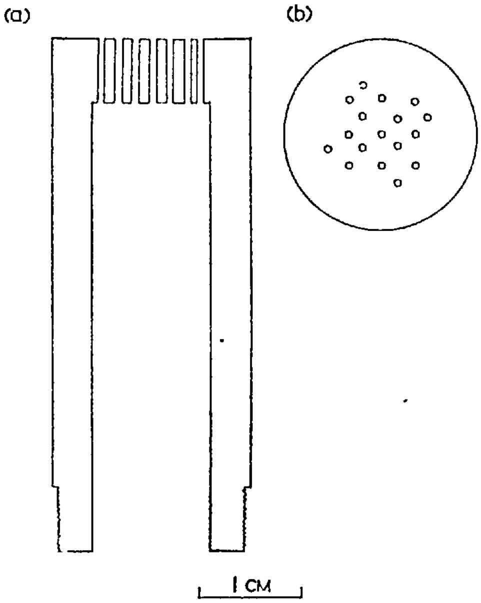


Diagram of the air-acetylene burner head. (a) Side view. (b) Top view.

<u>Figure 3.1</u>.

From the diagram (Figure 3.1) it can be seen that the burner is of the Meker type, consisting of a series of circular orifices drilled into the burner head plate to form a square pattern. The resultant flame at this burner then consists of separate reaction cones surrounded by a single stable secondary diffusion zone. When the flame is separated with nitrogen there is a tendency for the outer edges of the outer primary cones to be lifted off the burner rim. This effect is shown diagrammatically in Figure 3.2a :

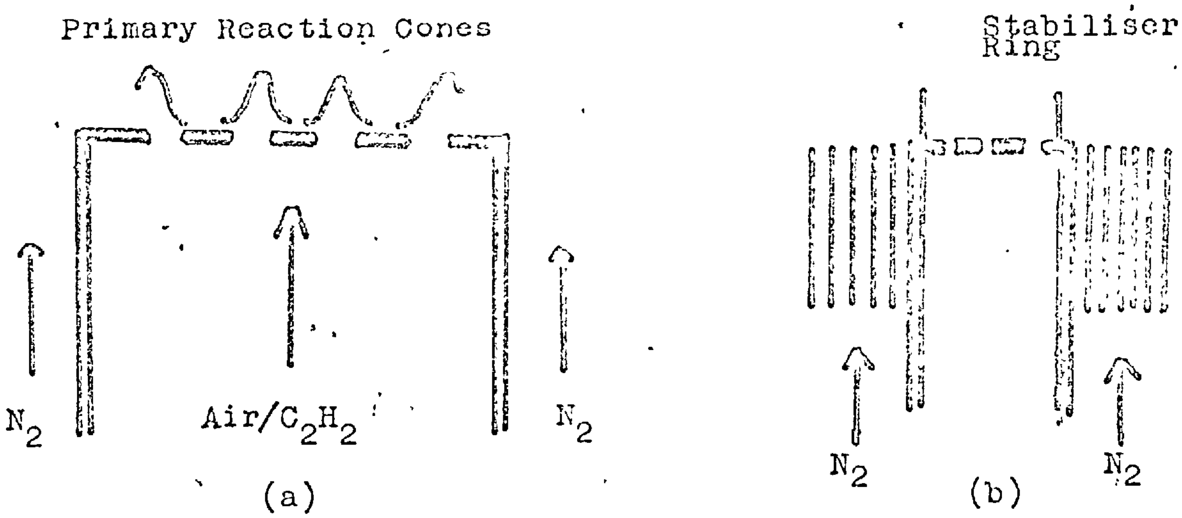


Figure 3.2.

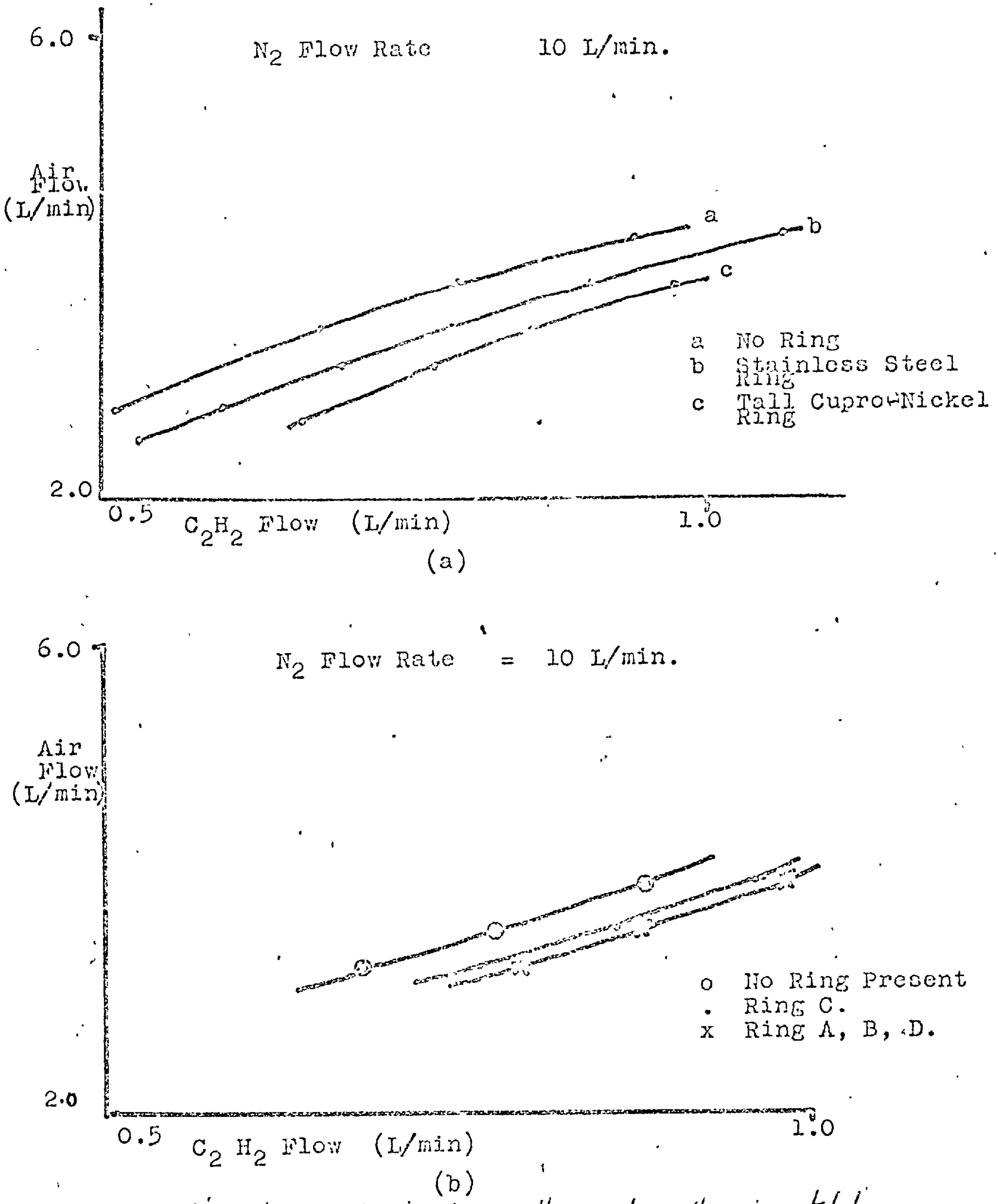
As the inner primary cones are protected from the shielding gas by the outer cones, they are not 'lifted-off.' However, if the fuel flow-rate is increased sufficiently, then the outer cones 'lift-off' completely and the inner cones are affected by the cooling and dilution effects of the nitrogen, resulting in the eventual 'lift-off' of the whole flame.

The first burner employed had thirteen holes, each 0.0635" in diameter, in the head plate. In the initial experiments a small cylindrical ring was constructed from thin cupro-nickel strip (thickness 0.06 mm. height c. 5 mm.) and placed on top of the burner so that it encompassed all of the holes of the burner (see Figure 3.2b). The nitrogen shielding gas flow-rate was kept constant, and then for various air flow rates the acetylene flow-rate at which the whole flame blew-off was noted. The experiment was repeated without the cupro-nickel ring. It was found that when the ring was present higher acetylene flow rates were required before the flame blew-off. These results were encouraging and suggested that the flame was in fact being stabilised by the ring; unfortunately, however, the cupro-nickel tended to be burned away relatively rapidly by the flame. A stainless steel cylindrical stabiliser ring was made, with the following dimensions: height 8 mm., outer diameter 12 mm., internal diameter 11 mm. The blow-off stability limits for the flame using this stabiliser were then obtained. As gaseous interdiffusion appears to play a part in causing instability of flames, increasing the height of the stabiliser ring should further protect the flame from the quenching effect of the nitrogen shielding gas. Stability limits were, therefore, obtained using a cupro-nickel ring of greater depth, i.e 12mm. The blow-off limits for this and those obtained using the stainless steel ring are shown in Figure 3.3a .

It can be observed that the deep cupro-nickel ring does provide more stability to the nitrogen separated air-acetylene flame than the stainless steel ring. However, the tall cupro-nickel ring was not of great practical value because of its short life-time and the fact that it blocks out much of the optimum flame volume to be used for analytical spectroscopy. A set of stainless steel stabiliser rings with varying dimensions was, therefore, made and their stabilising effect was evaluated. For this study a second circular air-acetylene burner, which had thirty holes (diameter mm.) drilled in the burner head plate, was employed. Four stainless steel stabiliser rings were used; the dimensions of these are listed in Table 3.1 :

Stabiliser	Height (mm.)	Internal Diameter(mm.)	Outer Diameter (mm.)
A	4	12	13
B	5	12	13
C	8	12	13
D	5	13	14

Table 3.1



The blow-off limits with and without stabiliser rings

Figure 3.3.

The stability limits obtained are shown in Figure 3.3b, along with the blow-off limits for the flame with no stabiliser ring present. It can be seen that there is no difference in the performance of rings A, B and D, although ring C is slightly better. This presumably is because the taller ring provides more protection to the base of the flame from the nitrogen.

3.3 THE STABILISATION OF THE NITROGEN SEPARATED NITROUS OXIDE-ACETYLENE FLAME AT THE BECKMAN LAMINAR FLOW BURNER.

The modification of the Beckman Laminar Flow burner head for the nitrous oxide-acetylene flame has been described in Chapter 2. It was noted that for good flame separation at high acetylene flow rates it was only possible to use argon as the shielding gas. On shielding this nitrous oxide-acetylene flame with helium it was found that even at relatively low acetylene flow rates the flame was very unstable. Only a small amount of helium was needed before the flame began to lift-off at the ends of the burner slot. This effect can be explained by the Lewis and von Elbe theory of flame stability in which interdiffusion of the gases plays an important role. The rate of diffusion of helium would be much greater than that for N_2 or Ar. When carbon dioxide was used as the shielding gas to minimise the diffusion rate, the flame was more stable than when helium was used, but in a slightly fuel-rich flame the 'red-feather zone' disappears. The entrained carbon dioxide presumably reacts with the flame species. Shielding with nitrogen was possible but only for the fuel-lean flame. The use of argon, however, did enable the fuel-rich flame to be separated.

An attempt was made, therefore, to improve the stability of the nitrogen shielded nitrous oxide-acetylene flame. Two 'horse-shoe' shaped stainless steel stabilisers were made and placed 3 mm. from each end of the burner slot, as shown in Figure 3.4 :

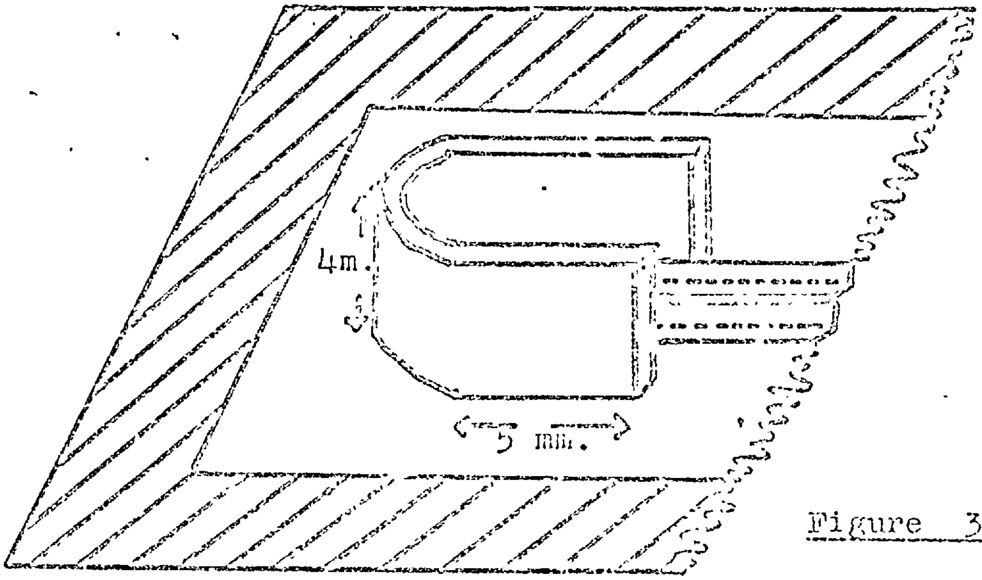


Figure 3.4.

At a given nitrogen flow-rate, the stability limits for blow-off were obtained with and without the stabilisers present. In these experiments the blow-off limit was defined as the acetylene pressure at which the flame base begins to 'lift-off' at the ends of the burner slot, for a given nitrous oxide pressure. The data obtained is shown in Figure 3.5 , and it can be seen that the stainless steel stabilisers do in fact allow a more fuel-rich flame to be used.

There is a further possible reason why the steel stabilisers are effective. Levy and Weinberg [93] studied flat flames by particle track photography and showed that the flame is stabilised at the burner rim by eddies of unburned and burned gas. A flat flame has a combustion wave which takes the form of a flat surface rather than the usual conical shape. Such flames are obtained with very lean mixtures and very low gas velocities. These workers noted that if the eddies were disturbed by an inert gas passing the base of the flame, then the flame stability is decrea sed. Therefore, the steel stabilisers used in this study might be considered to protect the flame base from such disturbance.

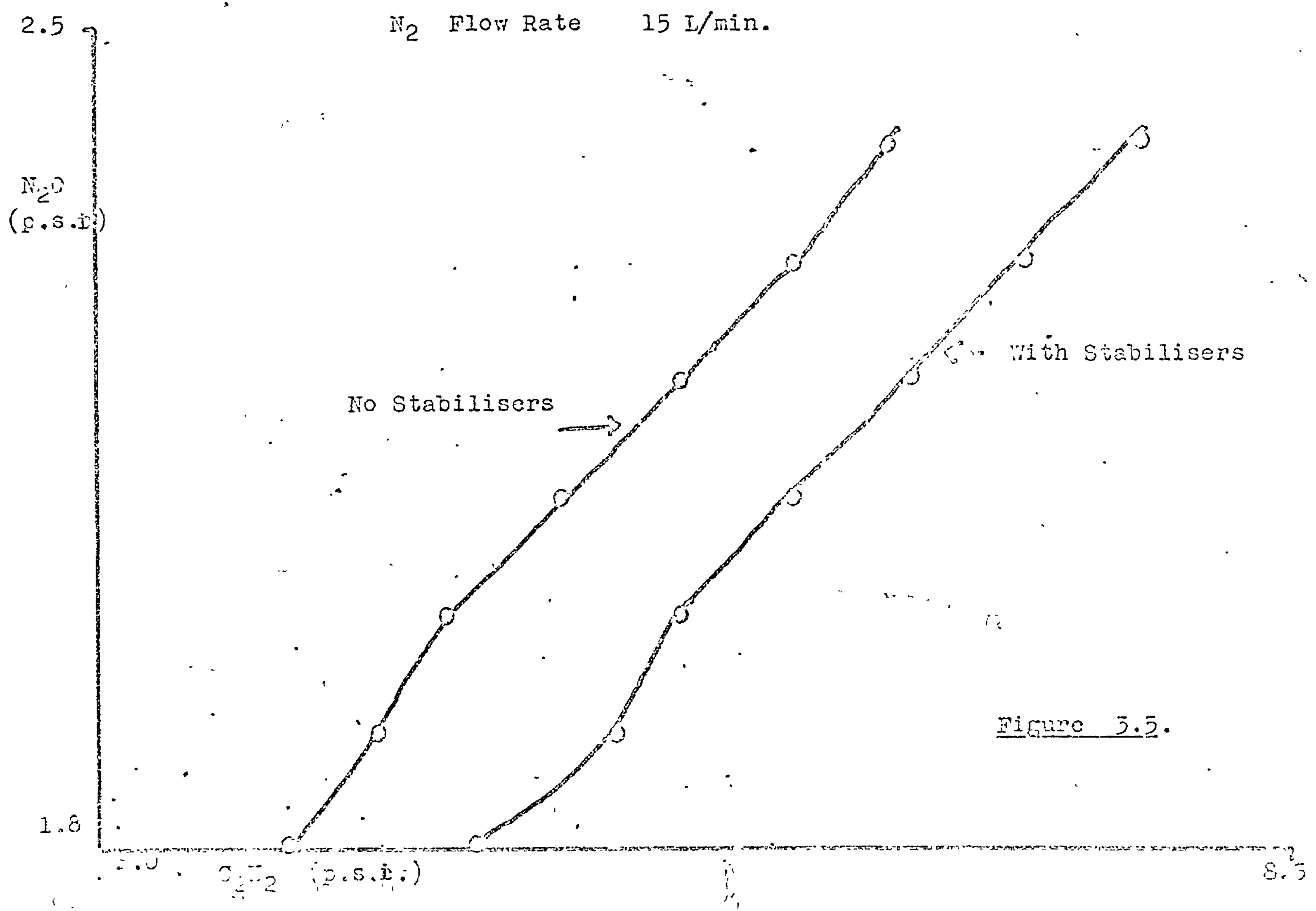
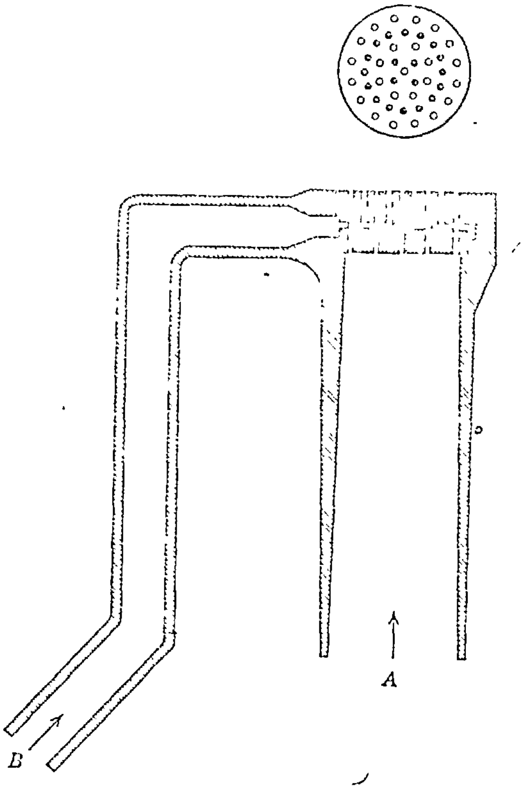

N$_2$ Flow Rate 15 L/min.
2.5
N$_2$O
(p.s.i.)
1.8
No Stabilisers
With Stabilisers
5.0
C$_2$H$_2$ (p.s.i.)
8.5

Figure 3.5.

3.4 THE DESIGN AND CONSTRUCTION OF A 'SCHUHKNECHT' TYPE BURNER.

In 1961 Schuhknecht[95] described the design and construction of a burner in which the aerosol is introduced directly at the base of the flame. A diagram of such a burner is shown in Figure 3.6.



Atomizer-burner of Schuhknecht. ○—openings for the aerosol; ∘—openings for the combustible mixture. Various combinations, producing premixed or diffusion flames, are possible: 1. C_2H_2-air through *A*; 2. H_2-air through *A*; 3. H_2 through *B* and air through *A*; 4. H_2 through *B* and O_2 through *A*; 5. C_2H_2-air through *A*, and additional O_2 through *B*.

Figure 3.6.

This burner enables various combinations of gases to be burned on the burner, as indicated in Figure 3.6. The main reason for the original design of this burner by Schuhknecht appears to be the need to reduce the danger of flashback with burners designed to support high burning velocity hot flames. In order to extend the study of experimental factors governing flame stability, and to provide a burner system of maximum versatility and flexibility in which the sample could be introduced into the flame independent of the fuel and oxidant gases, the construction of a burner based on similar principles was undertaken. The burner was constructed entirely from stainless steel capillaries. Other work on more conventional capillary burners has been described by Padley and Sugden[96] and Aldous et al[97].

A diagram of the burner design found to be most satisfactory is shown in Figure 3.7.

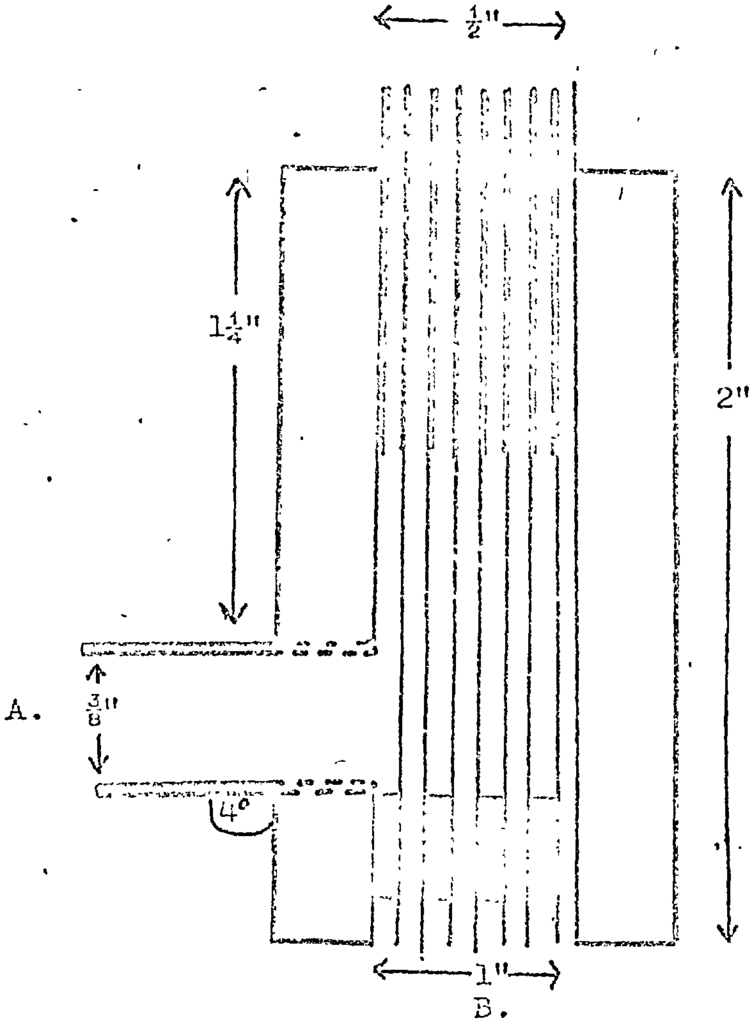


Figure 3.7.

Stainless steel hypodermic tubing (Accles and Pollock, Ltd.) was cut into 1" and $2\frac{1}{4}$" lengths. The 1" lengths were used to form the outlet holes for the side duct A. (Figure 3.7) and the $2\frac{1}{4}$" lengths were used for the outlet holes for the main duct B. The tubing was coated with high temperature epoxy resin (Araldite type AY 105 with hardener HY 953F, Ciba,Ltd.). A round burner was then constructed consisting of alternate long and short lengths of tubing. At the base of the assembly $\frac{1}{4}$" lengths of tubing were placed after being blocked with epoxy resin, in order to ensure that the chamber leading from the side duct A. was gas tight with respect to the duct B. The assembly was then fitted and sealed with epoxy resin into a stainless steel sleeve. Although two burners were constructed the only difference between them was that the second was of slightly greater diameter, and the side duct A. was inclined downwards from the horizontal in order to obtain improved drainage.

3.5 A STUDY OF SEVERAL GAS COMBINATIONS.

Various combinations of gases were employed with the burner. In the first a nitrous oxide-acetylene flame was burnt on the long capillaries. Theflame could be ignited directly, but after a few seconds there was a rapid build up of carbon on the burner head and a resultant luminous flame. The reason for the capillaries standing proud from the burner case is to prevent flash-back by air cooling of the capillaries. On grinding the capillaries down in stages, it was found that the length of time before carbon formation occurred increased, until a point was reached at which no carbon was formed. Therefore, there is both an optimum capillary height above the burner case before flashback will occur, and an optimum height before carbon formation will occur. The former appears to occur because the capillaries become too hot, while the latter occurs because they become too cool.

The burning of a nitrous oxide-acetylene flame on the short capillaries was attempted. The flame was stable but on switching the flame off the protruding capillaries became overheated. The reason for this was probably that the burner diameter was too large and the heat could not be dissipated sufficiently rapidly from the central capillaries. A stable air-acetylene flame could be burned at the short capillaries, but at the long capillaries low gas flow rates were required to permit a stable flame to be obtained.

With a nitrous oxide-acetylene flame at the long capillaries various gases were passed up the short capillaries. On passing nitrogen or argon up the short capillaries, i.e. diluting the burnt gases with inert gas, slight striations in the 'red feather' region of the flame were observed. The flame was more stable when argon was used than when nitrogen was employed, i.e. the flame did not tend to 'lift off' so easily, for the reasons discussed in Chapter 1. With air or nitrous oxide entering the short capillaries the nitrous oxide-acetylene flame became fuel lean. Hydrogen caused the appearance of an orange-red luminosity (possibly due to atomic hydrogen) which replaces the 'red feather' zone, and on increasing the hydrogen flow the flame tended to 'lift off'. The effect of carbon monoxide, passing through the short capillaries, on the nitrous oxide-acetylene flame was first to make the flame more luminous. This luminosity disappeared on increasing the carbon monoxide flow, resulting in a blue flame. Using this burner, it was also possible to burn an air-acetylene flame on the short capillaries and a nitrous oxide-acetylene flame on the long capillaries, simultaneously.

3.6 AN INVESTIGATION INTO THE PROPERTIES OF THE BURNER.

For the investigation the Beckman 440 Atomic Absorption Spectrophotometer was employed. A nebuliser chamber from a Techtron AA4 nebuliser system was connected to duct A and a chamber manufactured by Evans Electroselenium Ltd. was connected to duct B. The nebuliser heads were both manufactured by E.E.L. The burner and nebuliser assembly was placed in the position occupied by the Laminar Flow Burner. This meant that there was only one possible orientation of the burner assembly, due to the relatively small area which the Laminar Flow Burner can occupy.

An attempt was then made to study the effect on the atomic absorption of copper, when the mode of aspiration of the copper solution was varied. A 1000 ppm. copper solution (Anular copper sulphate reagent) and a Perkin-Elmer copper hollow cathode lamp was used. A nitrous oxide-acetylene flame was burned on the long capillaries, and the percent absorption noted for various flow rates of the nitrous oxide when the copper solution was aspirated via these capillaries. The sample solution was then aspirated into the flame at various flow rates of either nitrogen or argon via the short capillaries and the percent absorption again observed. All the absorbance values obtained were corrected for variation in sample uptake rate and nebulisation efficiency. The resultant curves are shown in Figure 3.8, together with the uncorrected values when argon was used. Argon gives a larger absorption signal than when nitrogen is employed as the aspirating gas, which can be accounted for by the specific gravities of the two gases. Table 3.2 shows the quantity of sample reaching the flame per unit time when the sample was aspirated via the short capillaries on either argon or nitrogen:

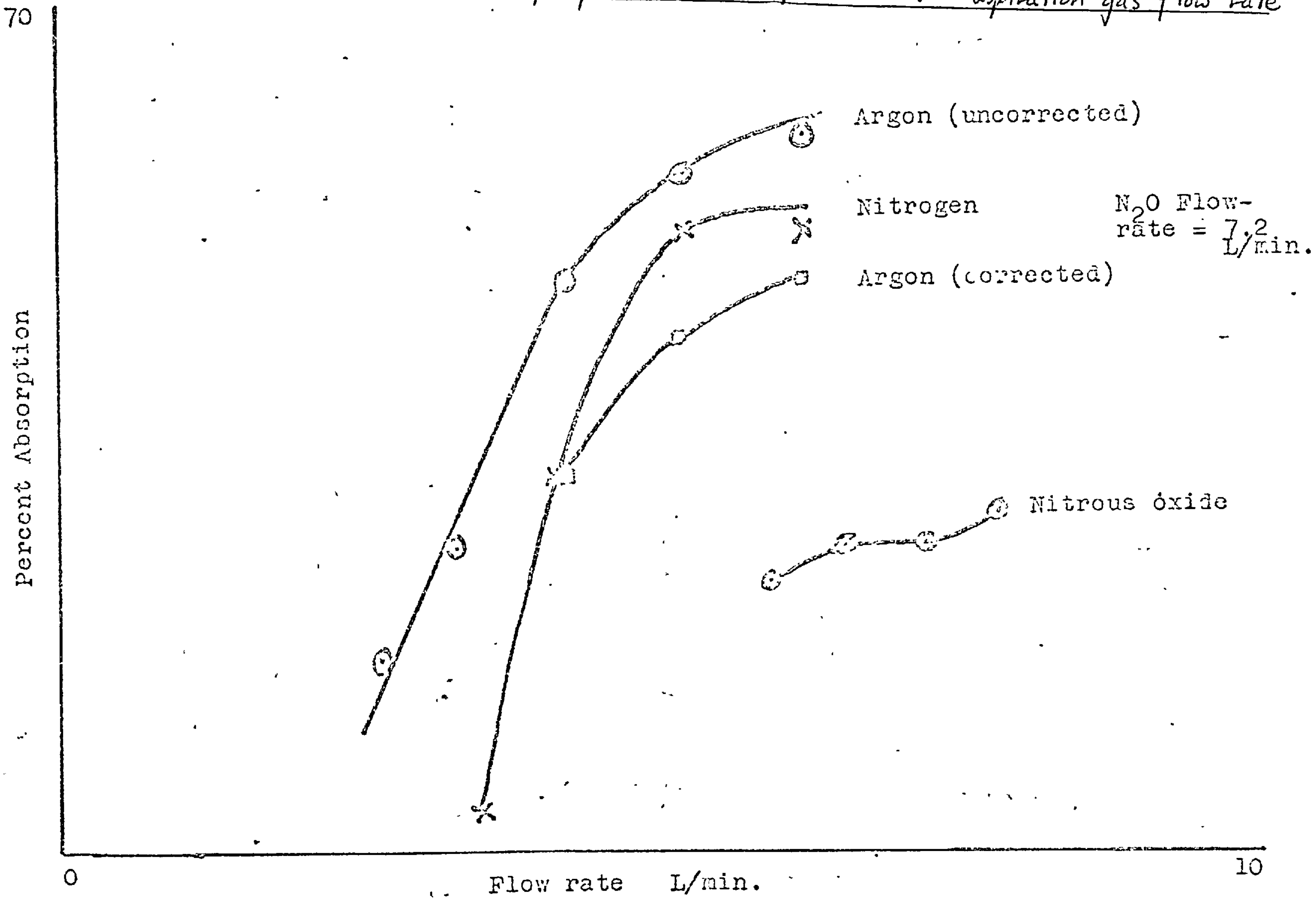
Quantity of Sample reaching Flame per min.(mls.)	Gas Flow-rate (L/min.)		
	6.2	5.2	4.2
1. Aspirating on Argon	0.50	0.40	0.26
2. Aspirating on Nitrogen	0.40	0.30	0.20
Ratio of 1. : 2.	1.25	1.3	1.3

Table 3.2.

It can be seen from Table 3.2 that the ratio of Argon to Nitrogen values for the amount reaching the flame per unit time is 1.3, which is the ratio of the specific gravities of Argon to Nitrogen. Because of the size and shape of the E.E.L. nebuliser chamber connected to duct A, there was a restriction in the horizontal movement of the burner assembly. This chamber was therefore replaced by a Techtron nebuliser chamber. The variation in the percent absorption across the top of the burner was studied with the

Figure 3.8.

The variation of percent absorption with aspiration gas flow rate



new arrangement. This was carried out by moving the burner across the path of the hollow cathode light beam, which was 5 mm. in diameter. The experiment was performed when the sample was introduced via the long capillaries into the nitrous oxide-acetylene flame by nitrous oxide, and when it was introduced through the short capillaries by argon. All percent absorption measurements were corrected for the differences in sample uptake rate and aspiration efficiency at each nebuliser chamber. The absorbance profiles obtained are shown in Figure 3.9, from which it can be seen that when aspiration is effected with argon there is a maximum absorption at one edge of the burner. This edge is directly opposite the inlet duct A. If the gas flow rates are adjusted such that there is 'lift-off' of the primary reaction cones, the first cones to 'lift-off' are those situated furthest away from the duct A. This suggests that a larger quantity of argon leaves the short capillaries in this particular part of the burner head.

Figure 3.9. The variation of percent absorption across the burner head.

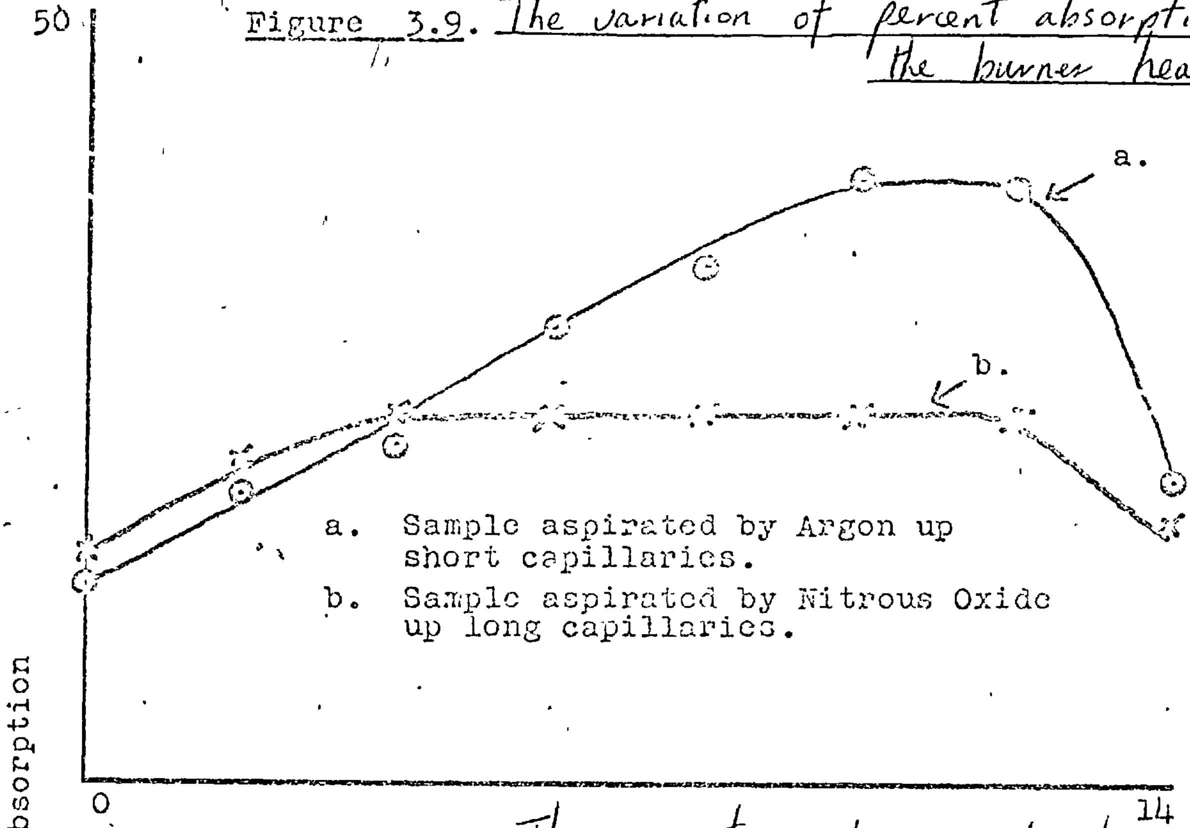
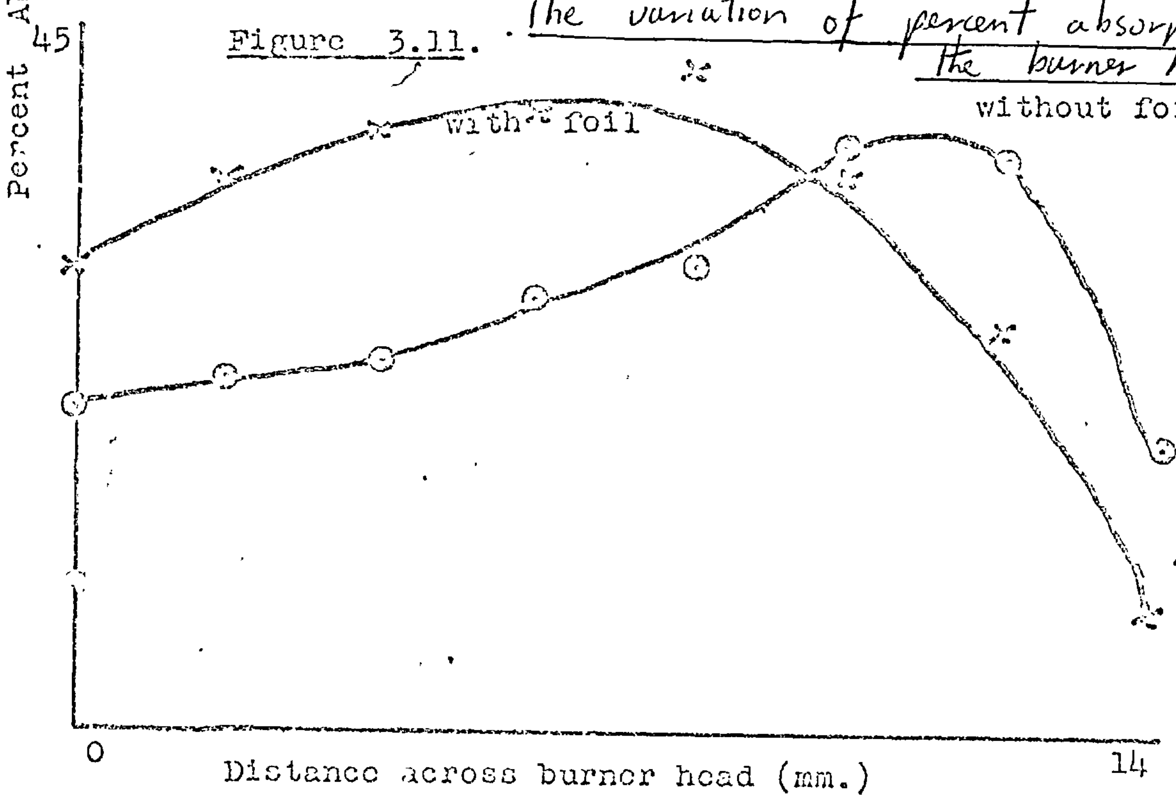


Figure 3.11. The variation of percent absorption across the burner head



In order to establish whether there was a non-uniform distribution of the argon in the short capillaries, a short piece of cupro-nickel strip was positioned in duct A. as shown in Figure 3.10:

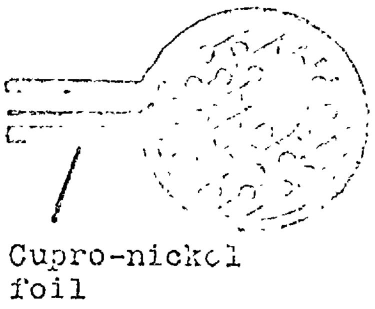


Figure 3.10.

It was envisaged that this foil might cause a tangential inlet flow in the gas stream, so that the ' swirling ' effect produced would cause a redistribution of the gas flow velocities across the burner head.

Figure 3.11 does show that with this arrangement the horizontal absorbance profile is indeed modified when the cupro-nickel foil is in position.

A further experiment to verify that an uneven distribution of gas occurred at the short capillaries involved the use of flameless atomic absorption for mercury. The burner assembly fitted with two Techtron nebuliser chambers was fitted to a Techtron AA.4 atomic absorption spectrophotometer. With no flame but using argon, which was passed over mercury before reaching the nebuliser, the absorbance for mercury at the 253.7 nm. line was observed. The same nebuliser was employed for aspiration via both the long and short capillaries. The experiment was performed twice. First the burner was in a position such that the maximum absorbance at the one edge of the burner was observed when aspirating via the long capillaries. This occurred when the axis of the inlet duct A. was at 90° to the optical axis of the Techtron AA.4 spectrometer; this will be denoted as position 1. The experiment was repeated with the inlet duct A. rotated through 90° , such that its axis was parallel to the optical axis, i.e. position 2. The results obtained are shown in Table 3.3:

Position	Absorbance	
	Long Capillaries	Short Capillaries
1.	0.035	0.055
2.	0.035	0.040

Table 3.3.

It can be seen from Table 3.3 that there is a maximum absorbance at one edge of the burner when the burner is in position 1 and the short capillaries are employed. In position 2. this maximum is reduced, as expected.

From these experiments it appears that the burner constructed is useful for study of different combinations of gases, but for analytical purposes an improved design for the introduction of sample into the short capillaries is required.

CHAPTER 4.

THE USE OF THE NITROUS OXIDE-ACETYLENE FLAME FOR THE DETERMINATION OF ARSENIC AND SELENIUM BY ATOMIC ABSORPTION SPECTROSCOPY.

4.1 INTRODUCTION.

The determination of arsenic and selenium by atomic absorption spectroscopy is well-known and has been studied by a number of workers,[98,99,100,101] Two of the principal difficulties encountered in these determinations which limit the A.A.S. detection limits attainable are the relatively low intensity and stability shown by many arsenic and selenium hollow-cathode lamp sources and the high flame background noise levels obtained at the resonance lines of these elements below 200 nm. With a hollow-cathode lamp source and an air-acetylene flame burning at a 10 cm. slot burner, commonly attained sensitivities (for 1% absorption) at the most sensitive arsenic line at 193.7 mm. are 1 or 1.5 p.p.m., while the detection limits observed by several workers under these conditions fall between 0.25 and 1 p.p.m.[98,99,59,101,102,103] Similarly in the air-acetylene flame, a commonly attained sensitivity at the selenium 196.0 nm. line is 1 p.p.m., while detection limits between 0.2 and 1 p.p.m. have been reported.

Several attempts have been made to overcome difficulties with low signal strength received at the detector, due to absorption of Ar and Se source radiation by the atmosphere, optical components and flame gases, and the relatively low sensitivity of commonly employed photomultipliers in the far U.V. region. The use of electrodeless discharge tube sources has been recommended by several groups of workers.[59,104,105,106] These intense line sources may present a greater signal intensity at the detector and allow operation at lower amplifier gain and spectral band-pass settings. Arsenic and selenium may be atomised efficiently for their determination by A.A.S. in argon-hydrogen or hydrogen-nitrogen diffusion flames burning with entrained air. These relatively cool flames exhibit greater transparency below 200 nm. than the air-acetylene flame, and fluctuations in the flame give rise to smaller variations in the signal; improved signal:noise intensity ratios are then obtained. Thus, for example, while as much as 60-75% absorption of the source radiation at 193.0 or 196.0 nm. may occur in the air-acetylene flame burning at a typical 10 cm. slot burner used

A.A.S.,[99,100,59,101,102,107] when an argon hydrogen flame is employed the flame background absorption at these wavelengths may be as low as 15-25%.[100] The determination of arsenic and selenium in these cool diffusion flames suffers from interference from foreign ions, however, particularly when high concentrations are present, owing to the inability of cool flames to vaporise or atomise the other elements present in the sample solution.

4.2 The Use of Single Pass Optics.

The use of the nitrogen shielded air-acetylene flame for the determination of arsenic and selenium by A.A.S. has already been described in Chapter 2. Separation of the oxidising secondary reaction zone of the air-acetylene flame by shielding with nitrogen results in lower flame background absorption and noise levels. The interconal zone, however, still contains significant partial pressures of absorbing molecular species (most probably oxygen) at high temperature; this results in significant absorption of the source radiation below 200 nm., even when a shielded flame is used. Thus even this flame was observed to produce approximately 30% absorption at

193.7 and 196.0 mm. when a 10 cm. slot-burner was employed.[59] The premixed nitrous oxide-acetylene flame, however, is effective for the atomisation of elements which form refractory oxides owing to the very low concentration of oxygen species in the interconal zone of the fuel-rich flame.[104] It was expected, therefore, that the background absorption of this flame would be very low, below 200 nm., particularly after separation of the secondary reaction zone by inert gas shielding. Although it might be expected that some loss of sensitivity (1% absorption) would result for As and Se from the use of this flame rather than the air-acetylene flame, with low background absorption and noise, superior detection limits and freedom from interferences could be anticipated. This chapter presents the results of a study of the determination of arsenic and selenium by A.A.S. in both conventional and nitrogen shielded fuel-rich nitrous oxide acetylene flames.

EXPERIMENTAL.

Apparatus. A Techtron AA4 flame spectrophotometer fitted with a Hanamatsu R213 photomultiplier was used in conjunction with a Servoscribe potentiometric recorder (Smiths Industries, Ltd., Wembley, England). Techtron 10 and 5 cm. path-length air-acetylene and nitrous oxide-acetylene slot-burners, and 5 cm. path-length shielded flame burner (Beckman-RIIC, Glenrothes, Scotland) suitable for use with a nitrogen shielded nitrous oxide-acetylene flame were used in this study. Hollow-cathode lamps (Perkin-Elmer Corp., Norwalk, Connecticut) for arsenic and selenium, and an electrodeless discharge lamp for arsenic, were employed. The electrodeless discharge lamp was operated in a $\frac{3}{4}$-wave resonant cavity Model 210L at 2450MHz with a Microtron 200 power generator (Electromedical Supplies Ltd., Wantage, England).

Reagents. 1000 p.p.m. arsenic and selenium stock solutions were prepared from arsenious oxide (AR grade) in 2N HCl and sodium selenite (AR grade) dissolved in distilled water. Dilute solutions were prepared from the stock solutions as required.

Operating Conditions in Nitrous Oxide-Acetylene Flame.

Arsenic.

Source: Electrodeless discharge tube operated at 35 Watts.

Resonance Line: 193.7 nm.

Monochromator Half-band pass: 0.99 nm.

Nitrous oxide Flow-rate: 7.0 litres/min.

Acetylene Flow-rate: 4.1 litres/min.

Burner: Techtron 5 cm. slot or Beckman-RIIC 5 cm. slot with inert gas shielding facility.

Shielding Gas Flow-rate: 15 litres/min.

Burner Height: Source radiation passes through red zone 2 - 7 mm.above burner head.

Sample Uptake-rate: 4 ml/min.

Selenium.

Source: Hollow-cathode lamp operated at 7 mA current.

Resonance Line: 196.0 nm.

Monochromator half-band pass: 0.99 nm.

Nitrous oxide Flow-rate: 7.0 litres/min.

Acetylene Flow-rate: 4.3 litres/min.

Burner: As for arsenic.

Burner Height: As for arsenic.

Sample Uptake-rate: 4 ml/min.

RESULTS.

Determination of Arsenic.

The operating conditions for the source, flame, monochromator spectral band-pass and detector which produced the highest sensitivity and lowest detection limits in the air-acetylene flame for the determination of arsenic at 193.7 nm. were established. When an arsenic hollow-cathode lamp source was employed at its recommended current (7mA) and with the maximum usable slit-width, due to low intensity and high flame background absorbance it was only possible to set the meter or recorder to zero absorbance using maximum gain. Under these conditions with a broad spectral band-pass the poor line signal:background intensity ratio of the lamp gave rise to poor sensitivity.[108] Even with the nitrous oxide-acetylene flame, where lower flame background absorbance permitted less gain to be employed, insufficient intensity was available from the hollow-cathode lamp to allow the use of a significantly narrower spectral band-pass to permit improvement in the 1% absorption sensitivity. For these reasons an electrodeless discharge tube source was employed for the arsenic determination. With optimised operating conditions this source was found to provide a better signal:background intensity ratio at the 193.7 nm. line and the absolute intensity of the resonance line emission was also greater.

Figure 4.1 shows the flame background absorption for the air-acetylene flame at 193.7 nm. after optimisation of the acetylene flow-rate to produce the best attainable detection limits for arsenic. Approximately 80% of the source radiation was absorbed by the flame; this value is in good agreement with previously reported data.[99,100,101,107] Even when an EDL source is used for arsenic, it is apparent that with the high flame background the noise level (Figure 1c) after setting the absorbance to zero by increasing the gain is equivalent to 2-3% absorption. With these operating conditions the sensitivity and detection limit for arsenic at 193.7 nm. in air-acetylene are shown in Table 4.1 . The detection limit was defined as that concentration of arsenic in aqueous solution which produced an absorbance signal equal to twice the standard deviation in the background noise.

Figure 4.2 shows the variation of the flame background absorbance at 193.7 nm. with acetylene flow-rate for the conventional premixed nitrous oxide-acetylene flame with the 5 cm. slot-burner. It is evident that high transmission is available as predicted in the 'red feather' region of the slightly fuel-rich flame. The lower transmission in the fuel-lean and very rich flames may be explained by the higher concentration of oxidising species in the interconal zone in the lean flame and in the secondary reaction zone of the luminous rich flame. The absorption signal observed for arsenic in the nitrous oxide-acetylene flame remained fairly constant as the acetylene flow-rate was varied, although less sensitivity is obtained in the very lean flame. The acetylene flow-rate used to provide minimum flame background absorption, therefore, also provided the optimum absorption signal for arsenic. Figure 4.1shows the flame background absorption and noise observed for arsenic at 193.7 nm. in the conventional and nitrogen shielded nitrous oxide-acetylene flames. The flame background absorption observed in the conventional flame was approximately 25%. When the flame was shielded with nitrogen the background absorption was observed to decrease to only 4%. It is also apparent from Figure 4.1 that the signal noise is substantially reduced in both nitrous oxide flames compared to the air-acetylene flame. The signal noise level in the conventional nitrous oxide-acetylene flame is equivalent to approximately 1% absorption, whereas in the nitrogen shielded flame it was found to be equivalent to approximately 0.5% absorption. Table 4.1 shows the sensitivity and detection limits obtained for arsenic in the nitrous oxide-acetylene flames under these conditions.

Determination of Selenium.

The operating conditions were optimised for the determination of selenium at 196.0 nm. in the air-acetylene flame. A selenium hollow-cathode lamp was employed with the maximum monochromator spectral band-pass of 0.99 nm. Figure 4.3 shows the flame background absorbance at 196.0 nm. for the air-acetylene flame after optimisation of the acetylene flow-rate to produce the best detection limits for selenium. Approximately 63% of the source radiation was absorbed by the flame; this value is again in good agreement with previously reported data.[100,59,102] The signal noise level obtained after setting the absorbance to zero by increasing the gain (Figure 4.3) is equivalent to 1.3% absorption. With these operating conditions the sensitivity and detection limit for Se at 196.0 nm. in the air-acetylene flame are shown in Table .

Figure 4.2 shows the variation of the flame background at 196.0 nm. with acetylene flow-rate for the premixed nitrous oxide-acetylene flame with the 5 cm. slot-burner. High transmission is available in the fuel-rich flame at this wavelength. The fuel flow-rate corresponding to minimum absorbance occurs at a somewhat higher acetylene flow-rate than for arsenic, and the absorbance at this point is substantially less than that for arsenic. As the selenium absorption signal was found not to be markedly dependent upon the fuel flow-rate the acetylene flow-rate for which low flame background absorbance is obtained also gives good sensitivity for selenium. Figure 4.3 shows the flame background and noise observed for selenium at 196.0 nm. in the conventional and nitrogen shielded nitrous oxide flames. The flame background absorption in the conventional flame was approximately 18%. When the flame was shielded with nitrogen the background absorption was observed to decrease to only 5%. A reduction in background noise is also observed compared to the air-acetylene or conventional nitrous oxide-acetylene flames. The signal noise level in the conventional flame is equivalent to approximately 0.5% absorption, whereas in the nitrogen shielded flame it was found to be equivalent to approximately 0.3% absorption. Table 4.1 shows the sensitivity and detection limits obtained in the nitrous oxide-acetylene flames under these conditions.

Table 4.1 Sensitivities and Detection Limits for Arsenic and Selenium.

Element Wavelength(nm)	Flame	Burner	Sensitivity (p.p.m./1% absorption)	Detection Limit (p.p.m.)
As 193.7	Air/C_2H_2	Techtron 10cm.	1.2	2.2
	N_2O/C_2H_2	Techtron 5cm.	2.0	1.1
	N_2O/C_2H_2	Beckman 5cm.	2.0	1.8
	N_2O/C_2H_2 (nitrogen shielded)	Beckman 5cm.	2.0	1.0
Se 196.0	Air/C_2H_2	Techtron 10cm.	1.3	1.3
	N_2O/C_2H_2	Techtron 5cm.	5.0	1.8
	N_2O/C_2H_2	Beckman 5cm.	6.5	2.5
	N_2O/C_2H_2 (nitrogen shielded)	Beckman 5cm.	6.5	2.0

Interferences.

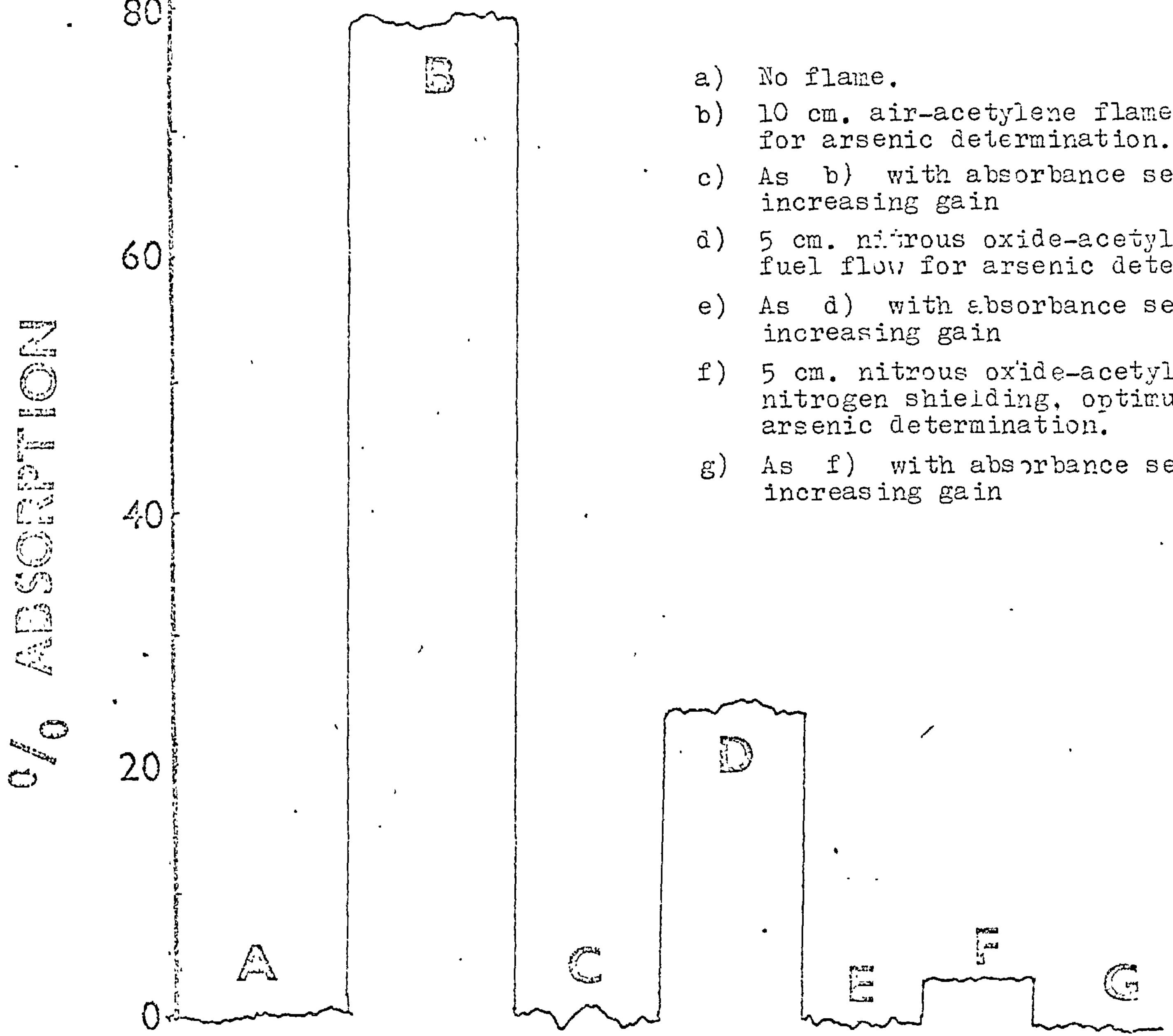
The effect of the presence of foreign ions on the determination of arsenic and selenium has been studied in the air-acetylene[109] and argon-hydrogen flames. In both of these flames numerous interferences are encountered for both elements. Johns[101] reported that selenium was less affected by interfering ions in the argon-hydrogen flame than in the air-acetylene flame and also observed very severe interferences when the argon-hydrogen flame was employed for the determination of arsenic. Kirkbright, Sargent and West[59] have reported the occurrence of interferences in the nitrogen shielded air-acetylene flame for the determination of these elements. As arsenic appears to suffer more severely than selenium from interferences in air-acetylene and argon-hydrogen flames we examined the effect of the presence of 100-fold weight excesses of 20 different cations and anions on the absorbance obtained for an aqueous 100 p.p.m. arsenic solution in the nitrous oxide-acetylene flame at 193.7 nm. The foreign ions chosen for study include those reported elsewhere to interfere with the determination of arsenic in air-acetylene and argon-hydrogen flames. No interference was observed at the concentrations employed for Al, Ba, Ca, Cd, Co(II), Cr(III), Cu, Fe(III), K, Mg.

Mn(II), Na, Ni, Sr, V(IV), Zn, Zr, PO_4(-III), SO_4(-II) and NO_3(-I). Of these Mg, Al, Ca, Fe(III), Co(II), Ni, have been reported to interfere in the air-acetylene flame[59], and Al, Ba, Ca, Co(II), Fe(III), Mg, Ni, Sr, and PO_4(-III) have been reported to interfere seriously in the argon-hydrogen flame.

Ionisation. As expected from the high ionisation potentials of the arsenic (I.P. 9.81 eV) and selenium (I.P. 9.75 eV) atoms no significant ionisation was detectable for these elements in the nitrous oxide-acetylene flame.

DISCUSSION

The results of this study show that the premixed nitrous oxide-acetylene flame forms an effective medium for the determination of arsenic and selenium by AAS. Although the sensitivity attainable is lower than that available with the air-acetylene or argon-hydrogen flames, presumably due to the high gas flow-velocity and short path-length necessary to support this hot flame, the low flame background absorbance and noise of the nitrous oxide flames permits detection limits which are comparable (for Se) or somewhat superior to (for As) those observed in the air-acetylene flame to be obtained. The argon-hydrogen flame may offer superior sensitivity and detection limits for the determination of both elements, but the results of this study indicate that the freedom from interference observed for arsenic in the nitrous oxide flame may make its use preferable to argon-hydrogen, or even air-acetylene for the determination of this element in complex matrices such as metal alloys, glasses, etc. When an atomising medium of low background and noise such as the nitrogen shielded nitrous oxide-acetylene flame or the argon-hydrogen flame is used for the determination of arsenic and selenium, the intensity and stability of the atomic line source employed limits the detection limits attainable. The argon-hydrogen flame produces a higher sensitivity (for 1% absorption) than the nitrous oxide-acetylene flame, so that when the same arsenic or selenium source is used for the determination of either element in each flame although the source noise is constant a lower detection limit is obtained with the argon-hydrogen flame. It should be possible to overcome the disadvantage of loss of sensitivity for arsenic and selenium in the nitrogen shielded nitrous oxide-acetylene flame by the use of multiple pass optics; this is not possible with the air-acetylene flame owing to its high background absorption.



a) No flame.

b) 10 cm. air-acetylene flame, optimum fuel-flo for arsenic determination.

c) As b) with absorbance set to zero by increasing gain

d) 5 cm. nitrous oxide-acetylene flame, optimum fuel flow for arsenic determination.

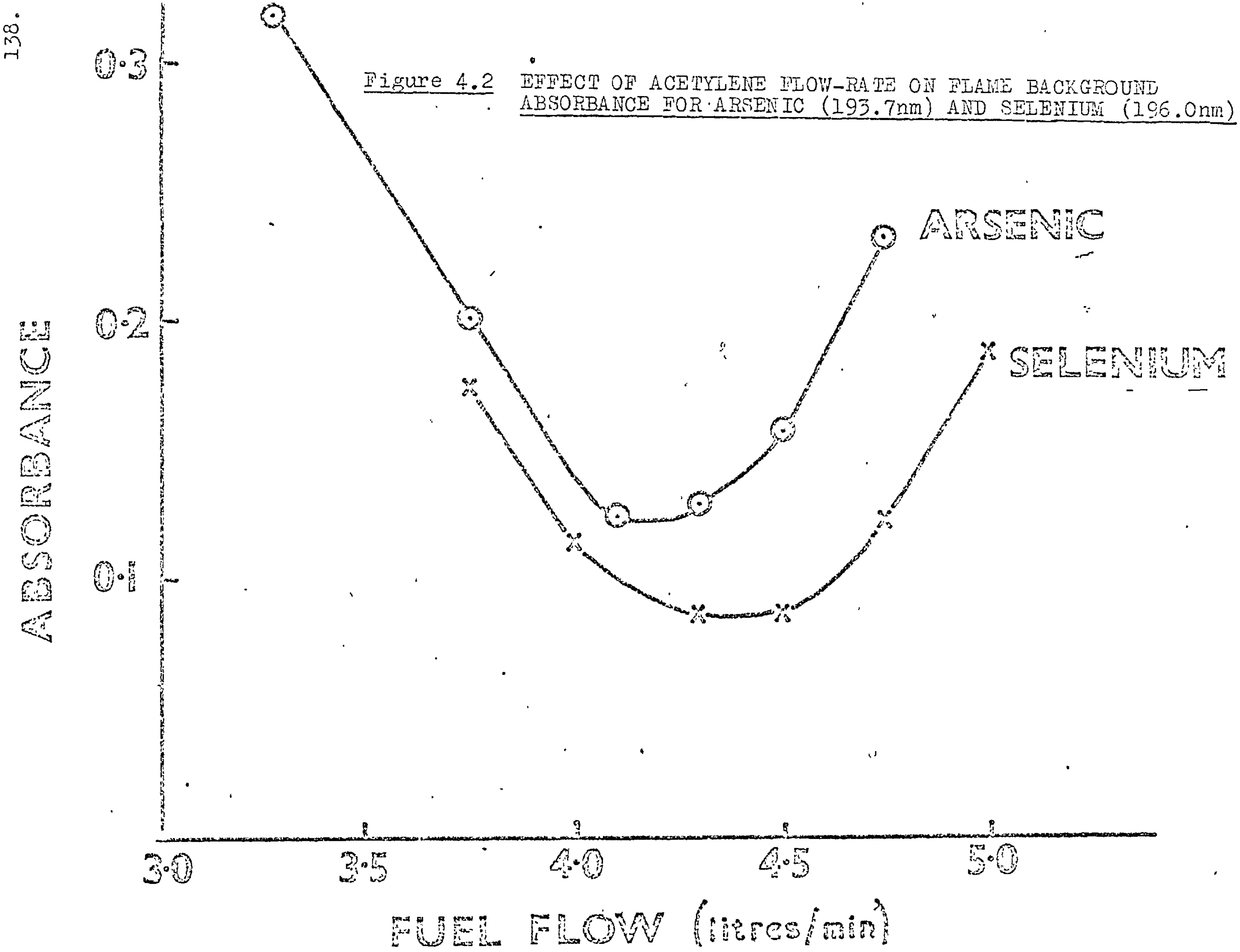
e) As d) with absorbance set to zero by increasing gain

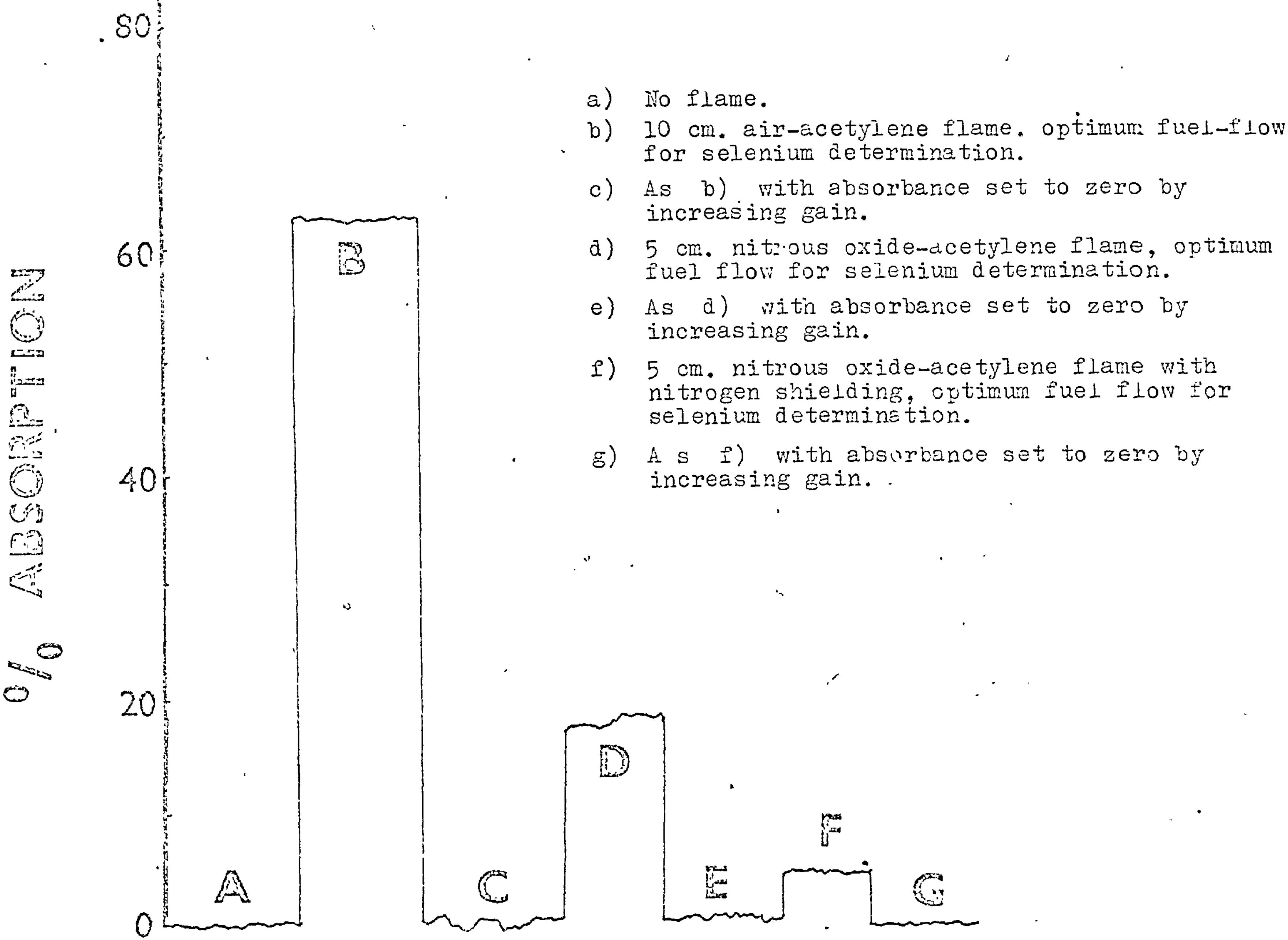
f) 5 cm. nitrous oxide-acetylene flame with nitrogen shielding, optimum fuel flow for arsenic determination.

g) As f) with absorbance set to zero by increasing gain

Figure 4.1 FLAME BACKGROUND ABSORPTION AT THE ARSENIC 193.7 nm. LINE.

Figure 4.2 EFFECT OF ACETYLENE FLOW-RATE ON FLAME BACKGROUND ABSORBANCE FOR ARSENIC (193.7nm) AND SELENIUM (196.0nm)





a) No flame.

b) 10 cm. air-acetylene flame. optimum fuel-flow for selenium determination.

c) As b) with absorbance set to zero by increasing gain.

d) 5 cm. nitrous oxide-acetylene flame, optimum fuel flow for selenium determination.

e) As d) with absorbance set to zero by increasing gain.

f) 5 cm. nitrous oxide-acetylene flame with nitrogen shielding, optimum fuel flow for selenium determination.

g) As f) with absorbance set to zero by increasing gain.

Figure 4.3 FLAME BACKGROUND ABSORPTION AT THE SELENIUM 196.0 nm. LINE.

4.3 The Use of Triple Pass Optics.

As described in Chapter 4.2, the Techtron A.A.4 flame spectrophotometer was employed for the investigation of the characteristics of the N_2O/C_2H_2 flame at the As 193.7 and Se 196.0 nm. lines owing to its great flexibility for optimisation of operating conditions; however, the Beckman 440 atomic absorption spectrophotometer has the facility of a triple pass mode of operation. The use of the nitrous oxide-acetylene flame for the determination of Arsenic and Selenium using the Beckman 440 spectrophotometer in conjunction with the Beckman Laminar Flow burner was, therefore, evaluated. It was expected that the loss of sensitivity in the determination of Arsenic and Selenium when using the nitrous oxide-acetylene flame as compared to the air-acetylene flame would be overcome when using both the triple pass and hot modes.

EXPERIMENTAL:

Apparatus.

A Beckman Model 440 Atomic Absorption Spectrophotometer equipped with the argon shielded nitrous oxide-acetylene Laminar Flow Burner was used in conjunction with a Beckman 5-inch strip-chart recorder (Model No. 93507). Electrodeless discharge lamps were used for both arsenic and selenium. The lamps were operated in a $\frac{3}{4}$-wave resonant cavity Model 210 L. at 2,450 MHz with a Microtron 200 power generator (Electromedical Supplies, Ltd., Wantage, England). The minimum power attainable with this power generator is 15 watts. In order to overcome this minimum power restriction a 3 db power attenuator (E.M.S.) was connected between the microwave generator and the cavity. This reduced the power output of the generator by 50%, thus decreasing self-absorption and short term noise of the resonant radiation . The arsenic and selenium stock solutions were prepared from arsenious oxide (AR grade) and sodium selenite (AR grade).

RESULTS:

The determination of Arsenic.

The percentual and fluctuational concentration limits (PCL and FCL) for Arsenic with the Beckman Laminar Flow unseparated air-acetylene flame at optimum conditions; i.e. flame conditions, burner height and electrodeless discharge lamp power in the cold and single pass modes, were determined. The P.C.L. obtained was 3.0 p.p.m. and the F.C.L. obtained was 15 p.p.m. with a response time of 2 sec. These values compare well with those previously obtained (Chapter 2); then the P.C.L. value was 2.00 p.p.m. and the F.C.L. was 16.00 p.p.m., with a response time of 2 sec.

The P.C.L. and F.C.L. values for Arsenic were then determined using the nitrous oxide-acetylene flame, all modes of operation being employed; i.e. single pass, triple pass, shielded, unshielded, hot and cold modes. The acetylene flow-rate and burner height were optimised to produce the best attainable detection limits. The P.C.L. and F.C.L. values obtained in all modes of operation are shown in Table 4.2 . The 193.7 nm. resonance line was employed and the E.D.L. was operated at a power of 20 watts in all cases.

In the single pass mode of operation 30% of the source radiation was absorbed by the nitrous oxide-acetylene flame; on argon shielding the flame this value was reduced to 10%, at the optimum conditions for the determination of arsenic. In the triple pass mode of operation the unshielded flame absorbed 75% of the source radiation, the shielded flame only absorbing 30%.

			PCL Values (ppm)			FCL Values (ppm)					
Element	Wavelength (nm)	Conditions	Air/ C_2H_2 Flame	Conventional Flame	Argon Shielded Flame	Response Time 2 sec.		Response Time 8 sec.		Response Time 16 sec.	
						Conventional Flame	Argon Shielded Flame	Conventional Flame	Argon Shielded Flame	Conventional Flame	Argon Shielded Flame
Arsenic	193.7	1-P Cold	3.0	6.0	6.0	12.5	12.5	6.2	6.2	3.1	3.1
		3-P Cold		7.0	3.1	75.0	22.0	37.5	9.0	22.5	6.0
		1-P Hot		2.2	2.0	4.4	4.0	2.2	2.0	1.1	1.0
		3-P Hot		1.2	0.7	12.0	5.5	7.5	3.5	5.0	2.1
Selenium	196.0	1-P Cold	2.3	14.0	14.0	28.0	28.0	14.0	14.0	7.0	7.0
		3-P Cold		10.5	8.1	94.0	48.4	42.0	24.0	2.1	12.0
		1-P Hot		2.5	2.5	7.5	7.5	5.0	5.0	2.5	2.5
		3-P Hot		1.8	1.5	18.0	12.0	7.2	6.0	3.6	3.0

Table 4.2 .

Mode:

1-P Single Pass
3-P Triple Pass.

The determination of Selenium.

A Selenium electrodeless lamp operated at a power of 25 watts was employed as the radiation source for the determination of Selenium using the Beckman Laminar Flow unseparated air-acetylene flame. The P.C.L. and F.C.L. values obtained at 196.0 nm. were 2.30 p.p.m. and 16.0 p.p.m. (Response time 2 secs.), respectively. The values obtained employing a selenium hollow cathode lamp were 2.09 p.p.m. and 12.5 p.p.m. (Response time 2 secs.), respectively. Thus the P.C.L. and F.C.L. values for Selenium using the unseparated air-acetylene flame in the single pass and cold modes of operation for both a selenium electrodeless discharge lamp and a selenium hollow cathode lamp compare favourably.

The P.C.L. and F.C.L. values for Selenium employing the unshielded and shielded nitrous oxide-acetylene flame were then determined for all modes of operation; the results obtained are shown in Table 4.2 . The nitrous oxide-acetylene flame was found to absorb 25% of the source radiation in the single pass mode of operation; on argon shielding the flame only 10% of the radiation was absorbed. The unshielded nitrous oxide-acetylene flame absorbed 85% of the source radiation when the triple pass mode was employed, but this reduced to only 20% on argon shielding the flame.

CONCLUSION:

Considering the single pass mode of operation for both Arsenic and Selenium, the P.C.L. values obtained using the nitrous oxide-acetylene flame are slightly worse than those attained in the air-acetylene flame. These values are considerably improved, however, on using the triple pass mode in conjunction with the argon-shielded nitrous oxide-acetylene flame.

4.4 The Analysis of Simulated Samples.

One of the main advantages of using the nitrous oxide-acetylene flame for the determination of Arsenic and Selenium is the freedom from interference effects which results; this is not the case for the air-acetylene and air-hydrogen flames[59,109,101]. The most common method employed to overcome interference effects when the latter two flames are used is prior chemical separation of the Arsenic or Selenium from the interfering matrix. Chakrabarti[109], for example, extracted Selenium into methyl- isobutyl ketone as the diethyl dithiocarbamate complex, and the selenium in the extract was then determined by atomic absorption spectrophotometry using the air-hydrogen flame. In 1968 Danchik and Boltz[110] determined Arsenic indirectly by forming molybdoarsenic acid at pH 1.8, extracting this into methyl-isobutyl-ketone and subsequently decomposing the acid with ammonical buffer solution. The molybdenum absorption was then measured using an air-acetylene flame. A similar method for the determination of Arsenic has been described by Ramakrishna[111] in which the arsenic is extracted selectively as the heteropoly-molybdo acid and the molybdenum determined by A.A.S. using the nitrous oxide-acetylene flame.

Holak[112], and more recently, Fernandez and Manning[113], have described methods of determining Arsenic and Selenium by producing arsine or hydrogen selenide. The arsine or hydrogen selenide is swept into an air-hydrogen flame[113], and the arsenic or selenium determined by atomic absorption spectrophotometry. Because the arsine and hydrogen selenide are released from the matrix, interference effects are, therefore, minimised.

Interference Studies:

Arsenic is often encountered in tin or lead based white metal alloys, whilst Selenium is often added to mild steels to make them more workable when being turned. Therefore, the effect of 500 or 1,000 fold excess of the various cations that may be present in such matrices on the absorbance of arsenic or selenium was investigated in the air-acetylene and nitrous oxide-acetylene flames. Both flames were operated in the cold mode and single pass optics were used. The interference effects are listed on Table 4.3.

Table 4.3 shows that at high concentrations of interferent ion, the air-acetylene flame at the optimum conditions for determining Arsenic and Selenium suffers from substantial interference, which is eliminated on using the nitrous oxide-acetylene flame. In order further to demonstrate the freedom of the nitrous oxide-acetylene flame from interference for both Arsenic and Selenium determinations, determinations were made for Arsenic in a tin based white metal alloy and for Selenium in mild steels. All determinations were made using triple-pass optics and the cold mode of operation.

In the case of the tin based alloy, a standard sample was obtained and analysed. A known amount of Arsenic was also added to the dissolved standard. It was not possible to obtain a mild steel sample containing a known amount of Selenium; therefore, simulated samples were examined.

Analyte Concentration (ppm)	Interferent Concentration (ppm)	Effect on Absorption for As or Se	
		Air-Acetylene Flame	Nitrous Oxide Acetylene Flame
Arsenic:			
40	Sn 20,000	25% depression	Less than 2%
40	Pb 20,000	Less than 2%	"
40	HCl (4N)	Less than 2%	"
Selenium:			
50	Mn 25,000	20% enhancement	Less than 2%
50	V 25,000	20% enhancement	"
50	Fe 25,000	21% enhancement	"
50	Ni 25,000	19% enhancement	"
50	Cr 25,000	19% enhancement	"
50	Phosphoric Acid 5% v/v	27% enhancement	"
50	Sulphuric Acid 5% v/v	25% enhancement	"
50	Hydrochloric Acid 5% v/v	Less than 2%	"
50	Nitric Acid 5% v/v	28% depression	"

Table 4.3.

For the determination of Arsenic in the tin based white metal, 2 gms. of the BCS.178/1 standard sample were dissolved in 25 ml. of conc. HCl and 4 ml. of conc. HNO_3 added to aid dissolution, care being taken not to lose the volatile chlorides of arsenic. A further 15 ml. of conc. HCl was then added, in order to prevent the precipitation of basic tin oxides. The solution was then made up to 100 mls. with distilled water. Further sample solutions were made by dissolving 1 gm. of the BCS.178/1 standard and adding various amounts of arsenic. For the Selenium determination 1 gm. each of BCS.320 and BCS.323 steel standards were dissolved in 5% v/v HNO_3/5%vv H_3PO_3 and 5%vv H_2SO_4 and selenium solution added such that the final solution on dilution to 100 mls. with distilled water contained 160 p.p.m. of Selenium. The results obtained are shown in Table 4.4 .

Sample Number	% Arsenic or Selenium found. Average of 2 Determinations:	% Arsenic or Selenium Present.	Other Major Constituents Present (%)
BCS.178/1	0.15_5	0.16	Pb, 3.23
BCS.178/1	0.68_7	0.70	Pb, 3.23
BCS.178/1	0.49_5	0.50	Pb, 3.23
BCS.323	1.6_0	1.6	Mn 0.29%;Cr 0.22%
BCS.320	1.6_5	1.6	Mn 0.19%,Cr 0.13% Ni 0.17%

Table 4.4

CONCLUSION.

The argon separated nitrous oxide-acetylene flame using the Beckman Laminar Flow Burner can be used successfully for the determination of Arsenic and Selenium in complex matrices, without the addition of the major constituents of the matrix to the calibration solutions.

CHAPTER 5.

THE USE OF AN OXYGEN SHEATHED HYDROGEN-NITROGEN FLAME FOR THE DETERMINATION OF BORON BY FLAME EMISSION SPECTROSCOPY.

5.1 INTRODUCTION.

The sensitivity attained in the determination of Boron by atomic absorption spectroscopy is relatively low, owing to the high thermal stability of the various oxides of boron; this results in a relatively low free B atom fraction in most flames. Even when a hot, fuel-rich nitrous oxide/acetylene flame was employed, Amos and Willis[114] were only able to obtain a sensitivity of 13 ppm.

The most important flame photometric methods for determining boron involve detection of the molecular band emission from boron species such as BO_2. The first comprehensive study of the use of flame emission spectroscopy for the determination of Boron was undertaken by Dean and Thompson[115]. Employing the three prominent boron oxide band systems (at 492, 518 and 546 nm.), an oxy-acetylene flame and 1:1 methanol-water solutions, detection limits of between 1 and 3 ppm. were obtained. Maek[116] extracted boron into methyl iso-butyl ketone as the tetrabutyl-ammonium boron tetrafluoride ion association complex and aspirated the extract into an oxygen sheathed oxy-hydrogen flame and obtained a detection limit of 10 ppm. Agazzi[117] formed a weak chelate between boron and 2-ethyl-1,3-hexonediol which was extracted into chloroform, the boron being determined by flame emission using an oxy-hydrogen flame.

From the above studies it is evident that a hot flame is required to form the lower oxides of boron and stimulate sufficiently intense emission from these species. The hot flames previously employed, however, such as oxy-hydrogen and oxy-acetylene, have extremely high burning velocities and may only be supported at total consumption nebuliser-burners as turbulent flames. Owing to the large mean average droplet diameter of solutions introduced into these flames, and the short residence time (high rise velocity) of the aerosol in the flame, considerable chemical and physical interference effects are encountered. In addition, the turbulent nature of these flames degrades the attainable signal:noise ratio. A cool flame, on the other hand, may be supported at burners of relatively large diameter. In order to provide for both low burning velocity, low rise velocity and high temperature, a cool flame with a hot outer zone may be obtained by oxygen sheathing a nitrogen-hydrogen flame.

Employing the Technicon A.F.S.6 spectrophotometer, which is capable of operating in both atomic fluorescence and flame emission modes, the determination of boron was investigated by flame emission with this flame using the separation facility of the normal burner to provide the oxygen sheathing.

5.2 EXPERIMENTAL:

A six-channel atomic fluorescence spectrophotometer (Technicon Corp., Tonytown, N. Y., Model A.F.S.6) was employed. This system is based on an original design described by Mitchell and Johansson [118]. Figure 5.1 shows the main features of the instrument. There are six excitation sources placed such that their radiation is focussed in the flame. A series of pulses of modulated radiation is emitted from each lamp in turn, resulting in fluorescence radiation from the corresponding atomic species in the flame. The fluorescent radiation is collected and passed through appropriate optical filters mounted on a rotating wheel to a photodetector. These pulses of radiation are converted to electrical signals which are processed and read out in digital form. A block diagram of the signal processing system is shown in Figure 5.1 , which also shows how the operation of the machine is controlled by digital timing and control circuitry. The following operations are required for both the fluorescence and emission modes of operation.

1. On aspirating a standard solution, the amplifier gain is automatically selected to give the optimum signal level for each channel.
2. Automatic zero setting on aspirating a blank.
3. Automatic calibration of the instrument on aspirating a standard solution.

4. Analog-digital conversion to enable digital readout.
5. Automatic measurement of samples.

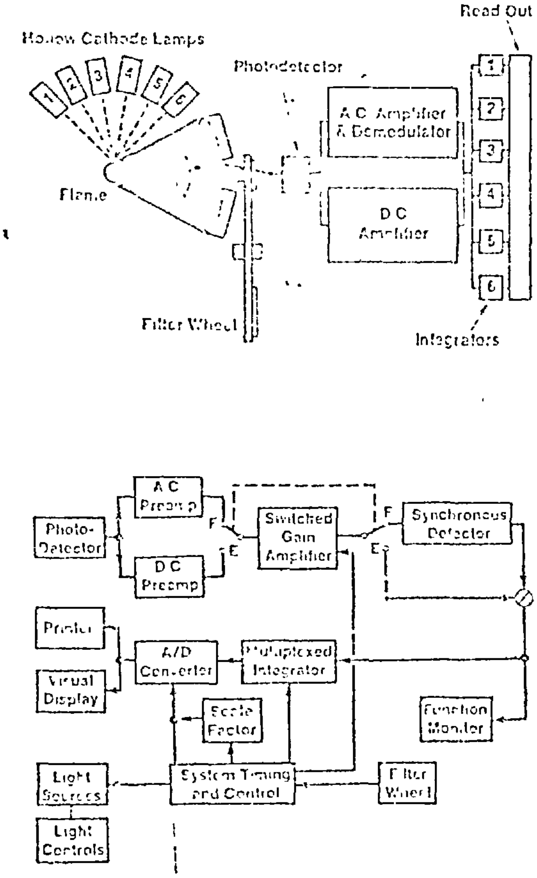


Figure 5.1.

The spectrophotometer employs an indirect nebuliser and premix chamber and for this study a circular titanium burner head with 19 holes, 0.029" in diameter. An oxygen sheathed hydrogen/nitrogen flame was used and the nebuliser uptake rate was 3.7 ml./min.

In order to remove any cation interferences, an ion exchange column containing analytical grade amberlite resin

(IR-120(H)) was used, activated with 0.1M HNO_3 in conjunction with the Technicon auto analyzer proportionating pump.

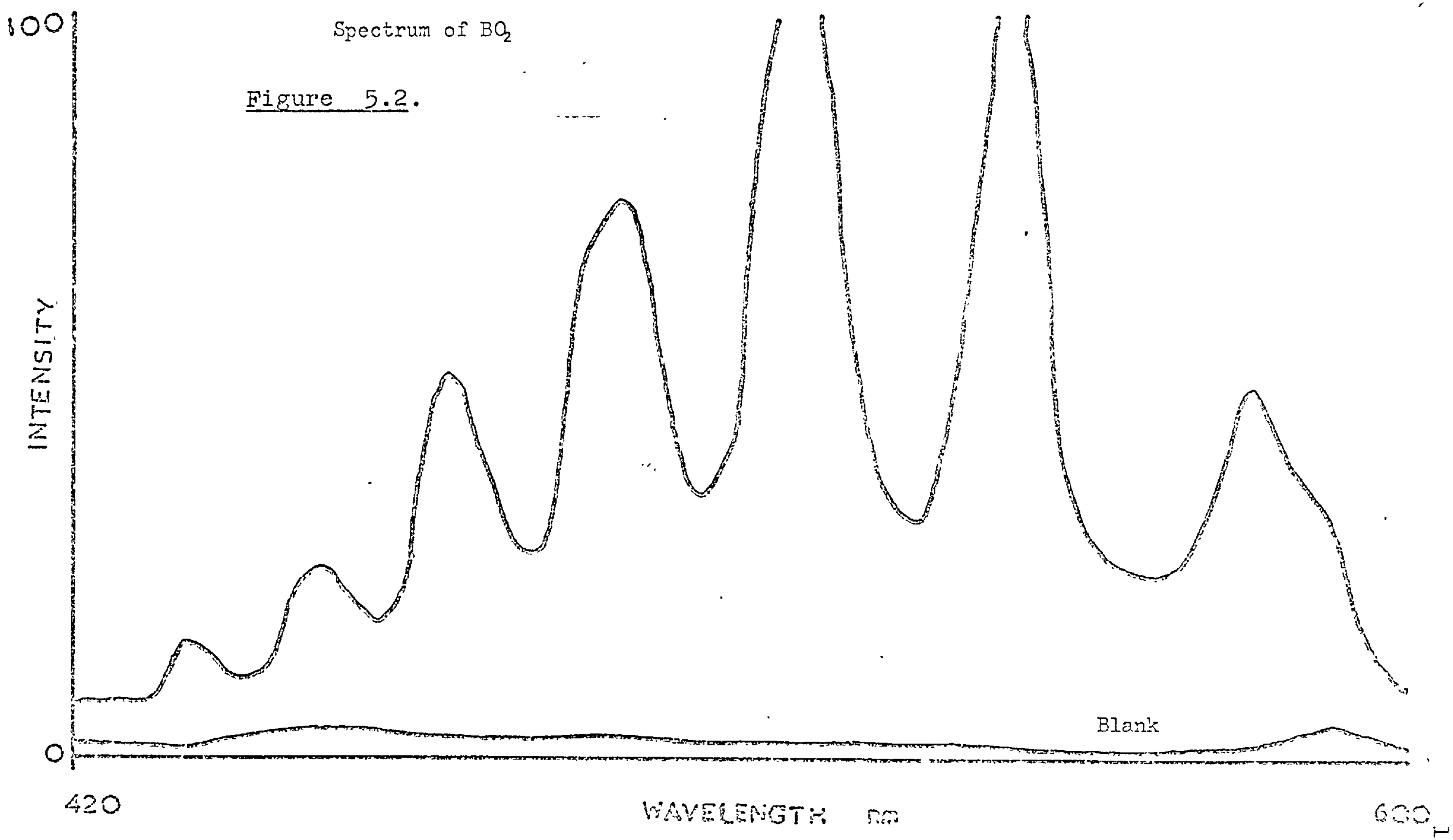


Figure 5.2.

5.3 RESULTS:

In order to examine the spectrum of the radiation emitted when 1,000 ppm. Boron was aspirated into an oxygen sheathed nitrogen/hydrogen flame, a Techtron A.A.4 spectrophotometer was used. The resultant spectrum is shown in Figure 5.2 , and it can be seen that the band heads occur at 580, 460, 518, 493, 471 and 452 nm.; these are in close correspondence with the band heads given for the BO_2 species by Pearse and Gaydon [119]. The best available filter for the A.F.S.6 instrument used had 70% transmission at 526 nm. and a 40 nm. half-intensity band pass. The nebuliser uptake rate, hydrogen flow and burner height were optimised to give the best attainable detection limit. This was defined as that concentration of boron which gave a 50% relative standard deviation after ten successive measurements. It was found that in the emission mode when a small signal was detected in the presence of a large background signal, before a realistic detection limit could be obtained any blank reading measured had to be subtracted from the actual signal reading. Using the above definition, the actual detection limit for boron was 2.5 ppm. Dean [115] observed that the emission intensity for the BO_2 species was substantially enhanced when methanolic solutions were employed. For instance, a 1:1 methanol to water solution of 100 ppm.

Boron gave a 7-fold enhancement of the BO_2 emission compared to an aqueous solution. Therefore, the effect on the relative standard deviations for various concentrations of Boron of using a 1:1 methanol to water solution was investigated; the results are shown in Table 5.1:

Concentration of Boron (ppm)	Aqueous Relative Standard Deviation %	1:1 Methanol:Water Relative Standard Deviation %
100	1 %	2.1%
50	3.7 %	6.4%
25	8.7 %	150%

Table 5.1.

The relative standard deviations shown in Table 5.1 were obtained after ten successive measurements. It can be seen that these are worse in all cases for the methanolic solution. This arises because although the BO_2 emission intensity increases the flame background at 526 nm. due to the introduction of methanol also increases. Hence when this background is subtracted from the measured BO_2 emission signal worse relative standard deviations are obtained.

5.4 INTERFERENCE STUDIES:

The effect of the presence of 10-fold weight excesses of a range of diverse ions on the determination of 200 ppm.

Boron was investigated. An ion was considered to interfere when it produced a variation in signal intensity of greater than twice the relative standard deviation for the concentration of Boron used. The effect of each ion is shown in Table 5.2 ; these values were obtained after subtracting any blank reading observed when the interferent only was sprayed into the flame.

Interferent	% interference
Th	- 13
Zn	- 9
Ba	- 99
Cd	+ 9
Pb	- 13
Mn	-100
Bi	- 9
Co	-100
Zr	- 4
Mg	- 16
Cr	-100
Al	- 16
K	Overload
Na	-100
Ca	-100
Cu	-100
Ni	-100
Fe	-100
Cl	-
SiO_2	- 20
NO_3	-
S	-
P	Overload

Table 5.2.

Effect of diverse Ions on signal produced for 200 ppm. of Boron.

A further experiment was performed to examine whether the interference effects could be reduced using lower concentrations of both Boron and the interferent. Therefore the interference caused by 500 ppm. of several cations on 50 ppm. Boron was examined. The results are shown in Table 5.3:

Interferent	% interferent
Mn	- 19%
Fe	+ 8%
Cu	- 47%
Ca	- 17%

Table 5.3.

The interference effects are reduced, but it appears desirable to remove any cations before the sample reaches the flame. An automatic ion-exchange system was, therefore, developed. This is shown schematically in Figure 5.3. A 10 ml. burette was packed with Amberlite (IR-120(H)) cation exchange resin, the eluant being passed directly into the flame *via* the nebuliser. A 200 ppm. Boron solution was employed and all interferents were 2,000 ppm. It was found that on using the ion-exchange column all interference effects were removed, except in the case of iron. In order to remove the iron a longer column was

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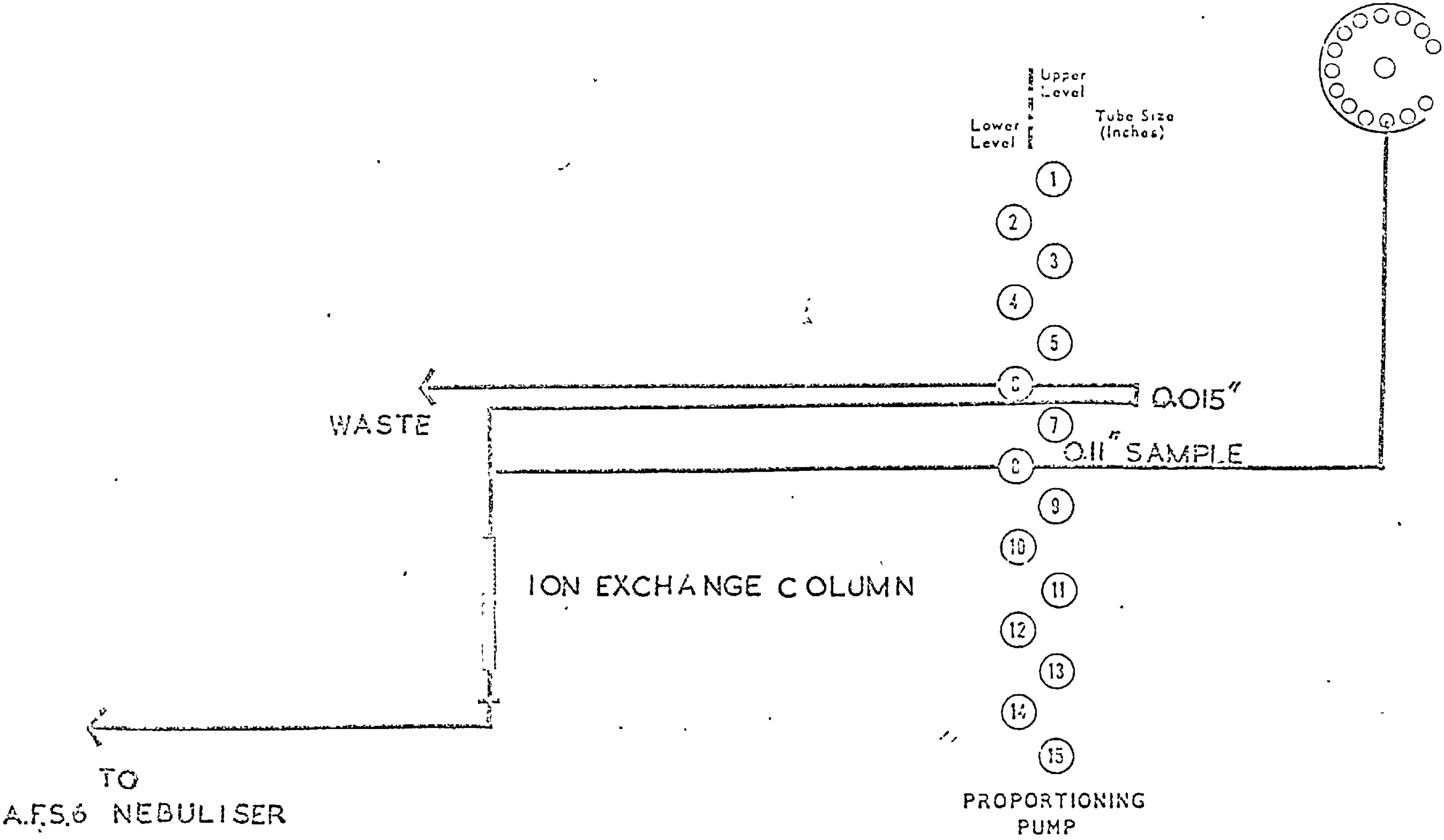
Figure 5.3.


Upper Level
Lower Level
Tube Size (Inches)
1
2
3
4
5
6
0.015"
WASTE
7
0.11" SAMPLE
8
9
10
11
ION EXCHANGE COLUMN
12
13
14
15
PROPORTIONING PUMP
TO A.F.S.6 NEBULISER

required. When a 25 ml. burette packed with Amberlite (IR-120(H)) resin was employed 2,000 ppm. of iron was removed from the sample solution without difficulty.

A further problem with the flame photometric method of determining boron is the spectral interference of Phosphate caused probably by the emission of continuum radiation from PO. The effect of 100 ppm. phosphorus on the determination of 100 ppm. Boron was studied and a method of overcoming this interference developed. It was decided to remove the phosphate by precipitating Lanthanum phosphate. 400 ppm. La (in the form of Lanthanum nitrate) was added to the solution containing 100 ppm. Boron and 100 ppm. Phosphorus as Phosphate. The interference effects of Phosphate on Boron, Lanthanum on Boron, and Phosphate plus Lanthanum on Boron are shown in Table 5.4:

Interferent	% interference
Boron + Phosphate	127%
Boron + Lanthanum	26%
Boron + Lanthanum Phosphate	7%

Table 5.4.

Effect of Phosphate on signal for 100 ppm. Boron in the presence and absence of Lanthanum.

The white Lanthanum phosphate was removed by centrifuging the sample solution, and the phosphate interference was considerably reduced. The pH dependence of the interference effect was then studied, by adjusting the pH of the solution with ammonium hydroxide. It was found that complete removal of the phosphate interference is obtained when the Lanthanum phosphate is precipitated in a solution with a pH greater than 4.0 but less than 5.0.

The depression of the Boron signal in the presence of silica was investigated. It was found that a 6-fold excess of SiO_2 on 50 ppm. Boron gave a 60% depression. However, when 2,000 ppm. Al was added to the sample solution, aluminium silicate was precipitated which, after removal by centrifuging, resulted in the interference effect being eliminated.

In order to evaluate this analytical method further, some simulated samples were examined. A casting alloy containing high percentages of Co, Cr and Ni and containing 1% B was simulated. Aluminium samples were dissolved and a certain amount of Boron added to the resultant solution. 0.25 gms. of the aluminium sample was dissolved in the minimum amount conc.HNO_3 and conc. HCl, and evaporated to near dryness. Then 2.5 ml. of 1,000 ppm. Boron was added and diluted with distilled water to 100 mls. The results of the experiments are shown in Table 5.5:

Sample	% B added	% B found (result of two determinations)	Other Major Constituents
Simulated Casting Alloy	1.00	1.0_6	30% Cr, 40% Co 39% Ni
Aluminium	1.00	1.0_0	

Table 5.5.

5.4 CONCLUSION:

In order to provide for both low burning velocity (low rise velocity) and high temperature, for the formation of the lower oxides of Boron, a cool nitrogen-hydrogen flame sheathed with oxygen may be used. Most of the cationic interferences encountered in the determination of Boron by flame emission spectroscopy can be removed by using a cation exchange resin, and the method can be automated.

CHAPTER 6.

THE SIMULTANEOUS SOLVENT EXTRACTION AND ATOMIC FLUORESCENCE SPECTROSCOPIC DETERMINATION OF SIX ELEMENTS.

6.1 INTRODUCTION.

The advantages of solvent extraction prior to the determination of elements by flame techniques are well known. The principal advantages being:-[120]

1. The elimination of interfering ions by selection of the appropriate chelating agent and pH.
2. To obtain an enhanced concentration of the element extracted by a suitable choice of sample/solvent ratio.
3. To obtain an increase in nebuliser efficiency due to the physical properties of the organic solvents used.

It was decided to investigate the possibility of automating the solvent extraction of six elements simultaneously, employing the Technicon A.F.S.6 and the Technicon Auto-Analyzer.

6.2 EXPERIMENTAL.

In a manual solvent extraction procedure[121] - the aqueous sample solutions are buffered to the appropriate pH in this case - pH5.0 and the chelating agent for the elements to be extracted is introduced. The complex formed is then extracted into an organic solvent by shaking

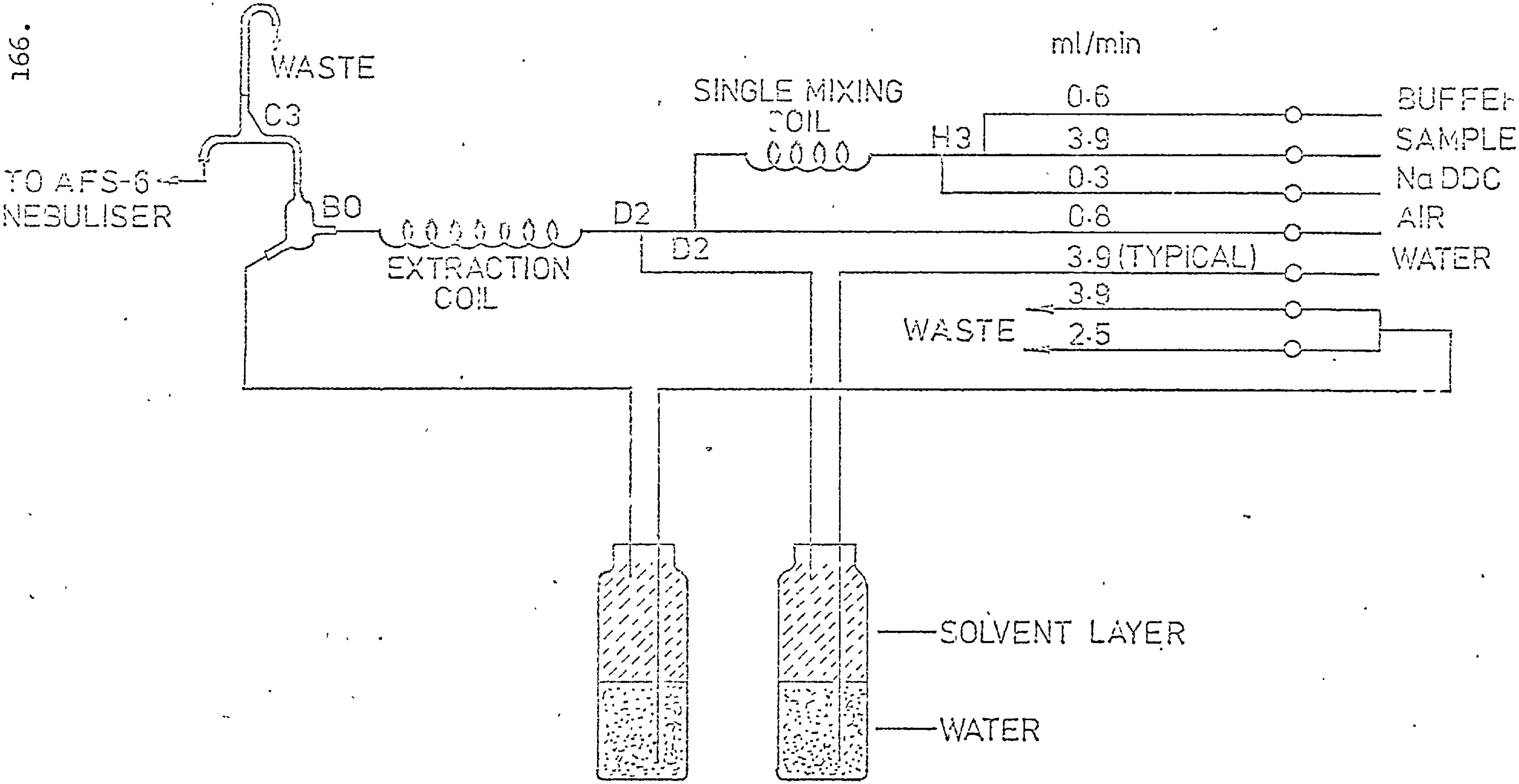


Figure 6.1 Solvent Extraction Manifold for Simultaneous Extraction and Concentration of Several Elements.

in a separating funnel or similar device. The organic layer is then removed for use by decantation or centrifuging. The choice of solvent clearly depends on the type of chelating agent used.

To automate this procedure, it was necessary to develop a manifold for use with the Technicon Pump which would perform the above steps on a continuous basis without the intervention of the operator.

The manifold developed is shown in Figure 6.1. Buffer and NaDDC are added to the sample at H3 and pass through a standard mixing coil.

Solvent is then added via a displacement bottle. Air segmentation is used, and using a 2:1 mixture of isobutanol and MIBK as a solvent, no problem with emulsification is encountered.

Extraction takes place in a glass coil containing glass beads - and the two phases are separated in a B.O. phase separator.

The stream is then de-bubbled using a C_3 fitting and the solvent extract allowed to aspirate into the AFS-6.

The aspiration rate is adjusted to ensure that air is not pulled through into the nebuliser. A small excess of solvent is allowed to pass to waste.

Reagents:

The concentration of NaDDC employed was 0.03M.

The solvent selected was a 2:1 mixture of isobutanol and MIBK.

The Buffer solution was prepared by mixing 100 mls. of 0.1M acetic acid with 200 mls. of 0.1M sodium acetate solution.

The ratios of sample:solvent were (a) 2:1 (b) 4:1

The take-up volume of the solvent extract was 1.2 ml. per minute.

The optimum volume for the AFS-6 nebuliser is approx. 3.3 ml. per minute.

To use the optimum flow rate and higher aqueous/solvent ratios would mean modification to the glassware involving a larger setting zone in the phase separator.

Operating Parameters:

The AFS-6 lamp currents were adjusted to one half the maximum rated current and an air/acetylene flame, separated with Argon, was used throughout. It was necessary to change the fuel/air ratio considerably when changing from aqueous solutions to organic solvents.

6.3 RESULTS.

Comparative results have been obtained by taking the standard deviations for each of the six elements in a group of ten consecutive samples.

Aqueous samples were run at concentrations varying from 6.0 ppm.to 0.08 ppm.

Each sample was run 10 times and each concentration was run at sample/solvent ratios of 2:1 and 4:1 and are compared with optimised aqueous runs. The % standard deviations for each group of ten have been plotted as log/linear graphs; this is shown in Figure 6.2 for Copper.

The accepted method of extrapolating these curves to a 50% standard deviation - which represents a signal/noise ratio of 2:1, gives an indication of the limits of detection. Precise extrapolation requires more results but the following curve indicates the enhancement obtained.

Copper, Nickel, Zinc and Chromium show clearly the increase in detection limits, i.e. approximately an increase by a factor of ten at 4:1 aqueous/solvent ratio over the aqueous detection limits. Manganese also shows a similar increase at 4:1 but gave anomalous results at 2:1 ratio. Results for Iron were also anomalous due, it is thought, to a noisy iron H.C.L.

6.4 CONCLUSIONS.

The automated procedure for simultaneous solvent extraction of several elements has a considerable time-saving value and relieves the operator from the tedium of manual extraction procedures. Results obtained to date show an improvement in detection limits by a factor of ten over those obtained for aqueous solutions. These detection limits could be improved further by using higher aqueous/solvent ratios and modified glassware.

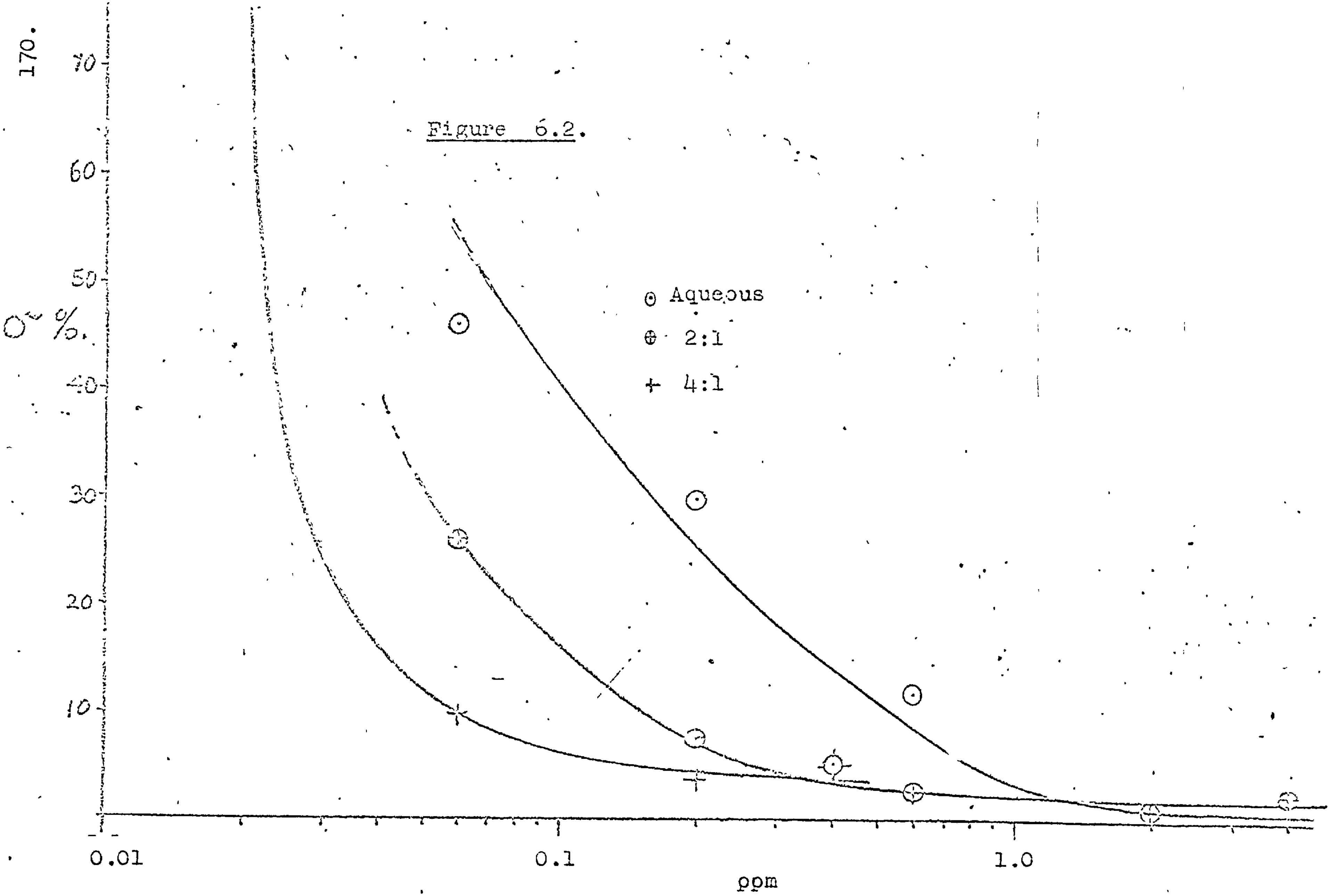


Figure 6.2.

CHAPTER 7.

CONCLUSION.

One of the most important facts presented in this thesis is that the inert gas shielded nitrous oxide-acetylene flame is almost completely transparent at the As 193.7 nm. and the Se 196.0 nm. resonance lines. Therefore, this flame is very useful for the determination of these elements by atomic absorption spectrophotometry. It would, therefore, seem very important to study the potential of this flame at even lower wavelengths. In fact, Sulphur has been determined by atomic absorption spectrophotometry employing the separated nitrous oxide-acetylene flame at the 180.7 nm. resonance line[122], giving a sensitivity (1% absorption) of 9 ppm.

The possibility of determining Phosphorus at the 178.3 nm. resonance line, Mercury at the 184.9 nm. line and Iodine at the 183.0 nm. resonance line, using this flame, should also be investigated. The main problem in such studies would be in trying to reduce the amount of air through which the source radiation traverses. This would mean taking such steps as purging the monochromator of the atomic absorption spectrophotometer with nitrogen.

A further investigation into the potential of the 'Schuhknecht' type burner for analytical atomic spectrophotometry could be most profitable. As discussed in Chapter 3, the burner design will have to be improved. The main feature of the design is that the sample is not aspirated through the primary reaction cones of the flame. Therefore, a study into this property of the burner could produce interesting results.

Although at the present time there is great interest in the use of non-flame atom cells, the flame still remains one of the most effective and versatile means of producing atoms for use in analytical atomic spectroscopy.

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