SOME ANALYTICAL APPLICATIONS OF VARIABLE PRESSURE FLAMES

by

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September, 1971.

ABSTRACT

The work presented in this thesis examines the effect of pressure on some of the flames which are commonly used for analytical atomic spectroscopy. The greater part of the work has been concerned with the effect of reduced pressures, below about half an atmosphere; particular attention has been paid to the low pressure nitrous oxide-acetylene flame, although many of the results thus obtained are of general applicability.

The main analytical disadvantage of a low pressure flame has been shown to be its inherently poor atomisation efficiency, resulting in a corresponding inability to generate a vapour phase atomic population of a sample from an aspirated solution. A number of ways of overcoming this inability are discussed, and a successful atomisation technique described. Using this technique, it has been shown that low pressure flames appear to be chemically more reducing than their atmospheric counterparts, and are thus very suitable for the analysis of those elements which normally form refractory oxides. A successful absolute method for the analysis of such elements has hence been developed. The practicality of this method has been improved by the development of a burner which can support

a low pressure flame without the aid of external mechanical pumps, and which is thus sufficiently compact to be used in conjunction with most commercially available spectroscopic instruments.

The low pressure flame has also been used for chemiluminescence studies, which have shown the particular value of the sample introduction technique developed here for examining the chemiluminescent excitation of foreign atoms within the reaction zone of a pre-mixed flame.

Finally, a preliminary examination has been made of the practicability of burning analytically useful flames at pressures in excess of atmospheric, and of the analytical advantages which might thus be obtained.

ACKNOWLEDGEMENTS

The work described in this thesis is entirely original except where due reference is made. No part of the work has been submitted previously for any other degree. The work was carried out in the Department of Chemistry, Imperial College of Science and Technology, between September, I969 and September, I97I.

I would like to thank my supervisor, Professor T.S. West, for his invaluable guidance and advice throughout this work. I would like to extend thanks also to Mr. R. Cescotti, of W.S.A. Engineering, for his advice on ejector performances, as well as to my colleagues in this department for many interesting and useful discussions.

I am grateful to the Science Research Council for the provision of a grant during the course of, and in support of, this work.

Finally, I would like to thank my wife, Jennifer, for her patience during the preparation of the manuscript, as well as for her help in typing it.

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CHAPTER ONE

I:I General Background.

Modern instrumental techniques, based on atomic emission, absorption or fluorescence spectroscopy in flame media, can provide methods of both qualitative and quantitative analysis which are applicable to most of the elements of the periodic table. The application of these spectroscopic techniques relies on the interactions between radiation and discrete atoms; thus the atoms involved must, as far as is practicable, be free from all interatomic interactions, and in particular from interatomic chemical interactions; this is a requirement which can only be satisfied within the vapour phase. The creation and maintenance of such a vapour phase atomic population is conveniently achieved by making use of the high temperature environment which is provided by a flame.

Historically, the colorations induced in alcohol / air diffusion flames after the introduction of various metal salts were noted by a number of early workers, but it was not until after the work of Bunsen and Kirchoff in I860, following the development of the pre-mixed air/coal gas burner by Bunsen, that the potential value of flame emission spectroscopy as an analyt-

ical technique really became apparent. The number of elements which can be thermally excited in a pre-mixed air/coal gas flame is however limited, and in consequence the interest in atomic emission work subsequently centred on arc and spark sources, until the work of Lundegardh in I928 (I). Lundegardh used a pneumatic nebuliser, based on the design of nebuliser described by Gouy in I879, in order to aspirate sample solutions into a pre-mixed air/acetylene flame. This technique proved to be very effective, and began to revive some of the earlier interest which had been shown in flame emission studies; an interest which was further stimulated following the introduction of photo-electric recording devices capable of replacing the photographic plates used in the earlier experiments.

The analytical applications of atomic absorption spectroscopy (2,3) and later still of atomic fluorescence (4,5), abruptly expanded the number of elements susceptible to spectroscopic analysis within a flame, and from this time an increasing amount of work has been devoted to the improvement of both the selectivity and the sensitivity of these techniques.

As mentioned previously, the above forms of spectroscopic analysis rely on the generation of a vapour phase atomic population from (generally) a solid sample. The work of James and Sugden, and others (6,7), has shown the efficiency of a flame in this respect to be very low; thus although a number

of other parameters of practical importance such as noise levels, interference effects etc. must also be considered when discussing the properties of atomisation media, the problem of poor atomisation efficiency still remains a most important and absolutely fundamental one. For this reason therefore, a great deal of work has been carried out in recent years to determine new techniques by which the efficiency of this atomisation process can be increased. Such work has lead for example to the development of new high temperature flames such as acetylene/oxygen (8) and cyanogen/oxygen (9), as well as to non-flame media such as the R.F. plasma (IO).

Virtually all atomisation media, including those given above, have been investigated within the confines of the atmosphere: i.e. they have been studied at pressures of around 760 mm/mercury. Nevertheless, it seems rather unreasonable to expect this to be an optimum pressure for analytical atomic spectroscopy, in particular when the diversity of the techniques thus classified is considered. Thus it was felt that an investigation of the pressure dependence of variables such as atomisation efficiency, as well as of other experimental parameters such as those mentioned above, warrented an examination. It is such an examination which is the major purpose of the experimental work undertaken in this study, in which the pressure dependence in a flame source of these analytical parameters

has been investigated.

Such an investigation required a flame which could be maintained over a range of pressures; however, for practical reasons this pressure variation has not been considered as a continuous function, but has been treated separately under the headings of 'high pressure' and 'low pressure' flames, with an arbitrary dividing line at one atmosphere.

No references at all appear to be available concerning the analytical chemistry of high pressure flames: indeed, with the exception of some isolated spectroscopic studies (II), the only work carried out in this field seems to have come from fuel technologists interested in the behaviour of hydrocarbon/air mixtures burning at elevated pressures in the combustion chamber of a gas turbine (I2,I3). Thus analytically speaking, high pressure flames are a completely unknown quantity, and nothing further will therefore be said concerning these systems at the present time.

On the other hand, low pressure flames are relatively well explored systems, which have been the subject of a number of spectroscopic investigations; they have been examined, albeit rather tentatively, to determine their analytical potential (see later), and were also a subject of considerable interest during the development of rocket motors suitable for use in space. Partly because of the availability of this

data, and partly for a number of other reasons which are discussed below, it was accordingly decided to look at the analytical possibilities of low pressure flames for the first part of this investigation.

The properties shown by a low pressure flame represent something of a departure from those observed with its conventional atmospheric counterpart. Although of themselves these properties are not of direct analytical significance, it is felt that they must be appreciated before an attempt is made to make any analytical use of such a system; for this reason therefore the properties of a low pressure flame are discussed in the following section of work.

I:2 Observed Physical Properties of the Low Pressure Flame.

The primary reaction zone (p.r.z.) of any pre-mixed atmospheric flame forms a hollow cone, whose base approximately follows the curvature of the burner head. The walls of this cone are very thin: thus the p.r.z. approximates closely to a two dimensional 'reaction surface'. In spite of its small volume, the cone is a source of extremely intense radiation: band emission is generally observed right through the visible and ultra-violet regions of the spectrum, indicating an extreme degree of molecular excitation. The implications drawn from

this must be that the p.r.z. is an area of fast chemical reaction, in which a great deal of chemical energy is liberated (see below), and in which a corresponding degree of chemical change must be undergone by the reacting gases. Thus it is a region of extreme interest, both with regard to any practical application of the flame, as well as from a purely theoretical point of view.

The observed effect of reduced pressure on the p.r.z. is seen as an increase in its physical dimensions. Wolfhard in fact gives as an approximate relationship that the thickness of the p.r.z. is inversely proportional to pressure (I4); thus its surface nature mentioned above tends to be lost as the pressure of the flame is reduced. Operation at low pressure also necessitates the use of larger diameter burners to permit stabalisation of the flame: thus both the diameter and height of the p.r.z. are correspondingly increased. This phenomenon of increased size renders the p.r.z. considerably more susceptible to spectroscopic examination; a property which attracted much of the early interest shown in low pressure flames.

The diffusion reaction zone, familiar with atmospheric flames, is generally lost at reduced pressure, due to the lack of oxidant in the atmosphere surrounding the flame; it is for this reason that subsequent references to low pressure flames refer specifically to the p.r.z. alone. However, it is possible to burn a low pressure diffusion flame if a suitable atmosphere

is provided (I5); a comprehensive description of the physical properties of such flames has been given by Gaydon (I5,I6) and others (I7).

I:3 The Chemistry of the Low Pressure Flame.

Chemically, the fact that the p.r.z. is a self-propagating system means that it can formally be described in terms of a series of chain reactions (see later), involving the standard steps of initiation, propagation, branching and termination. Spectroscopic studies (see later) have shown that the intermediate species participating in the various reaction stages are generally molecular fragments in high states of rotational, vibrational and electronic excitation. It is also well known that the p.r.z. is a non-equilibrium system (I6,I7), and that therefore this excitation is chemiluminescent. The departure from equilibrium in practice permits an extreme degree of molecular excitation, thus accounting for the high output of radiational energy from the p.r.z.

Levels of chemiluminescent excitation are a function of a given reaction, and are not particularly dependent on the environment in which that reaction takes place. Thus the energy changes occurring within the p.r.z. of a given flame can be reasonably assumed to be effectively pressure invariant (a

conclusion emphasizing that the p.r.z. is a system in which the validity of the results of equilibrium thermodynamics cannot, in general, be accepted).

In addition to this deduction, it has been pointed out by Gilbert and Lobdell (I8), among others (I5), that the number of collisions experienced by a given particle within the p.r.z. is approximately independent of pressure. Thus in the light of the observations above, it seems reasonable to suggest that the chemical reactions occurring within the p.r.z. of any given flame should themselves be correspondingly pressure insensitive.

This same conclusion has been arrived at by Gaydon, on purely experimental grounds (I5). He argues that the observed variations in the burning velocity of a given flame as a function of pressure are consistent with a constant reaction order over the pressure range considered. For example, fast burning flames such as acetylene/oxygen can be described by second order kinetics; i.e. their burning velocities are apparently pressure independent, and thus the chemical reactions occurring in these flames must be equally independent of pressure. Further evidence to this effect is given by Gilbert, who has measured the burning velocities of a large number of different flames over a wide range of pressures (I9); these results both support the data used by Gaydon, as well as

demonstrating the general applicability of the above conclusion.

Broida and Heath (20) have also suggested the possible chemical similarity between the p.r.z. of an atmospheric flame and that of its low pressure counterpart, on the specific grounds of a possible pressure-invariant mechanism for the chemiluminescent excitation of OH; an argument which was supported by the OH fluorescence results of Carrington (2I,22). However, they also present some data in the same paper which suggests that a possible departure from a fixed reaction mechanism (s) could occur at very low pressures, due perhaps to non-specific quenching processes associated with different types of burner head.

This latter observation may be related to the fact that no flame can burn at a true zero of pressure. As zero pressure is approached, molecular mean free paths correspondingly increase, and the reaction mechanism(s) of the flame must therefore change as radiative termination of chain processes becomes significant. That is, radiative heat loss consumes an increasing fraction of the energy output of the low pressure flame, resulting first in a change of reaction mechanism, and finally in the reduction of the burning velocity of the flame to zero.

Results such as those of Thomson and Enloe (23), however, show that this theoretical point of flame extinction

lies at very low pressures indeed (generally less than I mm/ mercury for flames with high burning velocities), and that even when practical considerations such as the quenching effect of the pressure vessel are allowed for, they can be expected to raise this limit only marginally.

Thus from the practical viewpoint of the work below, the minimum pressure limitation for flame combustion is considered to be sufficiently low for its implications to be neglected.

The discussion given above is therefore felt to lead to the conclusion that the chemical reactions occurring in the p.r.z. of a given flame are common to both the low pressure flame and to its atmospheric counterpart: i.e. chemically the p.r.z. is not a pressure dependent system. Although the general validity of this conclusion cannot be said to have been thus demonstrated beyond dispute, all the experimental evidence available is in its favour; furthermore, the assumption of a pressure invariant chemistry in the p.r.z. forms a valuable starting point for the analytical investigation of low pressure flames (see below), and, while recognising the possibility of error, it has therefore been accepted as such; an approach which has been justified by its success in subsequent experimental work.

Although the above discussion is sufficient for the present purposes, it is felt that a further brief consideration

of the individual reactions thought to occur in the p.r.z. would be of some interest. No information thus found is known to modify the generality of the conclusion that the chemistry of the p.r.z. is pressure invariant, and the following remarks are therefore equally applicable to both the low pressure flame, and to the p.r.z. of the corresponding flame burning at atmospheric pressure.

Spectroscopic evidence has shown the identity of the majority of the species present in the p.r.z. For example, pure hydrocarbon/oxygen flames generate radicals such as C_2, CH, OH, CHO, as well as a number of similar species at lower concentrations. The nature and concentrations of such radicals depends entirely on the type of flame considered; thus for instance the presence of nitrogen in the reactant gases gives rise to species such as CN, NH, NH_2 etc. A detailed consideration of the spectra of the p.r.z. at both atmospheric and reduced pressure, together with the species which can thus be deduced to be present, their levels of excitation, and other related data, have been given by Gaydon for a large number of different types of flame (I6).

Radicals such as those mentioned above are unique to the p.r.z. in that they occur in this region of the flame in high concentrations and in very high states of excitation; thus it seems reasonable to identify such species with the chain

reaction carriers mentioned earlier. However, although the natures of the chain intermediates are thus well known, the elementary reactions in which they participate are still uncertain. The reason for this uncertainty lies partly in the large number of elementary reactions making up a single chain mechanism, which, together with the possibility of the simultaneous existance of a number of such mechanisms, creates a highly complex situation. However, such complexity would not necessarily be insurmountable if thermodynamic considerations could be used to determine a minimum free energy (equilibrium) reaction sequence; unfortunately, the chemiluminescent excitation processes in the p.r.z. preclude this approach.

Despite these difficulties, it is possible to determine with reasonable certainty some of the major reactions occurring in the p.r.z. The procedure adopted is to consider the reactant compounds, and the reaction products (known by e.g. mass spectroscopic analysis (24-26)), and then to try and link the two via the known p.r.z. intermediates in a series of elementary reactions. The law of conservation of energy still applies to the p.r.z., and hence it is possible to determine the maximum energy which can be given to any intermediate formed in such an elementary reaction; for the postulated reaction scheme to be acceptable, the maximum excitation energy thus calculated as being available to a reaction intermediate must be at least

equal to the observed spectroscopic value. For example, Gaydon (I3) has suggested a reaction $CH + O_2 \longrightarrow CO + OH^*$, as a process whereby overexcitation of OH could occur. This reaction can be shown to be 6.9 eV (I59 Kcals/mole) exothermic: an energy release sufficient to produce OH in $A\,^2\Sigma+$, $v' = 2,3$ or 4 states, with a high additional rotational energy, as demanded by spectroscopic evidence.

A more detailed consideration of the nature of the basic reactions occurring in the p.r.z. is not felt to be pertinent to the present discussion. It will simply be pointed out that by use of the techniques outlined above, a number of very plausible reaction schemes can be written to account for the presence of the species spectroscopically observed in the p.r.z., and that a number of works exist in which such schemes have been examined in detail, and in which a full consideration of the evidence leading to their formation has been given (I7,27).

I:4 Some Non-Equilibrium Effects in the P.R.Z.

At the beginning of the previous section of work, it was mentioned that the intermediate species occurring within the p.r.z. were subject to chemiluminescent rather than thermal excitation, reflecting the fact that the p.r.z. was a system of

non-thermal equilibrium.

It is now proposed to examine some other relevent aspects of this non-equilibrium behaviour a little more closely.

The first result of analytical significance which is considered is the fact that the chemiluminescent excitation of the p.r.z. can extend to include foreign atoms externally introduced into this region (I7,28), although whether such excitation occurs as a result of true chemiluminescence or for example by energy transfer processes is not known.

While bearing this uncertainty in mind, the term chemiluminescence will be used equally in the future in this work to refer to the non-thermal excitation of species naturally occurring in the p.r.z. as well as to the non-thermal excitation of any foreign atoms which might also be present.

A second phenomenon which is of relevance to the present work is the high concentration of ions known to exist within the p.r.z. (29); this concentration is far higher than its equilibrium value, and has therefore been considered to be the result of chemi-ionisation.

Current work on chemi-ionisation (30) suggests such processes generally result in the production of positive molecular ions, accompanied by the simultaneous generation of free electrons; the latter however in general rapidly attach themselves to the nearest acceptable free radical to give a negative

ion.

It was pointed out previously that the chemistry of the p.r.z. should be pressure invariant, and thus the total rate of ion generation at low pressure should be comparable to that observed in an atmospheric flame; a supposition which has been largely born out by experiment (31-34). Nevertheless, at low pressure the electron/radical collision frequency must be reduced as the molecular mean free path increases, and it must therefore be expected that a low pressure flame will contain an abnormally high concentration of free electrons, as well as the positive and negative ions mentioned above. Although the analytical use of this deduction is not immediately obvious, except perhaps with regard to the possible suppression of sample ionisation, the electrical properties of the low pressure flame were subsequently utilized in this investigation; the phenomenon of ion/electron generation has therefore been mentioned at the present time for this particular reason.

The final aspect of the lack of equilibrium in the p.r.z. to be considered is the resulting inability to define a specific (thermodynamic) temperature for such a system. It was in fact the discrepencies between the rotational and vibrational temperatures required by different band systems of given species which led early workers in this field to deduce the non-thermal nature of the excitation (20); a deduction

confirmed by the even more spectacular differences observed between rotational, vibrational and electronic excitation temperatures of these species (35). For example, Broida and Heath (20) have reported the discrepencies summarised in Table I between rotational and vibrational temperatures for a number of species occurring in a low pressure flame; these results were obtained at a pressure of 5 mm/mercury in an acetylene/ oxygen flame.

TABLE I

Radical	Rotational Temperature	Vibrational Temperature
OH	3500 low K	-
OH	6000 high K	-
C_2	3400	4200
CH	2400 (0,0)	2200
CH	I900 (I,I)	-

Some workers have tried measuring 'thermal' gradients in the vicinity of a low pressure flame using a thermocouple (36), and meaningful results have been claimed from such work (37). However, while it must be admitted that the thermo-couple does indeed possess a real thermodynamic temperature

under such conditions, it is nevertheless felt that the temperature thus recorded is not a meaningful parameter, but merely reflects a state of balance between the (collisional) energy received from the flame, and the rate of heat loss by (forced) convection, conduction and radiation; similar reservations must be held concerning any macroscopic body heated within the p.r.z.

Thus it must be concluded that the concept of temperature as it is normally understood can be applied to the p.r.z. only as a means of describing the energy distributions deduced from spectral intensity measurements. Thus the idea of a 'temperature of the p.r.z.' is meaningless; rather, one has to consider the energy changes of the process of interest within the p.r.z., bearing in mind the possibility that the process might show a sufficient degree of consistency for those energy changes to be described in terms of a specific 'process temperature'.

Although the above discussion of non-equilibrium phenomena within the p.r.z. has now been carried far enough for the (analytical) purposes of the present work, it is felt that a further, more theoretical consideration of the chemical origins of these phenomena could be of some interest. Such a consideration has therefore been outlined in the following section .

I:5 Reaction Mechanisms in the P.R.Z.

The following remarks examine the p.r.z. as a chain reaction, and use the chain reaction terminology of initiation, propagation, branching and termination in the usual sense. Nevertheless, it must be emphasized that experimental knowledge of the chemistry of the reactions occurring in the p.r.z. is insufficient to say whether the chain mechanism can in fact be described in terms of purely chemical elementary reactions, or whether some other form of elementary process has to be invoked.

The pre-mixed reactant flame gases do not ignite spontaneously, and thus it can be deduced that in order to initiate combustion, some activation energy has to be overcome. While the flame is burning, the required ignition energy is supplied by the energy released after combustion, and the flame is thus sustained by an energy feedback process. In common with other (practical) feedback mechanisms, this process is not 100% efficient; thus branching reactions have to occur, to make up the inherent losses of the system, as well as termination reactions to account for the energy losses in the first place. The energy feedback process is considered as a propagation reaction, and leads to further initiation, thus repeating the cycle.

Propagation may well be purely chemical in nature,

simply involving diffusion of excited species from within the p.r.z. towards the unburnt reactant gases; the degree of excitation of these intermediates is sufficient to overcome the activation energy of initiation, and further reaction then occurs. In this case, termination can be viewed as resulting from the loss of excited intermediates on the burnt side of the p.r.z., and by quenching reactions on the surface of the burner head; branching occurs as a chemical phenomenon, specific to a particular system, some time after initiation, and the system thus becomes exactly analogous to other normal (chemical) chain reactions. On this model therefore, the closer the p.r.z. is to the burner head, the greater is the probability of termination rather than initiation, and vice versa; thus the stability of a flame on a burner over a range of conditions becomes immediately explicable.

On the other hand, it is equally possible to explain the propagation reaction in terms of purely physical heat transfer through the p.r.z. causing self-initiation of the reactant gases; a view supported by the results of studies of flame propagation as a function of the thermal conductivity of the reactant gases (38-40); branching, termination and flame stability are all then explicable in exactly the same way as before.

A number of other possible propagation mechanisms

have been advanced, usually with regard to specific systems; a full account of these theories can be found elsewhere (I6). Although initiation mechanisms are discussed at length below, it is not intended to discuss the mechanisms of propagation, branching and termination any further, except to point out that it has not so far proved possible to relate theoretical calculations to the elementary reactions of the p.r.z. deduced from spectroscopic studies (see above). For this reason there is a tendency to consider 'elementary reactions' as one isolated field for study, and 'theoretical chain reaction mechanisms' as another; an unnatural dichotomy showing the extent of the limitations of present experimental, and in particular theoretical, knowledge concerning the p.r.z.

From the analytical point of view, the mechanism of initiation is perhaps the most important of the chain processes mentioned above, since it is during the initiation reactions that the chemical energy of the fuel first becomes available, resulting in the formation of analytically useful chemiluminescent (and chemi-ionised) species. Unfortunately, the mechanisms of initiation are even less well understood than those of the other chain reactions, and are certainly less susceptible to even hypothetical explanation. Because of its relevence however, such work as is available on the mechanisms of initiation, and hence on the origins of chemiluminescence, is discussed

below.

Despite their mutually independent and isolated treatment in the literature, the phenomena of chemiluminescence and chemi-ionisation, already discussed, must clearly be related processes, if only because they both give rise to transient, non-thermally excited species which are unique to the p.r.z. Thus for instance it is possible to explain the existence of chemiluminescent and chemi-ionised species in a completely analogous manner in terms of a reasonable series of elementary reactions, based on conservation of energy calculations (I7) (see above). On these grounds therefore, it might prove possible to deduce empirically a reaction mechanism whereby the elementary reactions suggested by the separate chemiluminescence and chemi-ionisation studies can be related to a common initiation reaction.

The possibility of a (qualitative) link between chemiluminescence and chemi-ionisation was pointed out by Gaydon in I95I (4I), and has since been repeated by a number of other workers (42,43). Recently, an attempt was made to relate the observed ionisation energies of species in the p.r.z. to the theoretical energy available from the total oxidation of the carbon skeleton of the fuel gas molecules; a type of relation which has been independantly noticed during the development of flame ionisation detectors in gas chromatography (44,45).

Such work should clearly be equally applicable to chemiluminescence, at least in principle, and could thus lead to just such an empirical relationship between chemi-ionisation, chemiluminescence and the nature of the fuel as was suggested above. However, this latter work has been the subject of some controversy (46,47), and thus, although such results may well ultimately prove to be of theoretical value, further conclusions cannot be safely drawn until more evidence is available.

Thus although an empirical approach towards explaining the mechanistic origins of chemiluminescence and chemi-ionisation seems to be quite realistic, more experimental work is needed before the true worth of such an approach can really be evaluated.

The problem has also been approached in a completely theoretical way, by the application of transition state theory. The calculations involved are complex, and are only applicable to rather idealized, or at best very simple practical, cases; for this reason, no more than an outline of the technique will be given here.

For the purposes of calculation, reaction is considered to proceed through collisional formation of an activated complex, in which the chemical energy of the reactants is released as vibration. Under suitable conditions an electronically excited product can then be formed, whose electronic

energy is gained at the expense of the vibrational energy lost by the parent complex; after the manner given by Eyring and Polanyi (48), the energy changes surrounding the activated complex are described on what is effectively a three dimensional potential energy surface.

As already mentioned however, this approach to the origin of electronic excitation in a flame is quantitatively difficult, and for this reason it is considered to be a method of largely academic interest, at least with regard to the present work.

Thus on balance the following conclusions are proposed. Firstly, experimental work suggests chemiluminescence and chemi-ionisation to be qualitatively related processes, deriving their energy directly from the chemical energy released during the initial stages of oxidation of the flame fuel gases, possibly via a vibrationally excited complex intermediate. The observed lack of thermal equilibrium described by these phenomena is a result of the rapid release of this energy, which occurs at a rate greater than that at which equilibration can occur by normal inter- and intra- molecular processes. Experimental evidence also enables reasonable elementary reaction schemes to be given relating the existance of (many of) the transient species observed in the p.r.z. to the relatively stable final products, and to the initial reactants. Mechanistically,

propagation, branching and termination steps can be described, at least in principle if not in detail; however, attempts to use experimental results to deduce mechanisms for the elementary initiation reactions have so far had little success, and theoretical attempts to derive such mechanisms, although probably valid in principle, are too complex to be applied generally.

Considerable emphasis has been laid above on the lack of thermal equilibrium associated with chemiluminescence and chemi-ionisation processes, and the resulting inapplicability of conventional methods of calculation, relying on a specified temperature. However, Mavrodineanu and Boiteux (I7) have suggested the following approach whereby Boltzmann-type formulae can be applied to chemiluminescent excitation 'temperatures'; quite apart from any mechanistic implications, this approach is of value in that it offers at least some chance of giving a quantitative discussion of chemiluminescence at a relatively unsophisticated level.

The argument is based on the empirical result shown in equation (I); this equation was derived from the data on the chemiluminescent excitation of iron given by Gaydon (4I).

Put N_i = number of iron atoms in the i th energy level

N_o = number of iron atoms in the ground state

and g_i, g_o and E_i, E_o are the corresponding statistical weights

and energies respectively of those species.

$$\text{By experiment,} \quad \log_e \left[\frac{N_i \cdot g_o}{N_o \cdot g_i} \right] = a - b.E_i \qquad \text{——— (I)}$$

$$\therefore \quad N_i / g_i = (A . N_o / g_o) . \exp (-E_i / B)$$

where A and B are empirical parameters determined by experiment. Relations are now suggested of the form

$$A = \exp (-E_o / B) \qquad \text{——— (2)}$$

$$B = k . T_i \qquad \text{——— (3)}$$

where k is Boltzmann's constant, T_i is the 'excitation temperature' of the i th state and A thus becomes equivalent to an activation energy term.

$$\therefore \quad \frac{N_i}{N_o} = \frac{g_i}{g_o} . \exp \left[\frac{-(E_i + E_o)}{k . T_i} \right] \qquad \text{——— (4)}$$

Although equation (4) can be used in this existing form, a more accurate procedure is suggested by comparing equations (3) and (4), and defining a new temperature T_r, such that

$$E_i / k . T_r = (E_i + E_o) / k . T_i$$

$$\text{i.e.} \quad \frac{I}{T_r} = \frac{I}{T_i} . (I + E_o / E_i) \qquad \text{——— (5)}$$

Thus a plot of I / T_r against I / E_i should be linear, with an intercept at $E_o / E_i . T_i$; a result which agrees with that observed experimentally by Gaydon and Wolfhard (4I), from their observations of the chemiluminescent excitation of iron, mentioned above. Using this data, in conjunction with an equation of the form of (5) above, gives rise to experimental values of $T_i = 8600^{\circ}$ K, and $E_o = 7.5$ eV.

In support of equation (5), it may be noted that 7.5 eV is exactly that value of E_o which qualitative examination of the chemiluminescently excited lines suggests as the energy which must be released to give the degree of overexcitation observed. Furthermore, the value of T_i thus obtained agrees fairly well with the OH rotational temperatures observed in similar flames (ca. 9000° K) (49).

Although this method of calculation is rather a 'stop-gap' treatment, which pushes existing formulae beyond the regions in which they can justifiably be expected to be valid, it does offer a means of quantitative examination in a field where no other such means exists; as such, these formulae accepted in the course of the present work, and in fact subsequently proved to be of immense value in the interpretation of some otherwise inexplicable results.

I:6 Potential Analytical Uses of the Low Pressure Flame.

The p.r.z. has been presented above as a region of chain reaction, in which the intermediate species are formed in chemiluminescent, and chemi-ionised, states, via complex series of elementary reactions of a hypothetical nature and of even less certain mechanism. The rate of reaction in the p.r.z. is very high, and the concentration of excited species in this region is therefore correspondingly large. The excitation of the intermediates is non-equilibrium; a phenomenon resulting in a total inability to define a specific (thermodynamic) temperature for the system. The chemistry of the p.r.z. appears to be pressure insensitive, and thus the effect of pressure variations on the system can be discussed in purely physical terms.

From the analytical point of view, Mavrodineanu and Boiteux (I7) as recently as I965 summed up the p.r.z. with the statement " The analytical flame spectroscopist has little or no interest in this region of the flame, except for the efforts he is making to avoid it ". More recently however, chemiluminescent excitation in the p.r.z. of atmospheric flames has been utilized for the non-thermal excitation of elements whose optimum analytical lines do not involve ground state transitions, or else lie at very high energies, and which are therefore not usually observed in emission (50-52).

The fact that the non-thermal excitation of the p.r.z. can thus be transferred to foreign atoms present within the system is clearly of analytical significance, and the phenomenon has in fact been recently utilized by a number of workers (53,54), whose results have shown that, despite its high radiational background, signal to noise ratios observed in the p.r.z. are not, perhaps contrary to expection, so low as to preclude the analytical use of this region of the flame.

A number of spectroscopic studies of foreign atoms in low pressure flames have been undertaken, and have included elements such as Fe, Pb, Tl, and Zn (4I). However, such work has generally been for theoretical purposes, and the samples to be investigated have invariably been introduced as volatile derivatives. No attempts appear to have been made to atomise a solution into a low pressure flame in the manner familiar with atmospheric flames; indeed, Gaydon has pointed out that atomisation of solid samples in a low pressure flame appears to be a very inefficient process, of uncertain practical viability (4I).

Thus the analytical investigation of the low pressure flame presents a novel problem, in which correspondingly little experimental work is directly available to act as a guide. For this reason, the information given in the previous sections of work will be utilized as far as possible below to show the line

of approach which it would seem reasonable for such an analytical investigation to follow.

Firstly, the deduction of a pressure invariant chemistry simplifies the issue, and suggests that primarily physical effects associated with a reduced molecular collision frequency will predominate. Thus for the sake of simplicity, and in the absence of any more concrete guiding principle, the validity of this deduction will be assumed, to provide a starting point for the present work. The (physical) effects which might, therefore, be expected to be observed have been summarised as follows.

(a) At low pressures, collisional (Lorentz) broadening of spectral lines becomes negligible in comparison to Doppler broadening. Thus spectral lines must become sharper, and the absorption coefficient at the centre of the line must be correspondingly greater. The combination of a greater absorption coefficient and a sharper spectral line suggests both improved sensitivity and a reduction of spectral interferences for atomic absorption spectroscopy to be attainable.

(b) The lower collision frequency must result in reduced collisional quenching of excited species by energy transfer processes; a requirement which can be described quantitatively from theoretical considerations (55). Thus a greater proportion of excited atoms will lose their energy as radiation as

the flame pressure is reduced, and thus the sensitivity of atomic fluorescence spectroscopy should also be correspondingly increased.

This effect applies in principle to atomic emission as well, but as Gaydon has pointed out (4I), the non-equilibrium environment of the p.r.z. appears to favour abnormal excitation of non-resonance atomic lines, and thus any conclusions concerning the enhancement or otherwise of A.E.S. have to be approached with some caution.

(c) Thermodynamically, the lower the pressure, the more the general reaction $MO \rightleftharpoons M + O$ is displaced to the right (Le Chatelier). Thus a low pressure flame may be expected to inhibit sample oxidation, and should thus offer a more chemically reducing environment, suitable for the atomisation of refractory oxides, than does its atmospheric counterpart. However, in view of the absence of equilibrium in the p.r.z., this deduction must be given as a suggestion, rather than as a thermodynamic requirement.

(d) Related to (c) above is the apparently reasonable supposition that, in general, vapour phase chemical interferences must be reduced, simply because the reduced collision frequency lowers the rate of the reactions necessary for such interferences to occur. Thus on purely qualitative grounds, (c) above is presumably correct, and is one instance of a general conclusion that, once formed, an atomised sample in the

vapour phase will increasingly tend to stay as such as the pressure of its environment is reduced.

(e) The radiational background of the p.r.z., which is very high at atmospheric pressure, is reduced at low pressure, partly because of the increased sharpness of spectral lines, and partly because a continuum, always observed in atmospheric flames, and thought to be caused by the presence of small dust particles, is lost; a continuum normally observed in the outer mantle of an atmospheric flame due to the recombination reaction $CO + \frac{1}{2}O_2 \longrightarrow CO_2 + h\nu$ is also lost (56), in a manner similar to that observed for a separated flame. Thus for a given signal level, the signal to noise ratio observed for a given sample in the p.r.z. should be higher in a low pressure flame than in its atmospheric counterpart.

Thus from the arguments given above, it seems reasonable to conclude that provided a vapour phase concentration of atoms can be obtained from a given sample in the first place; a requirement whose fundamental nature has already been discussed, then an increase in both the sensitivity and the selectivity of analytical spectroscopic techniques should be observed by use of a low pressure flame.

It is considered that the separation and independent evaluation of all the factors given in (a) to (e) above is too complex a problem to be attempted in the present work,

especially in view of the practical difficulties which also arise. Thus for the purposes of deciding on the analytical potential of the low pressure flame, it was decided to combine all these factors by using the signal to noise ratios of given samples as a single analytical parameter, whose value thus reflected the simultaneous effect of a number of independent flame variables. The experimental determination of these signal to noise ratios, and of their variations with pressure, together with the interpretations put on these results, are described below.

CHAPTER TWO

2:I The Apparatus.

The apparatus used here for the experimental work on low pressure flames has already been described in detail (57), and is basically very similar to other low pressure burners used elsewhere (I4,I6,58). The flame was burned within a cruciform glass pressure vessel (Q.V.F. Ltd.), of I5 cms. internal diameter at the point closest to the flame; quartz windows at opposite ends of one arm of the vessel permitted either absorption or emission studies to be undertaken. A second vessel of cylindrical cross section, with quartz windows suitably placed for emission, absorption or fluorescence work, was also available, but was not extensively used, for a variety of reasons (see later).

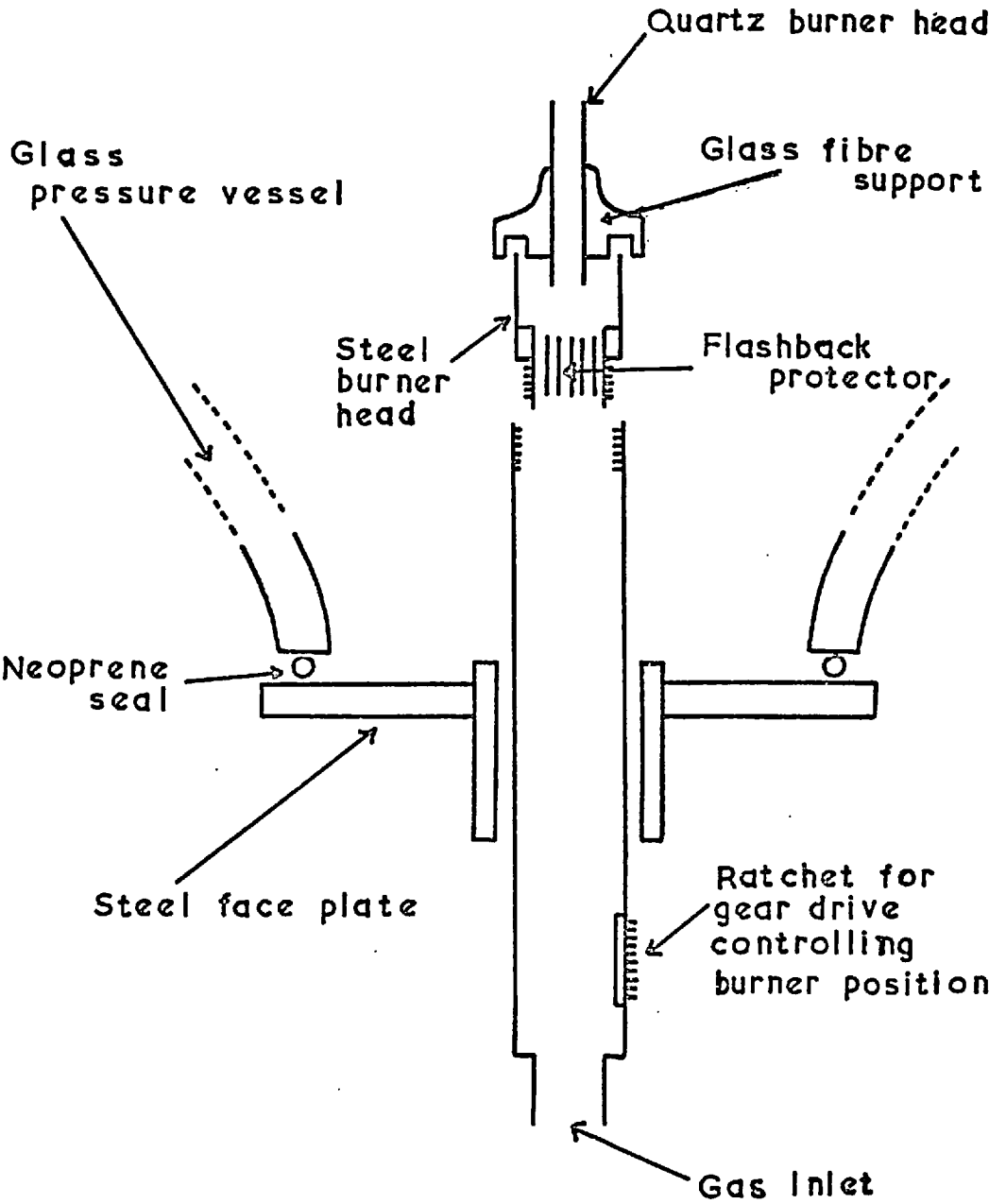
Tandem pumps (Edwards High Vacuum Ltd.; Speedivac I S 450 A rotary oil pumps, with non-return valves), with an individual capacity of 500 litres/minute, were smoothed through a vacuum reservoir of approximately 50 litres capacity, to maintain a steady vacuum and a smooth pumping flow. Flame pressure was controlled by bleeding air into the pumping line

via coarse and fine ballast valves; an arrangement which was found in practice to work very well.

Burner heads were mounted at the end of a gunmetal tube, carrying the fuel and support gases; the position of this tube could be adjusted by means of an external ratchet as required; one end of the tube was threaded to permit ready interchange of burner heads (see Figure I). Experiments covered a pressure range between about I5 and 300 Torr., and to stabalise flames over this range a series of burner heads of diameters varying between 0.3 and 4.0 cms. were required. The smaller burner heads were made from lengths of quartz or pyrex tube; these were mounted within the 2 cms. diameter mild steel burner head (itself threaded directly onto the burner carrying tube) by packing it with glass wool saturated with an epoxy resin (see Figure I): the glass fibre support thus formed prowed to be sufficiently thermally stable to give a burner head of the type described an almost indefinate lifetime. This method of construction also enabled the rapid exchange of burner heads to be effected, simply by 'unplugging' one head, and then pushing its replacement straight into the position thus vacated. Table 2 shows the approximate (practical) operating pressure ranges for the various burner heads thus constructed.

The largest burner (4.0 cms. internal diameter) was

FIGURE 1


Quartz burner head
Glass pressure vessel
Glass fibre support
Steel burner head
Flashback protector
Neoprene seal
Steel face plate
Ratchet for gear drive controlling burner position
Gas Inlet

made of brass, and was clipped over the 2 cms. head when required. None of the burner heads used had more than one

TABLE 2

Cms. Burner Diameter	Burner Material	Optimum Operating Pressure (Torr.)	
		C_2H_2/N_2O	C_2H_2/O_2
4.0	Brass	I8	—
2.0	Steel	33	I0
I.0	Pyrex	75	22
0.6	Pyrex	I30	45
0.3	Pyrex	320	I05

Note:- (I) The results in Table 2 were obtained at C_2H_2, N_2O and O_2 flow rates of 0.8, 4.0 and 2.0 litres / minute respectively, corrected to 20 ^{o} C and I atmosphere pressure.

(2) At low pressures, ignition of the flame can be achieved much more easily at the upper pressure limit of the burner used (I6).

(3) The (approximate) inverse proportionality between burner diameter and pressure enables burners to be designed to operate at any desired pressure.

nozzle, unlike a conventional atmospheric burner, and thus only a single flame cone was observed at any one time.

Reactant gases were passed through a packing of corrugated steel strip; this strip acted as a flashback protector, as well as providing a laminar gas flow to the burner head during normal operation. Ignition of the flame was achieved by passing the support gas alone through a high voltage discharge, and gradually introducing increasing amounts of acetylene until ignition occurred. This procedure was quite adequate at pressures below c.a. 100 Torr., since any explosion caused by a build-up of acetylene prior to ignition was not sufficiently violent to do any damage. At higher pressures however, increasing care had to be taken to achieve ignition as soon as acetylene reached the discharge (seen by a sudden green coloration due to C_2 emission); thus if the flame failed to ignite for any reason after C_2 emission was observed in the discharge when working at high pressures, the discharge had to be shut off immediately, and the pressure vessel flushed out with air to remove the excess acetylene.

The most common causes of non-ignition of the reactant

gases were either incorrect operating pressure (usually too low) for the burner head used, or else the fuel to support gas ratio was wrong (an easy error to make until the pressure dependence of the flow meters was known); the latter was not however particularly critical, and with practice could be gauged by the colour of the discharge prior to ignition. Air leaks in either fuel or support gas lines also caused a marked reduction in the burning velocities of both O_2 and N_2O supported flames, especially at pressures below about 100 Torr., and great care had to be taken to exclude all traces of air from the reactant gases when working with such high burning velocity flames at very low pressures.

2:2 The D.C. Flame Background.

The work below was carried out on a C_2H_2/N_2O flame, examined over a pressure range between about 15 and 300 Torr. The light output from the flame was chopped at 285 c/s, permitting it to be seen by the phase sensitive Tectron amplifier, and was pre-focussed to give a maximum output from the photomultiplier. Measurements were made on both line and continuum emission as a function of burner position, under conditions of variable pressure and variable fuel: support ratios. Under given experimental conditions, the emission to burner position curves

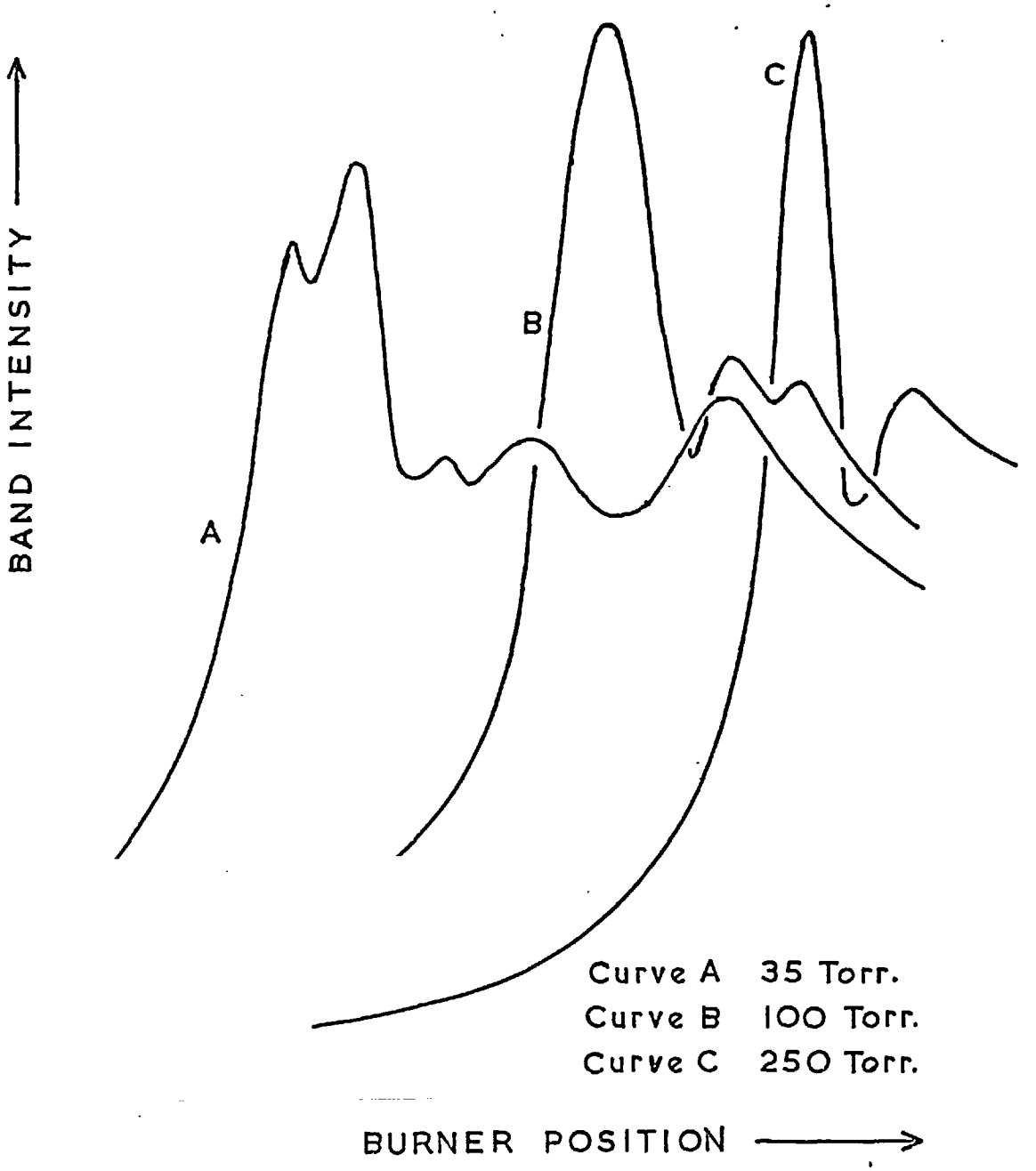
were found to be qualitatively independant of the band observed, although small (relative) quantitative differences were apparent: these results were determined by observing the emission intensity as the burner head was advanced by measured amounts, using the external ratchet.

The low pressure burner is extremely safe if conditions of either flashback or lift-off are reached for a given burner head; thus there was no difficulty in examining the D.C. profiles of the flame over all conditions between these two extremes, by repeating the procedure given above at a number of different fuel: support ratios.

The examination of the D.C. profiles as a function of pressure proved more difficult, since it was necessary to cover a pressure range between about 15 and 300 Torr; this involved the quantitative transfer of data obtained using different burner heads. Quite apart from the effect of the (inherently) very different flame dimensions between these pressure limits on the measurement of any absolute intensities, it was also found that results were quantitatively dependant on factors such as the material used for the burner head (e.g. quartz or pyrex), and even on its physical dimensions (e.g. a thick walled pyrex burner head was found to decrease C_2 emission at 516.5 nm. by about 20% compared with a thin walled burner of equivalent internal diameter, at a pressure of 150 Torr.). The present results were obtained using a series of thin walled pyrex

FIGURE 2

D.C. Flame Noise Profiles

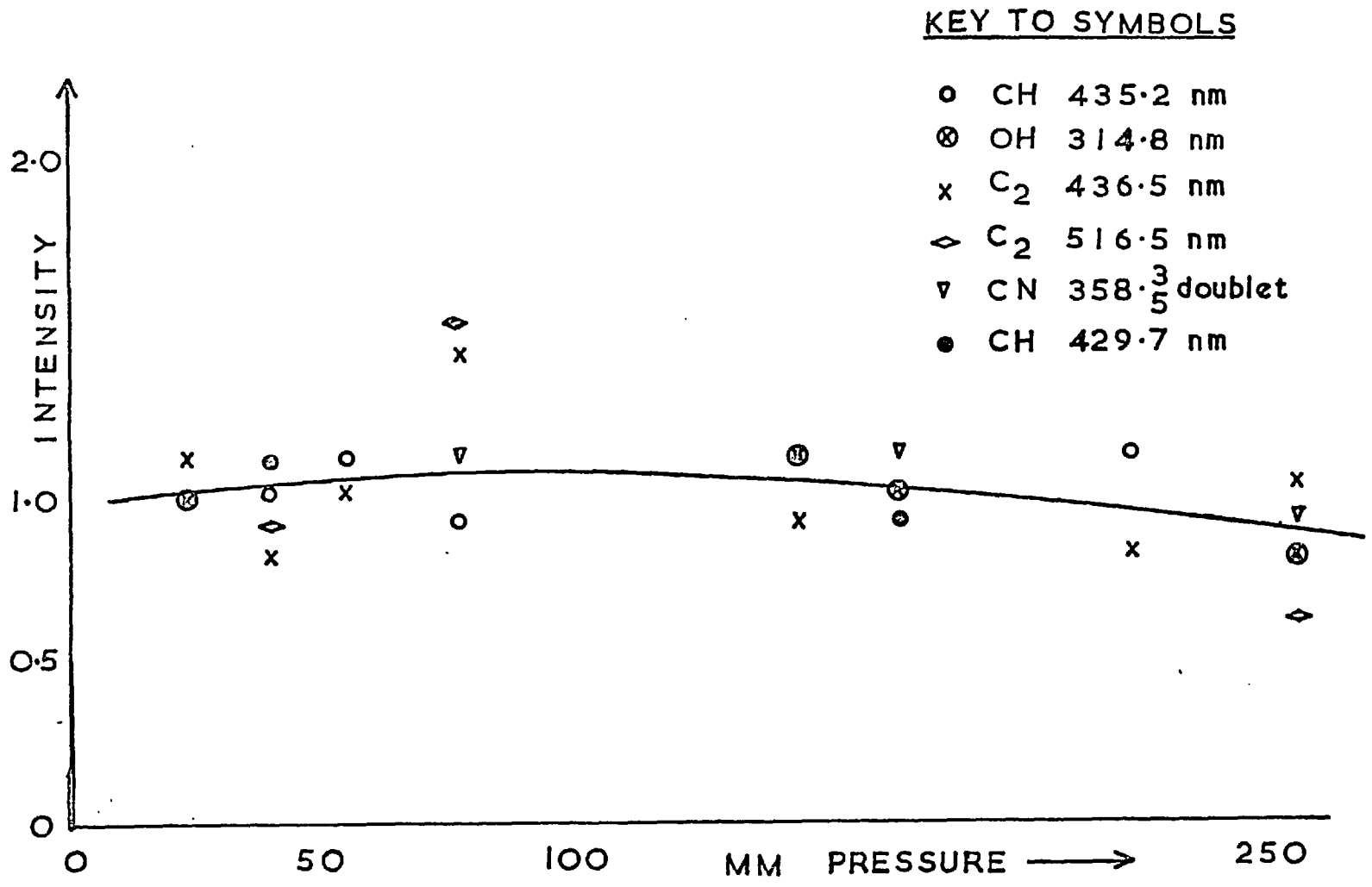


burner heads, used from new, and aged for a few minutes before any results were taken: a procedure which was subsequently adopted whenever it proved necessary to determine quantitative results over a wide pressure range. The pressure dependence of a number of the most intense lines emitted by the low pressure C_2H_2/N_2O flame are shown in Figure 3; each result was taken with the burner position adjusted for maximum emission of the line concerned.

In obtaining these results, no account has been taken of the reduction of a measured line intensity compared to its absolute value due to the increased size of the flame as pressure is reduced. Thus Figure 3 represents the effect of pressure on the D.C. background as seen by the instrument; although analytically useful therefore in deducing the noise levels likely to be seen in practice, these results do not lend themselves to any immediate conclusions concerning the variations of the absolute flame emission as a function of pressure.

The curves of Figures 2 and 3 show that the 'edge' of the flame is not, radiationally speaking, and hence presumably chemically as well, a true break; that is, the boundary of the p.r.z., although it is undoubtedly extremely sharply defined, certainly does not represent a discontinuity in the flame, and thus if it is required to make use of the low D.C. background existing beyond the p.r.z., the flame must be withdrawn for some finite distance beyond the field of vision of

FIGURE 3


KEY TO SYMBOLS
o CH 435·2 nm
⊗ OH 314·8 nm
x C_2 436·5 nm
◇ C_2 516·5 nm
▽ CN 358·$\frac{3}{5}$ doublet
● CH 429·7 nm
2·0
1·0
0·5
0
INTENSITY
0
50
100
MM PRESSURE ⟶
250

the monochromator.

The oscillations of emission intensity within the p.r.z., shown in Figure 2, are suggestive of the formation of a standing pressure wave induced at the burner head; a supposition which is strongly supported by the observed critical qualitative dependence of this oscillatory pattern on factors such as flame pressure, gas flow rates and burner position within the pressure vessel; the causes and results of such A.C. noise have been discussed at greater length below.

The level of the D.C. background does not appear to be particularly sensitive to pressure, although small reductions in intensity can be seen towards the limits of the pressure range examined (Figure (3)). The conclusion must therefore be drawn that the pressure dependence of the D.C. background of the low pressure flame is not, practically speaking at least, an important variable; furthermore, provided the high pressure trend of the curve in Figure 3 can be extrapolated, there is no reason for supposing that the low pressure flame offers any significant advantage over its atmospheric counterpart on the grounds of any improvement in the background emission intensity.

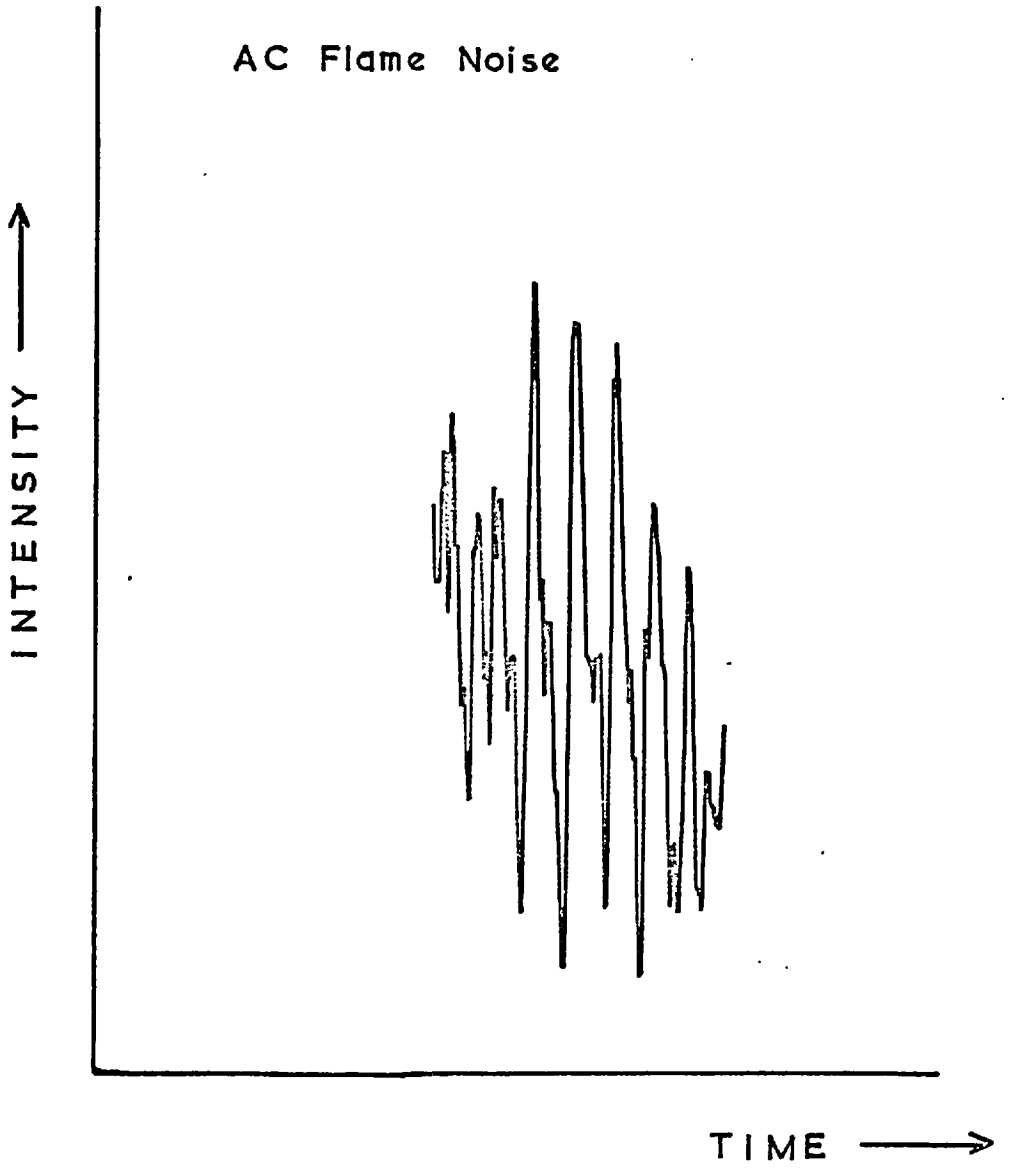
2:3 A.C. Flame Background.

Any gas jet issuing from a nozzle is susceptible to

time-dependent mass-perturbation effects, which may develop into a true oscillation as the system approaches resonance (59): thus for example A.C. frequencies of upto 5 Kc / s have been observed in the radiational output of conventional atmospheric flames (60). Even ideally, no flame supported on a tubular burner and mounted within an enclosing vessel can ever have a purely D.C. output (I6, 6I, 62); thus it must be expected that the present equipment will always impose some degree of (inherent) self-modulation on the low pressure flames examined.

The problem of A.C. noise was accentuated in the present experiments, firstly because the large sizes of some of the burners used reduced the natural resonance frequencies of the system, and secondly because the effect of pulses from the pumps could not be completely eliminated within the pressure vessel. These effects were especially noticeable at very low pressures (less than ca. 30 Torr.); at such pressures the 2 cms. diameter burner head was very commonly used, and the resonant frequency of this burner apparently lay quite close to that of the pumping system itself. Figure 4 shows a 3 c/s modulation, observed on the 5I6.5 nm. C_2 line in a C_2H_2 / N_2O flame burning on the 2 cms. head at 30 Torr, which was attributed to this joint resonance. The resonant frequencies of the higher pressure burners however were evidently rather greater, and at pressures above about 70 Torr. A.C. noise in the flame appeared to be mostly due to the pumps. Thus at higher pressures, A.C.

FIGURE 4



noise intensities did not appear to be particularly pressure dependent, and could be virtually eliminated by stopping the pumps (until the resulting rise in pressure brought the flame towards flashback, when some turbulence tended to occur).

The low frequency oscillation thus induced in the flame, quite apart from generating an excessively high noise level under resonance conditions, could even cause the flame to lift off, or, less often, to flash back. Thus when working under conditions where coupled oscillation could occur, some care had to be taken with the mechanical layout of the gas supply lines to the burner, to avoid this region of critical mutual resonance.

The A.C. noise discussed above clearly represents a severe disadvantage of the low pressure flame in comparison with its atmospheric counterpart. The lower mechanical resonance frequencies of large diameter burners means that, even if the A.C. noise due to pumping fluctuations could be eliminated, an inherently increasing A.C. background must occur as the flame pressure is reduced. Any sample present in the flame must follow the physical mass distribution of the flame gases, and thus even if the effect of background noise due to flame emission can be negated (e.g. by means of atomic fluorescence spectroscopy, using a modulated source and a phase sensitive detector), the flame noise must still be carried by the sample itself, and

therefore such noise cannot be prevented from creating a correspondingly poor signal to noise ratio.

Therefore the conclusion reached after an examination of the A.C. and D.C. background emission levels in a low pressure N_2O/C_2H_2 flame must be that no definate reduction in background intensities is likely to be attained by working at reduced rather than atmospheric pressure; in fact if anything these intensities are likely to be worse at low pressure. Although the results leading to this conclusion were obtained specifically from the low pressure C_2H_2/N_2O flame, their rationalisation is quite general, and thus it seems reasonable to consider this conclusion to be of corresponding generality; thus if a low pressure flame is in fact to be of any analytical use, it seems likely that it will be through some factor other than an analytically favourable background noise level.

CHAPTER THREE

3:I The Nebulisation of Solutions into the Low Pressure Flame.

Before any sample emission studies could be undertaken, it was necessary to devise a satisfactory means of nebulising a sample solution into the low pressure flame. The standard Techtron nebuliser was initially used for this purpose, although sample solutions could not be aspirated directly through the pressure gradients involved without some modification to this unit. During the original experiments, the analyte solution was fed to the nebuliser inlet through a throttling valve; however, the use of transparent couplings to this valve revealed that its action did not give rise to a steady but reduced flow of sample solution, as required, but rather that the solution was broken up into a series of globules; these globules entered the atomiser as separate, discrete particles, with a consequent irregularity in the rate at which the sample was finally fed into the flame.

The problem of absorbing the excess energy available to an aspirated solution due to the pressure gradient across the inlet to the nebuliser was first overcome satisfactorily by packing the inlet capillary with 'Litz' wire, obtained from a

radio tuning coil. 'Litz' wire is made up of very fine individual strands, and by using a sufficient number of these strands to pack the inlet capillary, sample delivery rates as low as around 0.05 ml/min. could be achieved on direct aspiration from the atmosphere. The aspiration was continuous, and, of even more importance, it was also found to be quantitatively reproducible.

The only drawback occuring with this arrangement was that when the nebuliser blocked up, which was a fairly frequent occurrence, the inlet capillary had to be unpacked, each strand of wire washed, and the whole thing re-assembled again; this was not only a lengthy operation, but it also destroyed the continuity of any results being taken, since the characteristics of the inlet system could never be exactly duplicated once it had undergone such treatment. The problem was finally solved by replacing the multi-strand packing with a single piece of stainless steel wire, of such a diameter as to provide an exact and very tight fit between the walls of the inlet capillary. Thus instead of providing a number of very fine channels between the individual strands of 'Litz' wire, as before, the channels occured between the surface of the wire and the capillary walls. This arrangement was found to have all the advantages of the old inlet system; in addition, it could be unblocked by simply twisting the wire within the inlet capillary; a process which could be achieved in a few seconds, and without any apparent

deletorious effect on the performance of the nebuliser. Finally, this new arrangement permitted some control to be excercised over the rate of sample uptake, by adjusting the length of wire inserted into the inlet capillary; such variation in the length of the surface channels of the wire controlled the force required to push a given volume of fluid through those channels, or alternatively controlled the volumetric flow rate of fluid occurring under the action of a given force.

The performance of the nebuliser described above was quite adequate, and it was accordingly used without any further modification during subsequent work. It was however found with this nebuliser that organic solvents tended to vapourise so quickly that any water also present tended to freeze; also, the presence of such organic vapour appreciably reduced the burning velocity of the flame. Thus the aspiration of any organic solvents required careful pre-drying of the nebuliser, and was accompanied by a (usually) visible movement of the flame front away from the burner head; thus the noise levels of analytical work were correspondingly increased. Under extreme conditions (with solutions containing e.g. benzene or toluene as solvents) the flame would lift off altogether; for these reasons therefore, the following work was carried out exclusively with aqueous solutions, and no experiments at all have been attempted using non-aqueous solvents.

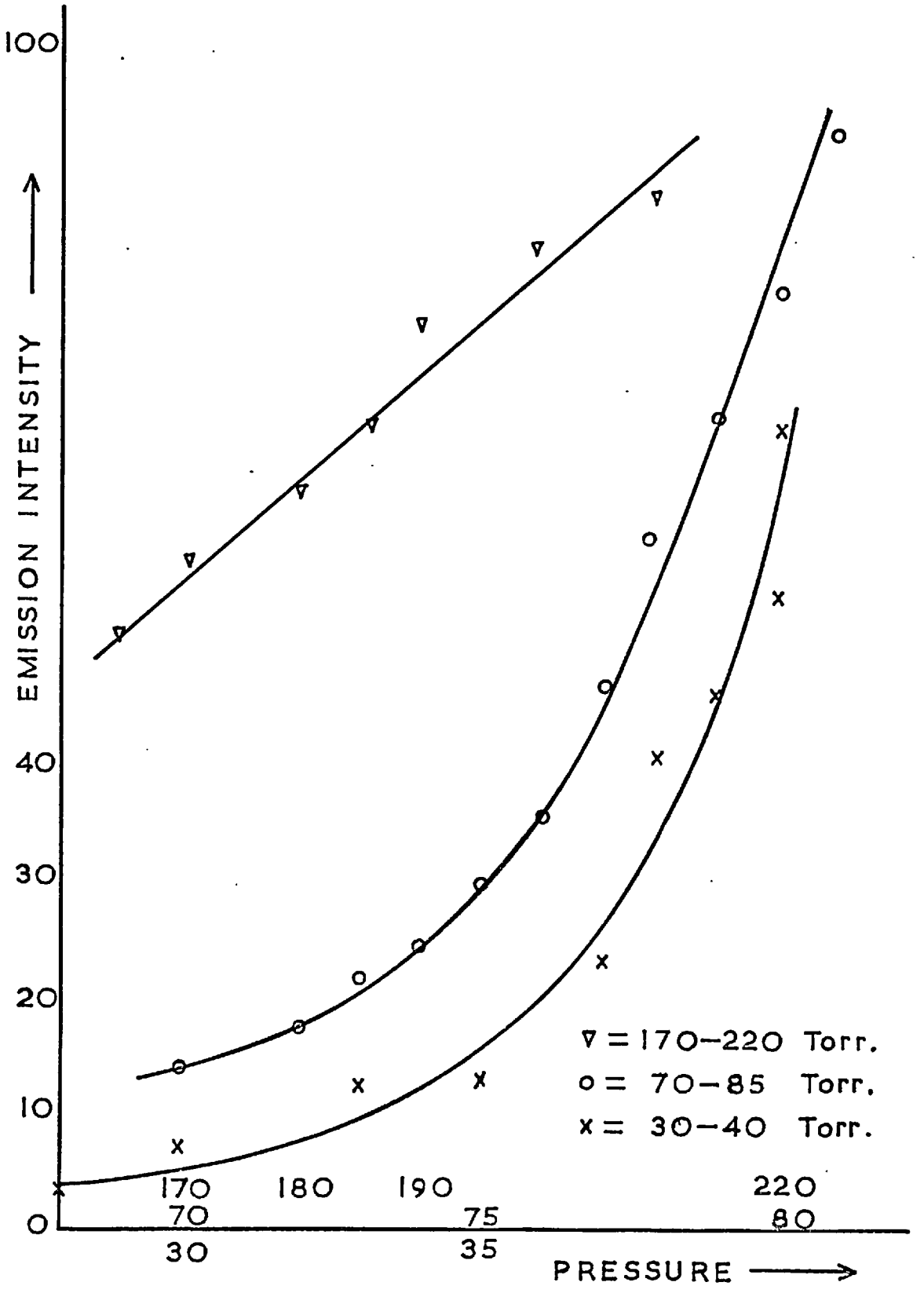
3:2 Sodium Emission as a Function of Pressure.

The first experiments undertaken using the above equipment determine the emission signal, as a function of flame pressure, given by some of the alkali and alkaline earth metals; these results subsequently proved to be of fundamental importance to the consideration of any general analytical application of the low pressure flame. The alkali and alkaline earth metals were initially chosen because of the relative volatility of their salts, and also because of the ease of excitation of their resonance lines; a point of some importance, since the reportedly poor results given by atomic absorption spectroscopy in low pressure flames (57), and the technical complexity of atomic fluorescence in combination with the low pressure burner, made examination by atomic emission virtually obligatory at this stage of the work.

Results obtained for sodium are shown in Figure 5; these results are typical of those obtained both for other elements, and over a variety of conditions, but for numerical reasons (see later) only the results given by sodium have been considered at the present time.

For the purposes of the present work, the edge of the flame was considered as the burner position at which the D.C. background at 589.0 nm. had risen to twice the value observed

FIGURE 5


100
40
30
20
10
0
EMISSION INTENSITY
▽ = 170–220 Torr.
o = 70–85 Torr.
x = 30–40 Torr.
170
180
190
220
70
75
80
30
35
PRESSURE

with the burner fully withdrawn from the field of vision of the monochromator (see Figure 2 above); an analagous method of definition of the flame edge has subsequently been adopted during later experiments, unless specifically stated to the contary.

The results for sodium emission as a function of pressure were obtained by measuring the intensity of the 589.0 nm. line at the flame edge during the aspiration of aqueous solutions of Na Cl; results were obtained over a variety of conditions of flame composition and pressure, and of solution concentrations aspiration rates (see Table 3). The suggested interpretation of these results is given below.

The curves of Figure 5 have the form of an exponential rise of the sodium emission intensity with pressure; if true, this result clearly implies that the analytical senstivity of atomic emission spectroscopy, and perhaps of the other spectroscopic techniques as well (57), is inherantly reduced by working with a low pressure rather than a conventional atmospheric flame. For this reason therefore it is felt to be essential that the curves of Figure 5 be given a quantitative, physical, interpretation if it is at all possible to do so.

It was pointed out in Chapter I that overexcitation in the low pressure flame has been successfully quantitatively interpreted by the use of a set of Boltzmann-type equations: this success therefore suggests the use of a similar approach

to the present problem. Using such an approach, the sodium emission may be described by an equation of the form

$$\log_e I = \text{constant} / T + \text{constant}' \quad \text{——————} \quad (I)$$

where I is the observed emission intensity, and $T^{\circ}K$ is the 'sodium temperature' of the flame.

To account for the curves of Figure 5 by means of equation (I), T must be expressed as a function of the pressure, p, leading to the equation

$$\log_e I = \text{constant} / f(p) + \text{constant} \quad \text{——————} \quad (2)$$

A graphical plot of the results in Figure 5 fitted to equation (2) suggests that f (p) can be expressed as a power function of the form $T = \text{constant} \cdot p^x$ —————— (3)

Thus by comparison of equations (I), (2) and (3),

$$\log_e [I / A] = + B / p^x \quad \text{——————} \quad (4)$$

where A and B are constants.

Although it is possible in principle to calculate an exact value of x from equation (4), given a set of values for I and p, by means of a graphical method, in practice this approach is precluded by the scatter of the points due to experimental error; a factor to which equation (4) appears to be particularly sensitive. It was in fact for this reason that the quantitative correlations attempted below have been restricted to the results for sodium emission, since these were found to be the least susceptible to random errors.

To minimise the effect of such experimental errors, a numerical solution for x was effected by use of the University of London I.B.M. 7094 computer.

By the use of the computer, a specific value of x could be determined giving a minimum standard deviation of experimental results from the values required by equation (4). The results of this numerical analysis are shown in Table 3 below.

In Table 3, A, the pre-exponential term in equation (4), can be shown to be dependent on the experimental conditions used (see below). Thus its numerical value is governed by parameters such as amplifier gain, flame temperature, solution concentrations etc., as well as including the normal Boltzmann probability factors; the values of A observed in Table 3 cover almost six orders of magnitude, giving at least some indication of the extent to which the parameters mentioned above have altered between different experiments.

The value of B in equation (4) above corresponds to an activation energy term; the variations of B observed in Table 3 can be shown (see below) to result, at least in part, from a non-constant nebuliser performance. That such behaviour should be observed is not perhaps too surprising when it is considered that the energy available for nebulisation is directly dependent on the pressure gradient across the inlet capillary of the

TABLE 3

Experiment Number	Pressure Range Considered (Torr.)	Conditions Used	$A.10^{-6}$	-B	-x
I	75 - 90	S / I00	87	I20	0.36
2	70 - 80	L / I00	82	270	0.56
3	80 - 92	R / I00	0.2	I00	0.55
4	80 - I02	S/I0,000	0.0027	3500	I.5I
5	64 - 73	S / I000	0.0064	3200	I.5I
6	70 - 82	L / I0	77	290	0.58
7	78 - 92	R / I0	0.0028	3200	I.5I
8	28 - 40	S/I0,000	0.00I5	2800	I.79
9	28 - 40	S / I000	2.2	II0	0.66
I0	I03 - I35	S / I00	I00	II0	0.35
II	I65 - 220	S / I00	.00026	3200	I.5I
I2	270 - 330	S / I00	.000I6	4I00	I.60

Key to Experimental Conditions Used:-

S = stoichiometric flame
R = fuel rich flame
L = fuel lean flame

I0 = I0 ppm Na aspirated at 0.5 ml/min.
I00 = I00 " " 0.5 "
I000 = I000 " " 0.I "
I0,000=I0,000 " " 0.I "

nebuliser, and that this pressure gradient varies between about a half and one atmosphere; in view of this, variations in B by the observed factor of up to 40 are not felt to be unreasonable.

Finally x, although ideally a constant, can be seen in Table 3 to vary between -0.35 and -I.79; however, in view of the numerical variations of the A and B terms seen above, such discrepancies are not considered to be excessive.

The results in Table 3 give an average value of $x = 0.994$; a value which is felt to justify the hypothesis of a 'true' value of x equal to unity. That is, the apparent sodium temperature in the low pressure flame is directly proportional to pressure.

However, when the complexity of the factors giving rise to the observed sodium temperature in the low pressure flame are considered, it appears most unreasonable to expect a relationship as simple as $T \propto p$ to be valid over a range of conditions as wide as that examined. Furthermore, there is another variable in the low pressure flame which is also linearly dependent on pressure, namely, the molecular collision frequency, z, and in the light of these observations it seems to be demanding too much of coincidence to assume that the relationships $T \propto p$ and $z \propto p$ are unrelated results. The conclusion which is therefore suggested from these arguments is that the curves of Figure 5 do not result from any temperature change at all,

but that they somehow reflect the changing molecular collision frequency with pressure in the flame.

This conclusion seems to be not unreasonable if a particle, introduced into a region of high molecular thermal energy but of low mass density, is considered. Conservation of energy principles require the heating rate of the particle to be linearly dependent on the molecular collision frequency, at least initially, and to fall to zero as the pressure of the particle environment also falls to zero; thus the fraction of the particle mass simultaneously volatilising must be correspondingly pressure dependent. Hence the variations of a spectroscopic emission signal with pressure can be explained very plausibly in terms of a varying vapour phase concentration of sample, provided the pressure is sufficiently low, without resorting to the violent temperature fluctuations apparently demanded by Figure 5. It is therefore suggested that the curves of Figure 5 indeed fulfil this low pressure condition, and hence that the variable parameter being observed in Figure 5 is simply the changing atomisation efficiency of the flame in converting solid particles of salt into a vapour phase atomic population, by energy transfer from the flame to the particle <u>via</u> molecular collision processes.

In order to achieve a quantitative interpretation of this hypothesis, it is necessary to have some physical model

on which calculation can be based. For the purposes of the present work, the model chosen considers a (single) sample particle, heating up at a finite rate, but without losing a significant fraction of its mass by evaporation, as it travels through the flame.The temperature of the particle then becomes steady as evaporation commences and volatilisation cooling balances the rate of heat transfer to the particle from the flame gases. The layer of vapour created around the particle during either of the above processes is permitted to diffuse away, to give a vapour phase sample population distributed throughout the flame: at no stage is any account taken of possible changes of state occurring while the particle is in the condensed phase.

For the sake of mathematical simplicity, the above processes have been considered to be mutually exclusive, to the extent that while all three can be simultaneously considered, if required, only one can be a rate determining process. Given this degree of simplicity, calculation then suggests that a result of the form of equation (4) above can never be achieved if the particle has reached a state of balance between the heat gained from the flame and the heat lost by evaporation. Thus to explain the experimental occurrence of equation (4) on the model outlined above, it is necessary to consider a particle which gradually heats up as it passes through the flame, but

which never reaches an equilibrium temperature; the (small) amount of sample vapour generated during this process then diffuses away. Since 'energy balance' conditions are never achieved, energy considerations cannot represent a rate determining step, and therefore under such conditions the diffusion of the vapour phase population away from the particle surface must be rate determining. The quantitative interpretation of this model is given below.

Let z $sec^{-1}.cms^{-2}$ be the molecular collision frequency in the flame.

$\bar{E}$ the mean energy transferred per particle/molecule collision.

A the instantaneous surface area of the particle

m the instantaneous mass of a particle

T the instantaneous temperature of a particle

S the specific heat of the sample

d the density of the sample

Neglecting evaporation and surface energy effects, the rate of temperature increase of a sample particle is given by:-

$$z \cdot \bar{E} \cdot A = \frac{d}{dt} \cdot (m \cdot S \cdot T) \quad \doteq m \cdot S \cdot \frac{dT}{dt}$$

$$\text{but} \quad A = 4\pi \cdot \left[\frac{3}{4\pi \cdot d}\right]^{2/3} \cdot m^{2/3}$$

$$\therefore \; z \cdot \bar{E} \cdot 4\pi \cdot (3/4\pi \cdot d)^{2/3} \cdot m^{2/3} = S \cdot m \cdot \frac{dT}{dt}$$

$$\therefore \text{ integrating, } 4\pi \cdot z \cdot \bar{E} \cdot (3/4\pi \cdot d)^{2/3} \cdot t = S \cdot m^{I/3} \cdot (T_t - T_o)$$

$$\therefore \quad T_t = T_o + \frac{4\pi \cdot z \cdot \bar{E} \cdot (3/4\pi \cdot d)^{2/3} \cdot t}{S \cdot m^{I/3}}$$

But the molecular collision frequency, z, is known to be directly proportional to the flame pressure, p_f (63)

$$\text{i.e.} \quad z = K_I \cdot p_f$$

$$\therefore \quad T_t = T_o + K \cdot p \cdot t / m^{I/3} \qquad \text{——— (5)}$$

$$\text{where } K = K_I \cdot 4\pi \cdot \bar{E} \cdot (3/4\pi \cdot d)^{2/3} / S$$

The Clausius-Clapeyron equation (64) gives the saturated vapour pressure, P_s, of a condensed phase sample in terms of its temperature, T, and its heat of evaporation, L_v, as

$$-\frac{d(\ln P_s)}{d(I/T)} = L_v / R$$

$$\text{i.e.} \quad \ln (P_s)_t / (P_s)_o = -(L_v / R) \cdot (I/T_t - I/T_o) \qquad \text{——— (6)}$$

$\therefore$ for $T_t \gg T_o$, and combining equations (5) and (6),

$$(P_s)_t = (P_s)_o \cdot \exp(-L_v \cdot m^{I/3} / R \cdot K \cdot p \cdot t)$$

Finally, it is necessary to calculate the fraction of sample diffusing to the defined point in time and space at which it is experimentally observed. Crank (65) relates the vapour pressure at such a point to the saturated vapour pressure, P_s, of the sample by an equation of the form

$$P_{x,t} = C_{x,t} \cdot P_s / D$$

where $C_{x,t}$ is a constant, and D is the diffusion coefficient of the vapour phase sample in the flame gases.

$$\therefore P_{x,t} = C_{x,t} \cdot (P_s)_o \cdot \left[\exp(-L_v \cdot m^{I/3} / R \cdot K \cdot p \cdot t)\right] / D \quad \text{———(7)}$$

When equation (7) is compared with the experimentally determined equation (4) above, it can be seen that A is proportional to $C_{x,t} \cdot (P_s)_o$, as well as to the purely experimental parameters, neglected in the above derivation, such as nebuliser efficiency, amplifier gain etc.; also, $B = L_v \cdot m^{I/3} / R \cdot K \cdot t$, and x is unity as required. The derivation also provides at least an indication of the complexity of the A and B terms in equation (4), thus showing perhaps the origins of the experimental variations observed with these parameters.

The discrepancies between equation (7) as p approaches infinity, and the Lykov equation (66), derived to describe

particle volatilisation in the more conventional atmospheric flame, are presumably due to the different assumptions necessarily chosen for the physical models from which the two equations were obtained. For instance, the gradual heating stage of a particle lifetime, apparently of supreme importance at low pressure, can reasonably be assumed to occur so fast at atmospheric pressure that its effect can be ignored, and only thermally steady state conditions need to be considered (66,67).

3:3 Conclusions.

By use of the arguments above, the following conclusions are suggested.

Firstly, experimental results show that the dependence of sodium emission intensity on pressure requires a relationship of the apparent form temperature proportional to pressure.

Secondly, it is argued that this linear relationship occurs because 'temperature' in the present context refers to a molecular collision frequency; thus the emission / pressure dependence simply reflects the changing atomisation efficiency of the flame.

Thirdly, although a rigorous quantitative solution to the problem of sample atomisation in the low pressure flame appears impractical, it does seem that the only way of arriving

at a result as simple as temperature proportional to pressure is to correspondingly simplify the original equations describing atomisation in the flame; this can be done by adopting the assumption given previously. These assumptions require that the solid particles of the sample gradually heat up as they pass through the p.r.z., losing only a small fraction of their mass by evaporation on the way; on this model therefore the bulk of an aspirated sample must pass through the flame while still in the solid state.

Even though the evidence so far presented was, during the original experiments, sufficient to deduce the conclusions given above, it is not felt that the work is sufficiently numerically accurate to consider these conclusions to have been proved valid beyond all doubt. However, there is a great deal of further supporting evidence which is also available (see below), and in view of this support it is felt to be permissable to state with reasonable certainty that the work above locates the fundamental problem inherant in any analytical use of low pressure flames; namely, the extreme difficulty of atomising any sample initially existing in the flame as a solid; a problem arising directly from the low (macroscopic) energy density of the low pressure flame.

If the validity of the above work is thus accepted, a number of useful deductions can immediately be derived from it.

Firstly, in order to introduce an analytical sample into a low pressure flame, either the properties of the flame must be modified to permit a greater rate of energy transfer to occur between the flame and any solid particle existing within the flame, or else the sample introduction technique has to be altered so that the low energy density of the flame can be more readily tolerated. Various methods for putting these possibilities into effect are discussed at the end of the present section of work.

Secondly, if a solid particle can survive its passage through the reaction zone of a low pressure flame, then, in view of the discussion given in Chapter One, it must also be expected that similar particles will also survive in the reaction zone of the corresponding atmospheric flame. The suggestion is therefore proposed that a kinetic control of sample volatilisation processes may be of significance in conventional atmospheric flames (68,69), contributing appreciably to poor analytical sensitivity (at the base of the flame), even for samples as volatile as the sodium chloride used here. Such a kinetic control must be of even more importance when considering either high melting point samples, for which volatilisation rates must be correspondingly reduced (see equation (7) above), or else those elements which form refractory oxides, and for which only the (physically restricted) chemically reducing regions of a flame

can support a useful vapour phase atomic population; the deduction of such kinetic control therefore clearly emphasises the need to use highly efficient nebulisers, capable of generating a very finely dispersed solution spray (70 - 73), when working with such samples. In addition, and by similar reasoning, this deduction also perhaps accounts in part for the analytical success of separated flames (74,75), and in particular of the separated C_2H_2 / N_2O flame (76 - 78); in the latter case, the expansion of the (chemically reducing) interconal zone (79) extends the time over which particle evaporation can usefully occur, thus increasing the vapour phase atomic population of sample observed (80); i.e. by increasing (t) in equation (7) above, $P_{x,t}$ is thereby correspondingly increased as well.

The final point raised by the deduction of the inherently poor atomisation efficiency of the low pressure flame is the explanation of the poor reproducibility which was also encountered. That is, since only a small fraction of the sample mass reaching the flame is considered to be volatilised, a relatively small change in experimental conditions can be expected to have a disproportionately large effect on the fractional change of vapour phase sample concentration then observed, resulting in a correspondingly magnified effect on experimental reproducibility. The poor reproducibility encountered made extreme care in controlling all experimental conditions an

absolute necessity; e.g. the original attempts to use a throttling valve, to control solution flow rates, in conjunction with an unmodified Techtron nebuliser probably failed to give satisfactory quantitative results for this reason.

3:4 Further Evidence for the Poor Atomisation Efficiency of the Low Pressure Flame.

Figures 6 and 7 show the calibration curves obtained for Li, Na and Ca, Sr, Ba. These curves can be seen to become convex at relatively low concentrations, at a point rather closer to the detection limit than might have been expected from the corresponding results at atmospheric pressure (8I). This curvature is explained in terms of equation (7); increasing the sample concentration increases (m), thus decreasing the atomisation efficiency of the flame by the factor $\exp(m^{I/3})$. In physical terms, this reflects the fact that at increased solute concentrations, larger crystalline particles can be expected to enter the flame; although the particle volume increases linearly with the increasing particle mass, the particle specific area rises at a lower rate, and thus the relative rate of evaporation via energy transfer from the flame is correspondingly decreased.

Equation (7) requires the atomisation efficiency of the flame to be proportional to $\exp(-b \cdot m^{I/3})$. Thus for a

FIGURE 6

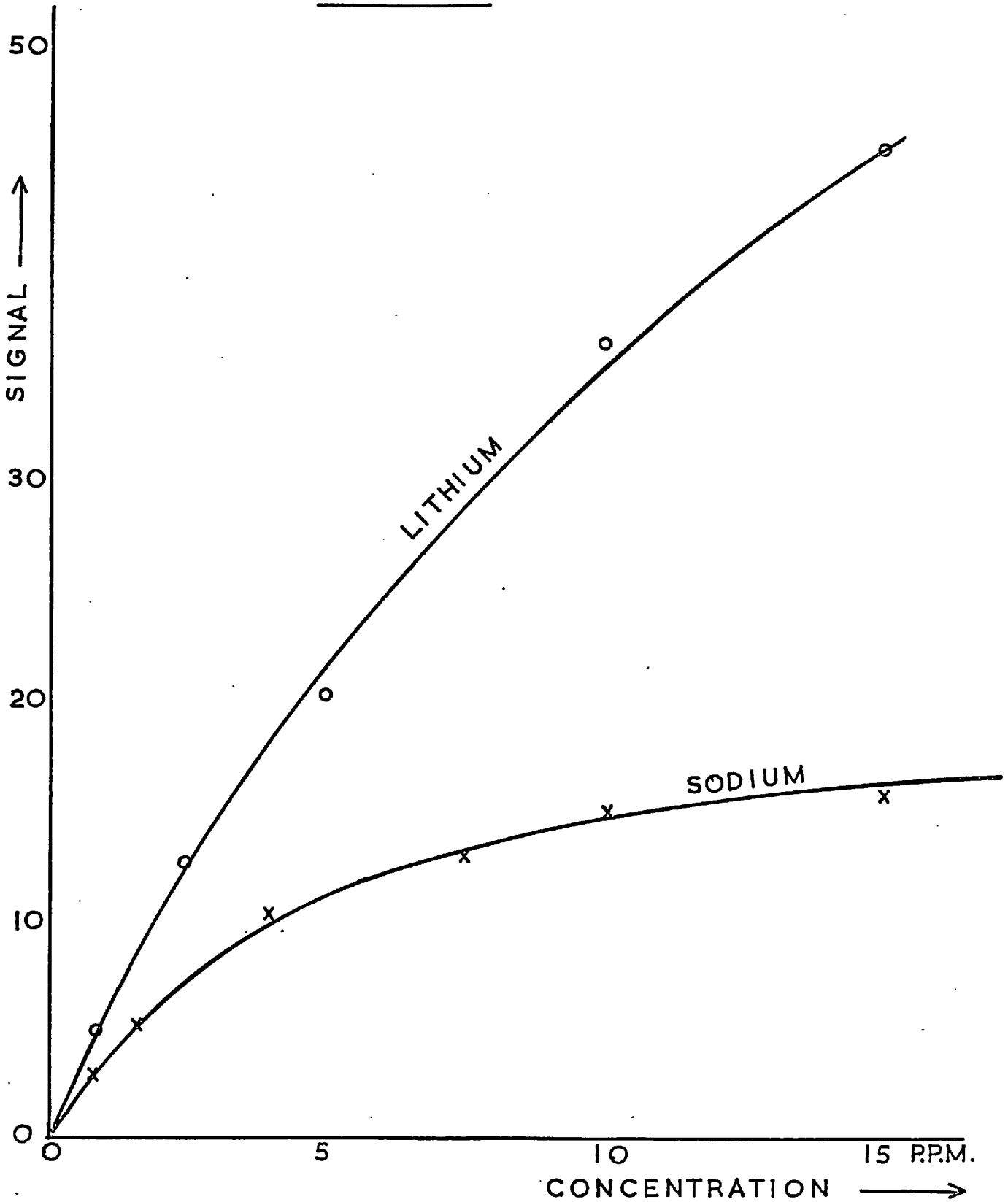

50
30
20
10
0
SIGNAL
LITHIUM
SODIUM
0
5
10
15 P.P.M.
CONCENTRATION

FIGURE 7

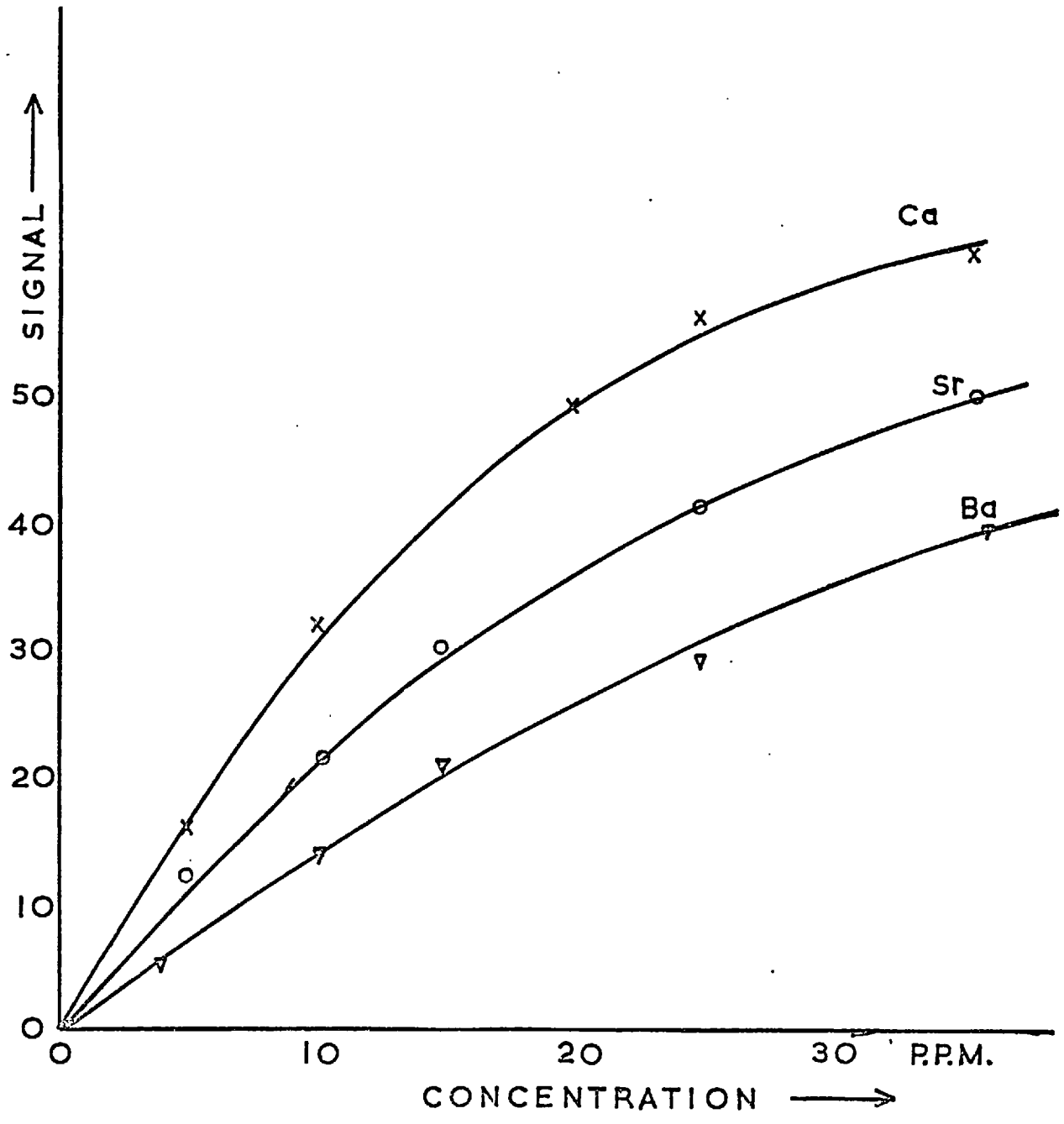


FIGURE 8

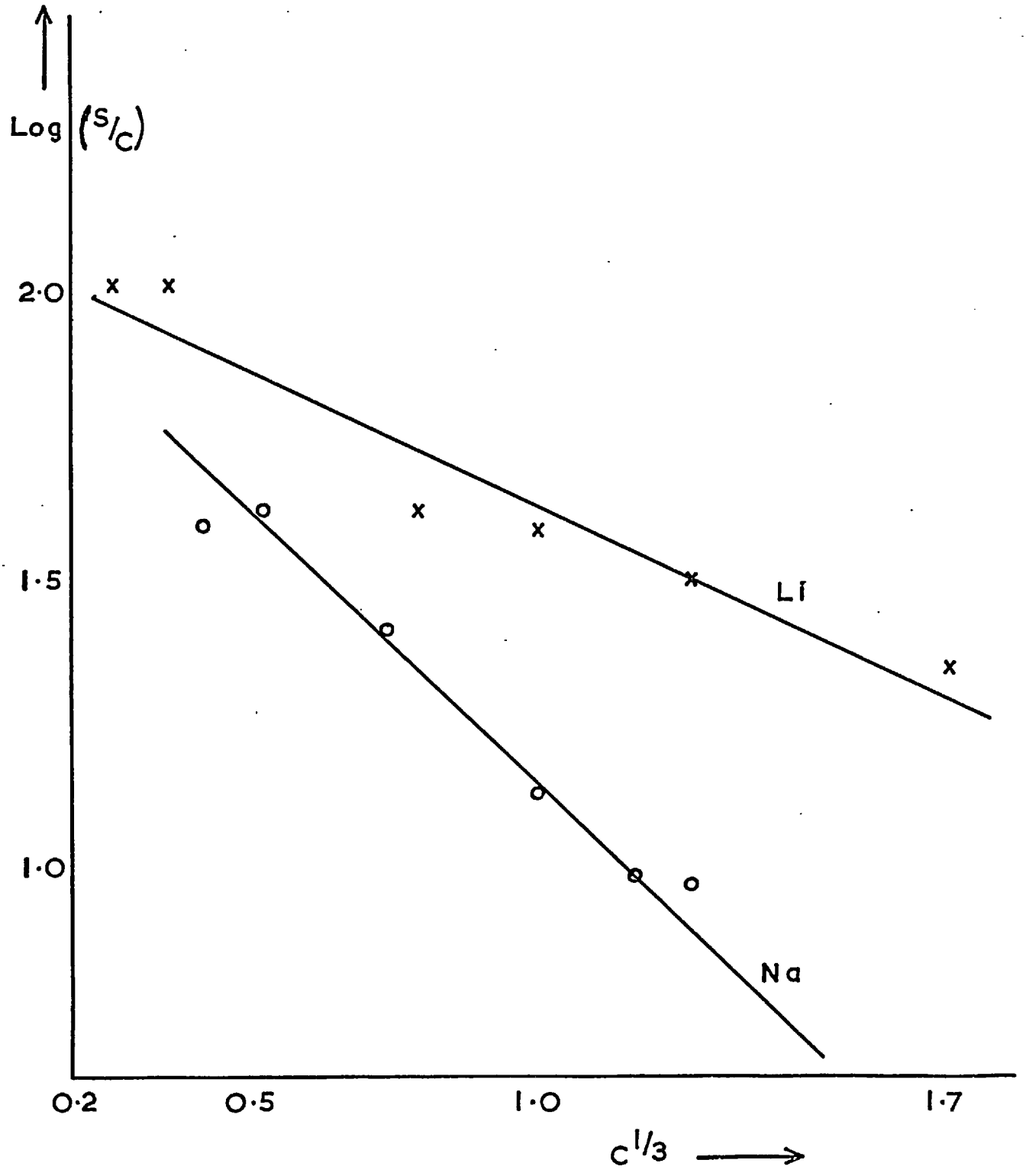
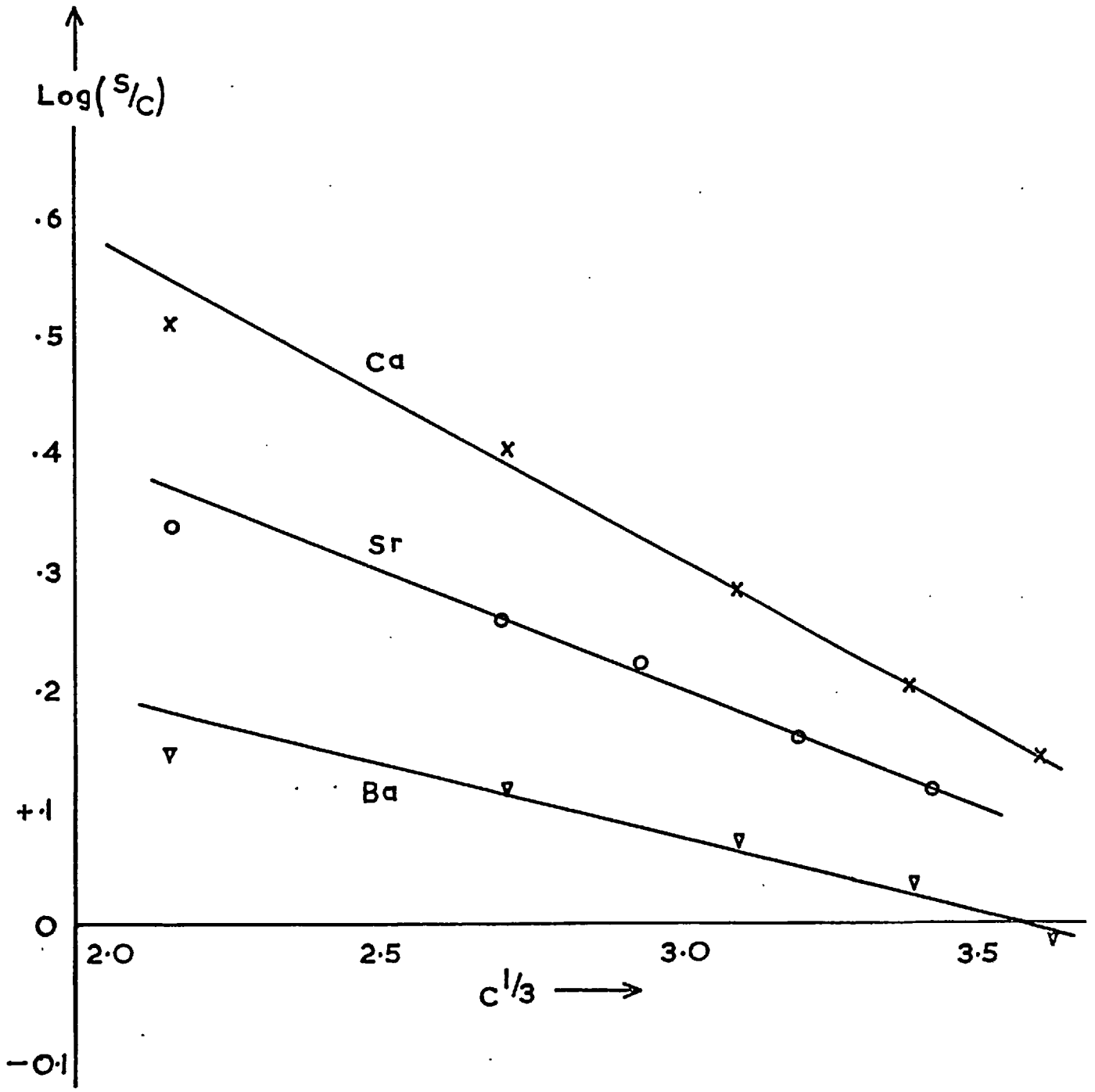


FIGURE 9



signal, S_c, observed for a sample of concentration C_s, the graph of log (S_c/C_s) against $C_s^{I/3}$ can be expected to be linear, with a slope proportional to (b). The curves observed in practice are shown in Figures 8 and 9.

Using the symbols given above, (b) is proportional to $\frac{L_v \cdot S}{4\pi \cdot R \cdot p \cdot \bar{E} \cdot t \cdot K_I} \cdot \left[\frac{4\pi \cdot d}{3}\right]^{2/3}$. The values of L_v, d and S are known for the samples considered here (82,83), and thus if p, $\bar{E}$, K_I, t and the proportionality constant between m and C_s are assumed invariant, it becomes possible to estimate the relative values of $\bar{E}$; i.e. a value for the relative efficiency of energy transfer between the flame gases and the solid particles of sample can be found for the different samples used. These values are given in Table 4 below. It can be seen from the results in Table 4 that the values found for $\bar{E}$ only bear a very approximate relationship to the corresponding detection limits, suggesting that even in a low pressure flame interatomic vapour phase interactions are still analytically significant processes. This is a rather unexpected result, in view of the deductions made in Chapter One, and it is one which implies that any reduction of chemical interference effects to be gained by working at the pressures examined here is not likely to be of outstanding magnitude.

The degree of curvature of the calibration curves of

TABLE 4

Sample Used	Slope of Curve $\log (S_c / C_s) : C_s^{I/3}$	Estimated Value of $\overline{E}$	Experimental Detection Limit (ppm)
Li Cl	-0.25	I.0	0.02
Na Cl	-0.89	0.7	0.05
$CaCl_2$	-0.3I	0.8	0.3
$SrCl_2$	-0.I8	0.5	0.2
$BaCl_2$	-0.I0	0.4	8

Note:- I) For the purposes of thermometric calculation, all samples were assumed to exist as non-hydrated particles before evaporation commenced.

2) The maximum value of $\overline{E}$ found was for Li Cl; this has been given an arbitrary reference value of unity.

Figures 6 and 7, together with the observed agreement between experimental results and theoretical requirements (Figures 8 and 9), provide the first pieces of supporting evidence for the conclusions reached in section 3:3 above.

Two further qualitative results supporting this conclusion are also available. Firstly, I000 p.p.m. solutions of some of the elements of the first transition series were

separately aspirated into a C_2H_2 / N_2O flame, as the flame pressure was increased from 30 to 300 Torr. The qualitative results thus obtained are given in Table 5 below.

TABLE 5

Element	Signal Observed			
	30 Torr.	100 Torr.	200 Torr.	300 Torr.
Ti	zero	zero	zero	zero
V	zero	T	S	S
Cr	zero	T	T	T
Mn	zero	zero	T	S
Co	zero	zero	T	S
Cu	T	S	S	S
Zn	S	S	S	S

T = Transient signal (see below)

S = Continuous signal observed.

In Table 5, a transient signal refers to a signal pulse observed at the moment when the solution was first aspirated, but which rapidly fell to zero with time. The phenomenon was attributed to an abnormally high initial nebuliser efficiency, caused by the (observed) high velocity acquired by the

solution front as it passed through an unobstructed inlet capillary; the impact of this fast-moving solution was then sufficient to give rise to the formation of a number of abnormally small solution droplets. When the inlet capillary was full, fluid frictional forces ensured that the solution flow velocity dropped to its reduced equilibrium value. This phenomenon can perhaps be considered to illustrate previous remarks concerning the possible application of very highly efficient nebulisers to the analysis of high melting point samples using conventional flame techniques.

Although no attempt has been made to give any quantitative significance to Table 5, a clear qualitative trend of results is apparent. Thus it can be seen that the higher melting point elements show a marked reluctance to give any analytical signals as flame pressure is reduced, and even at half an atmosphere (the practical upper pressure limit of the equipment), some of these elements still fail to give a satisfactory result. This qualitative trend is put forward as the second piece of supporting evidence for the conclusions given in section 3:3 above.

The final piece of evidence considered in this section of work is the fact that it proved possible to detect an increased light output after aspirating a sample into a low pressure flame irradiated by a chopper modulated I50 watt quartz-halogen lamp. All the light signals thus received were examined for

wavelength dependence (84,85), and it was hence concluded that the signals observed resulted from light scattered from solid particles within the flame. For salts of high melting point elements, such as chromium and vanadium, scatter signals could be obtained at solution concentrations as low as, or even below, 50 p.p.m. (85,86); for the more volatile salts such as sodium chloride, slightly higher solution concentrations were usually required before any signal was observed.

In the light of the arguments given above, it is thus concluded that, as suggested, the fundamental difficulty in the analytical use of low pressure flames is the inherent inability of these systems to volatilise a solid sample. A number of ways in which this problem might be overcome, to permit analytical work to be undertaken, are considered below.

3:5 Some Possible Techniques for Increasing the Atomisation Efficiency of the Low Pressure Flame.

Effectively the only way so far adopted for introducing a given elemental sample into a low pressure flame has been by the use of a volatile derivative of that element (41,49); in this way the sample is already in the vapour phase before it ever enters the flame, and simply requires molecular decomposition to generate the free vapour phase atoms required. Since

the energy available at the molecular level in the low pressure flame is ample for this purpose, all the inherent atomisation problems mentioned above are immediately overcome.

Although none of the complexing agents so far used for the synthesis of volatile derivatives can be combined with more than a few of the metallic elements, there seems to be no reason why greater generality could not be achieved by use of volatile (metal) halides (87). The major disadvantage of such a technique however is the amount of sample pre-treatment required (88), which, it was felt, would be of such a complexity as to render the technique impracticable. Thus although probably technically feasable, no attempt was made to explore such an approach, for this purely practical reason.

At this stage of the work, it was therefore considered that a method was required whereby normally available (ionic) compounds could be used as analytical samples, despite the apparent inability of the flame to generate free vapour phase atoms from such compounds. The various attempts carried out to achieve this end are discussed below.

(I) Use of a D.C. Discharge.

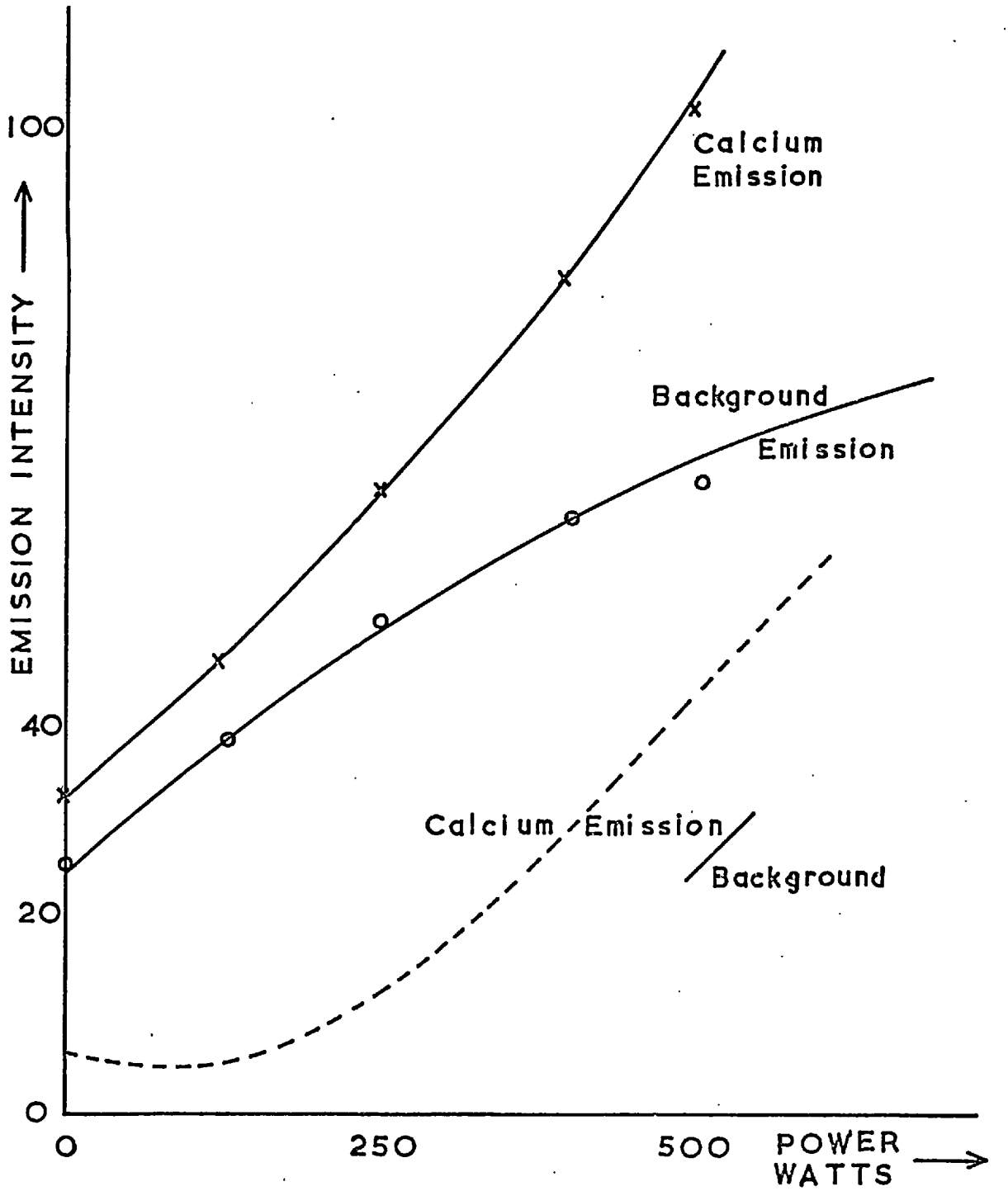
In Chapter One it was pointed out that the p.r.z. of the low pressure flame should contain an abnormally high concentration of free electrons. This supposition suggested using the

flame as the cathode of a D.C. discharge, set up in order to augment the low energy density of the flame with the external electrical power thus supplied (in a manner not unlike that already examined in conventional atmospheric flames (89,90)).

In order to minimise electron losses, all these experiments were carried out at the lowest practicable pressure; thus the effects considered are those of a D.C. discharge on a C_2H_2 / N_2O flame, burning at a pressure of 20 Torr., and supported on a 2 cms. diameter steel burner head. The discharge was set up between a $\frac{1}{8}$" diameter tungsten electrode, held about 10 cms. beyond the burner head, and the burner head itself. The tungsten electrode was surrounded by a quartz shield, to protect it from the direct impact of the electron stream; in the absence of this shield the electrode was found to be burned away at an excessive rate. D.C. power was obtained from a 500 watt maximum output supply, giving a voltage output variable between 0 and 1 KV.

Figure 10 shows the effect of a discharge of increasing power on the flame background beyond the p.r.z., and on calcium emission, at 422.7 nm., following aspiration of a 100 p.p.m. solution. It can be seen from Figure 10 that the observed signal to noise ratio does improve with input power, in accordance with expectation; it is however clear from Figure 10 that the maximum power of 500 watts which was available was insufficient to

FIGURE 10

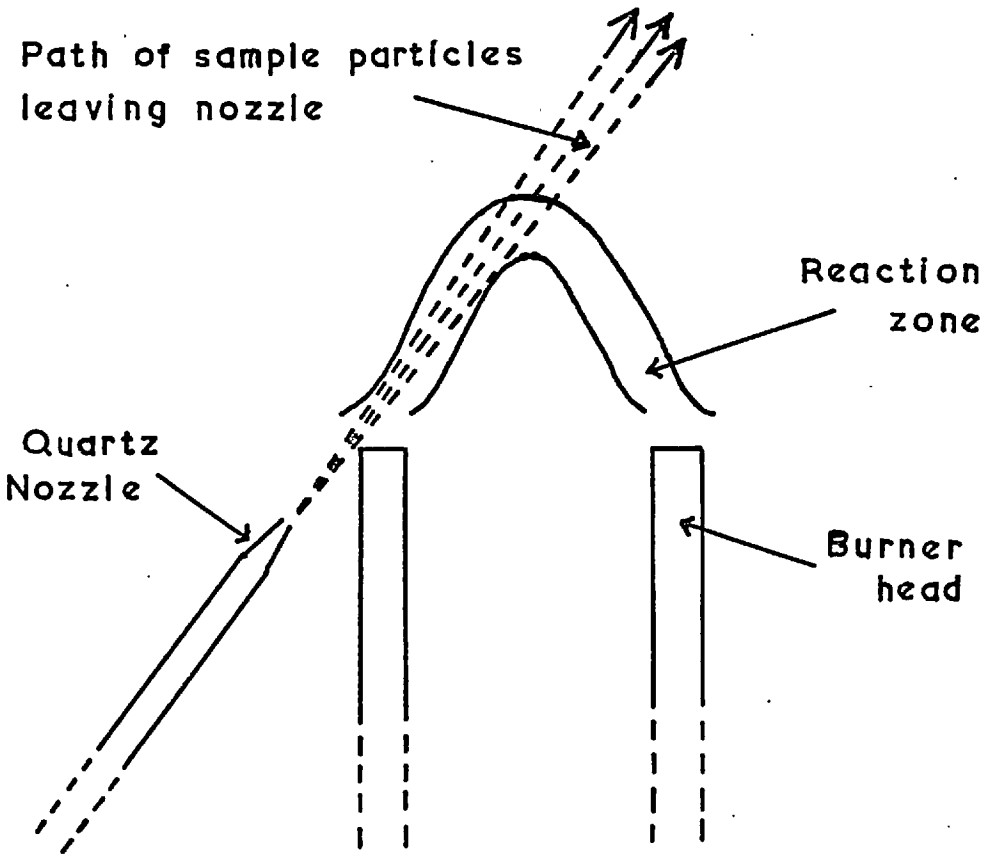

100
40
20
0
EMISSION INTENSITY
Calcium
Emission
Background
Emission
Calcium Emission
Background
0
250
500
POWER
WATTS

reach an optimum signal to noise ratio. Although in principle this power level could have been increased, it was considered that the resultant overheating of the pressure vessel prevented such an experiment from being attempted with the apparatus available; furthermore, the discharge was found to be very much less stable than is the normal case with low pressure gaseous discharges, presumably as a result of variable ionisation processes within the flame. Thus it became clear that, although in principle the technique appeared sound, in practice it would require a very great deal of specialised equipment to operate successfully: such specialisation was felt to represent too great a departure from the course of this work, and these experiments were accordingly discontinued.

(II) Use of an 'Expanded Flame'

If the residence time of the solid sample particles in the p.r.z. could be increased, then it seems reasonable to assume that the atomisation efficiency of the flame would also be increased. In order to achieve this result, the sample solution was aspirated directly into the flame at such an angle as to ensure that the sample remained within the boundaries of the p.r.z. for as long as possible (see Figure II); i.e. the system was converted to what was effectively a total consumption burner. In addition, the linear dimensions of the flame were increased

FIGURE II


Path of sample particles leaving nozzle
Reaction zone
Quartz Nozzle
Burner head

by simultaneously raising the flame pressure and the reactant gas flow rates; a satisfactory flame size was reached with a C_2H_2/N_2O flame burning on the 2 cms. head at a pressure of 100 Torr.

The system described suffered from a number of serious defects. Firstly, several practical difficulties were encountered, such as maintaining the sample jet alignment, providing sufficient cooling for the pressure vessel, and preventing the inlet jet from blocking up; the latter point in particular gave considerable trouble, because of the small jet diameters used. In addition, and rather more seriously, it was found that this method of sample introduction gave rise to a region of severe turbulence in the flame, even at very low solution flow rates; this in turn gave rise to a high background noise level. For these reasons therefore, the technique was felt to be fundamentally unsatisfactory, and accordingly these experiments were not pursued.

(III) The Tungsten Loop.

In this method, a film of sample solution is picked up on a loop of about $\frac{1}{4}$ mm. diameter, wound from a strand of 0.1 mm. tungsten wire (91). Having picked up the solution on the loop, the solvent is permitted to evaporate, and the loop is then introduced into the edge of the flame. The tungsten

wire rapidly reaches a temperature in the region of 2000 ^{o}K, and can be left in the flame for however long the sample requires to volatilise completely.

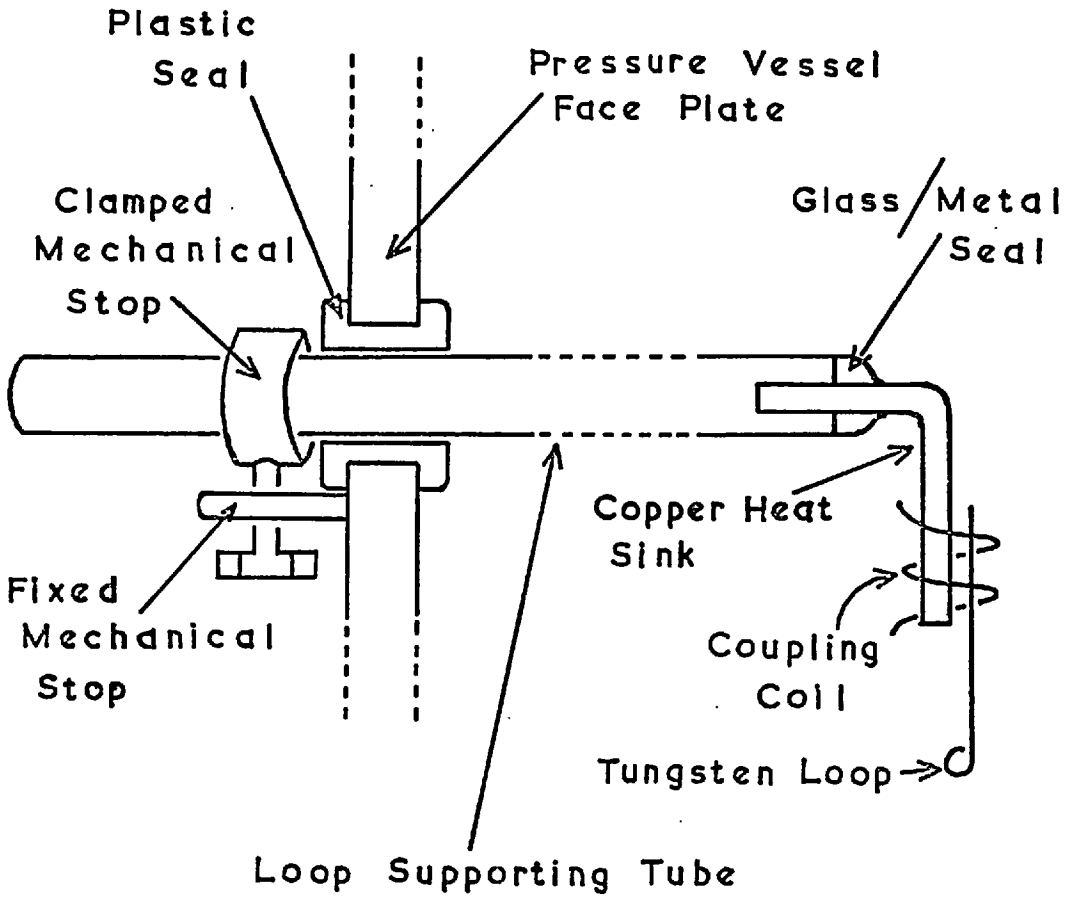
The technique was found to be quite successful, and this method of sample introduction was used throughout the remainder of this work. A fuller description of the operation of the tungsten loop, and of the associated equipment also required, is given the following chapter.

CHAPTER 4

4:I The Tungsten Loop Atom Reservoir.

Loops were made from 0.I mm. tungsten wire, by winding a single turn round a length of 28 gauge nichrome wire; because of the relative lack of reproducibility of this technique, new loops were calibrated before use, by measurement of the emission signals given by a standard strontium solution (see below), when comparison of numerical results with previous data was required. Loops were attached to a I mm. diameter copper rod by wrapping a closely fitting copper coil over the whole assembly (Figure I2); this arrangement gave a good thermal contact between the tungsten and copper, enabling the loop to be cooled by conduction to the heat sink provided by the copper rod. The final temperature of the loop could then be controlled by varying the position of the (thermally coupling) copper coil. The copper rod was held within a length of pyrex tubing by a glass-metal seal; the pyrex tubing passed out of the vacuum chamber into the atmosphere (Figure I2), and was used for external manipulation of the loop. In the original experiments, water was passed through the pyrex tube to cool the copper heat sink, but this precaution was subsequently found to be unnecessary and was

FIGURE 12


Plastic Seal
Pressure Vessel Face Plate
Clamped Mechanical Stop
Glass / Metal Seal
Copper Heat Sink
Fixed Mechanical Stop
Coupling Coil
Tungsten Loop
Loop Supporting Tube

therefore discontinued.

Samples were introduced into the flame by dipping the loop into a reservoir of solution, during which process it picked up a film of solution (9I); the solvent was then allowed to evaporate, and the loop was advanced to a position beyond the burner head and dipped into the flame. The relative orientations of the sample reservoir, the pyrex tube carrying the loop assembly, and the burner head were so arranged that all these operations could be carried out by combined longtitudinal and rotational movements of the pyrex tube, from a point outside the flame pressure vessel. Mechanical stops were clamped as required to the pyrex tube, enabling reproducible positioning of the loop to be effected.

In the present work, samples were detected by their thermal emission beyond the reaction zone. The solid sample carried by the tungsten loop only survived for a few milliseconds before volatilisation was complete (see later); thus the resulting emission pulse was of correspondingly short duration, and it therefore required the use of an integrating amplifier to analyse and store the output signal from the photomultiplier. The amplifier used here was designed and built specifically for the present experiments; the mode of operation of the circuit is described at length in the appendix.

Figures I3 and I4 show the equipment used to transfer

sample solutions from the atmosphere to the reservoir within the flame pressure vessel, from which the loop picked up its film of solution. The transfer of analytical solutions was achieved in two stages: the first was a vacuum line, external to the pressure vessel, but evacuated to the same pressure (Figure I3); the second was a capillary carrying the sample solution to the solution reservoir. The second stage was built within the flame pressure vessel, and therefore required extensive cooling to prevent evaporation of the sample solution before it reached the reservoir (Figure I4).

In order to introduce a sample, solutions were transferred from the funnel (Figure I3) into the vacuum line by opening the tap T_I; approximately I ml. of solution was used at any one time, and the whole of this sample was released into the vacuum line; the solution was then temporarily stored in the section of the line between valves V_I and V_2. With V_I shut and V_2 fully open, the pressure gradient forcing the solution through the inlet capillary was zero; however, by partly closing V_2 and then opening T_I, a pressure gradient could be gradually built up across the inlet capillary which forced solution from the vacuum line down to the reservoir in the flame pressure vessel; the magnitude of this pressure gradient was controlled by the settings of V_I and V_2. Once sufficient sample had been forced through to the reservoir, T_I was shut, and the flow of

FIGURE 13

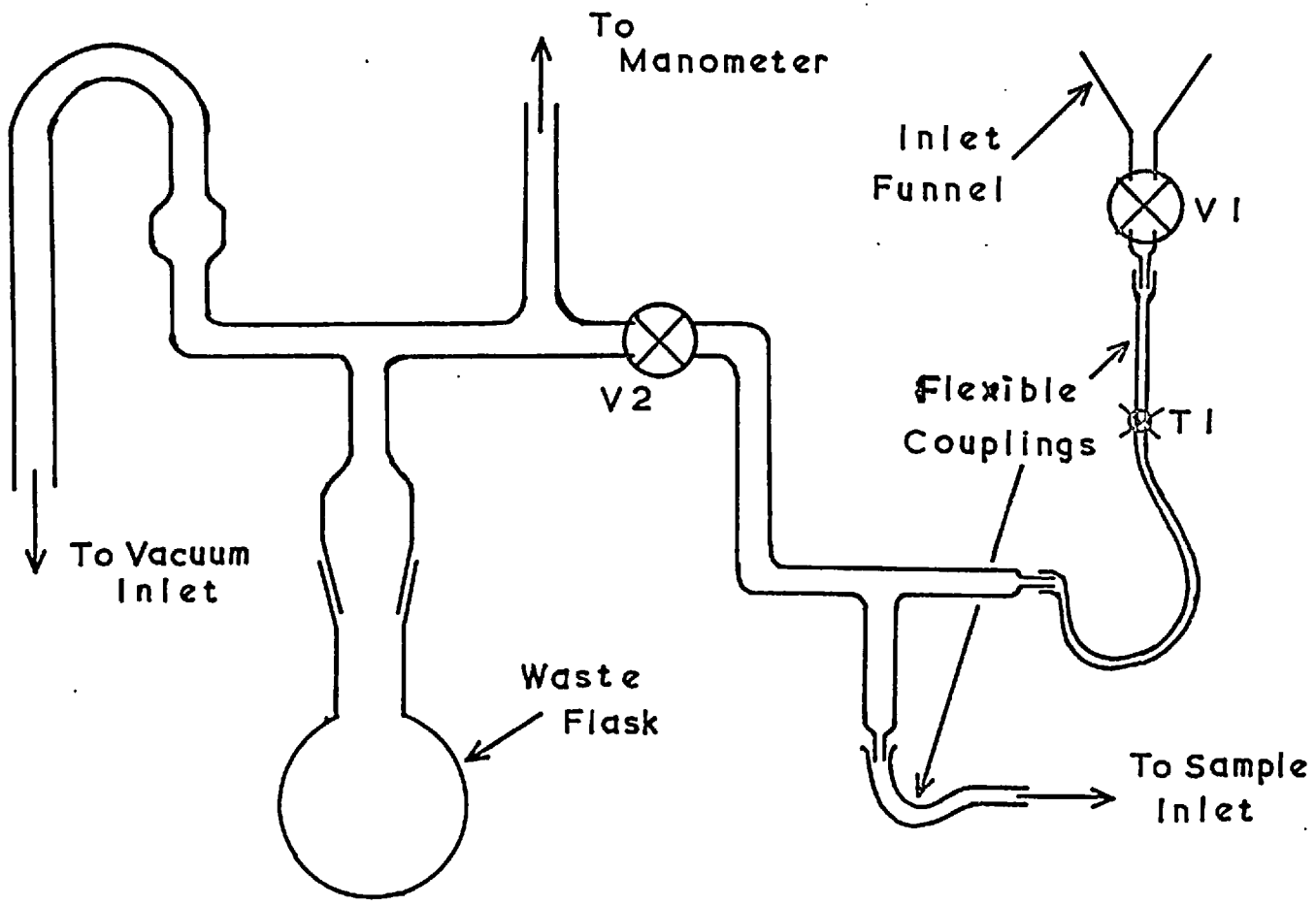
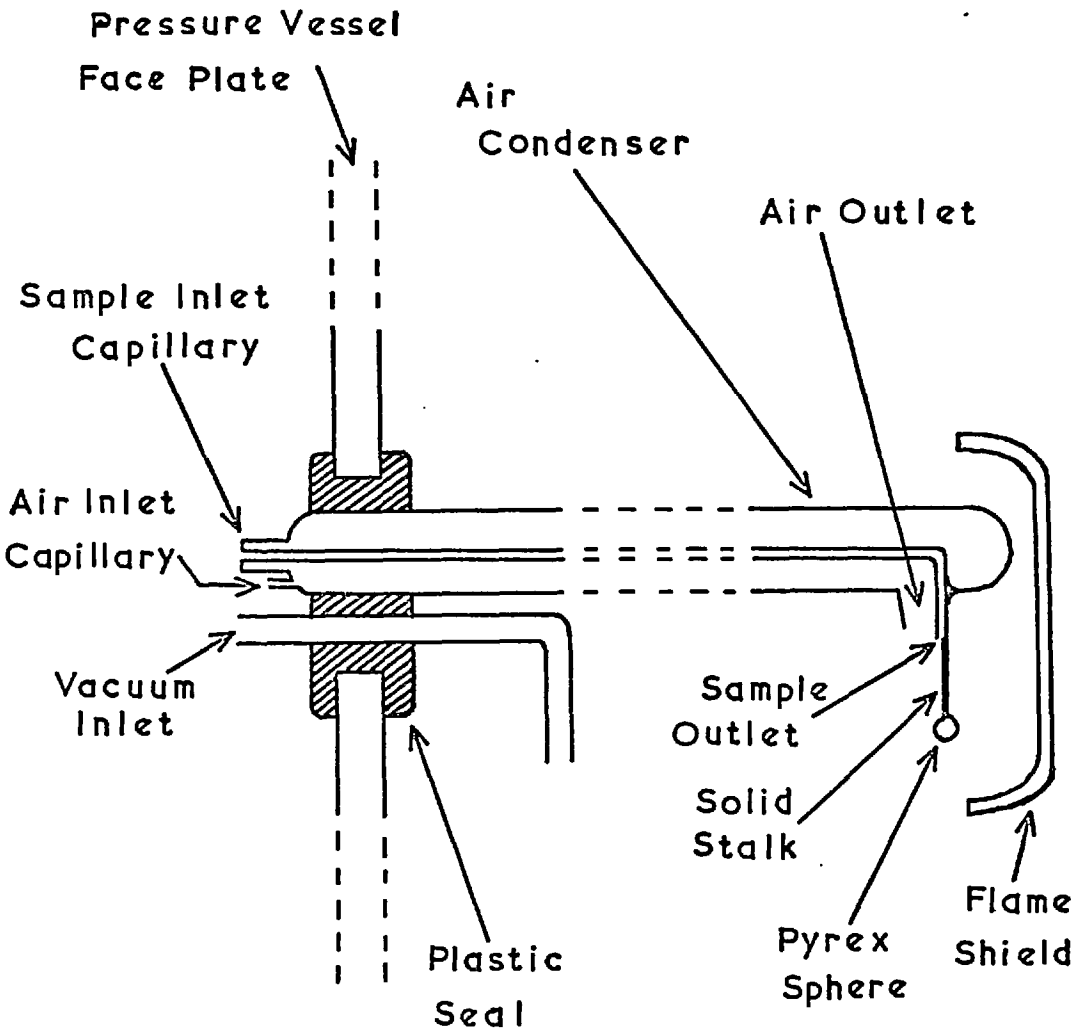

To
Manometer
Inlet
Funnel
V 1
V2
Flexible
Couplings
T 1
To Vacuum
Inlet
Waste
Flask
To Sample
Inlet

FIGURE 14


Pressure Vessel
Face Plate
Air
Condenser
Air Outlet
Sample Inlet
Capillary
Air Inlet
Capillary
Vacuum
Inlet
Sample
Outlet
Solid
Stalk
Flame
Shield
Pyrex
Sphere
Plastic
Seal

solution stopped; backlash in the system was kept to a minimum by making the diameter of the inlet capillary as small as practicable in comparison with the effective diameter of V_2. Further amounts of sample were transferred to the reservoir when required by opening T_I.

In order to change samples, V_I and V_2 were fully opened, T_I was opened, and the remaining solution was flushed into the waste flask. The system was then washed out with distilled water and the new sample solution, and the cycle repeated.

As mentioned above, the inlet capillary within the flame pressure vessel was cooled, to prevent evaporative concentration due to constant boiling of the solutions from occurring. In the original equipment, cooling was achieved by using a stainless steel inlet capillary surrounded by I mm. internal diameter copper tubing carrying a flow of cooling water; this arrangement however was later superceded by the air-cooled design shown in Figure I4.

In this later design, the sample solution leaving the inlet capillary trickled down a solid, unprotected pyrex stalk, terminating in a 3 mm. diameter pyrex sphere. The sphere acted as a solution reservoir, since drops of solution accumulated at this point as a result of surface tension forces, and hung free in the space below the sphere; hence a solution film could easily be picked up on the tungsten loop by passing the loop

through the solution drop hanging below the pyrex sphere. The sphere was illuminated by a 6.3 panel bulb, which enabled the whole assembly to be readily examined, to determine whether the loop had in fact picked up a film of solution, or whether it had for instance picked up too much solution, as a spherical drop instead of a surface film: such visual examination proved subsequently to be of considerable value when the causes of the initial non-reproducibility of the system were investigated (see below).

Although protected by the pyrex flame shield (Figure I4) from the direct impact of the burnt gases, forced convection within the pressure vessel resulted at first in considerable local heating of the solution reservoir, with the consequent problems of solvent evaporation. However, by directing the coolant air down from the outer jacket of the inlet capillary, it was possible to displace the burnt gases away from this region of the pressure vessel; by the use of this technique, it was found possible to cool the solution reservoir satisfactorily without using such high coolant gas flow rates as to accentuate evaporation of the sample solutions, or to impair seriously the very low pressure operation of the equipment.

4:2 The Causes of Non-Reproducibility using the Tungsten Loop.

Even with the apparatus described above, which, by providing both efficient cooling of the sample at all stages of handling, and visual observation of the amount of solution initially carried by the tungsten loop, ensured a reproducible sample delivery to the flame, the degree of signal reproducibility at first obtained was very poor: e.g. it was not uncommon originally to observe order of magnitude differences between successive readings. The present section of work describes the experiments carried out to locate the causes of this non-reproducibility.

The first factor investigated was the response of the integrating amplifier used. For the reasons discussed in the appendix, this unit could not be built to any standard specifications, but had to be designed specifically to handle the type of signal given by a loop-in-flame technique. Because of the unusual circuitry thus demanded, the equipment exhibited a number of unforseen characteristics, one of which was manifested in the form of a non-linear response. In fact, the integrator output depended exponentially rather than linearly on the input, and thus, although it was electronically reproducible, the amplifier had the effect of disproportionately magnifying all the other causes of error in the system; correction of this electrical

distortion immediately improved the reproducibility of the apparatus, to the point where it became possible to look successfully for the other causes of error.

The investigation of the other sources of non-reproducibility of the equipment required the use of a standard sample, to give emission pulses of constant amplitude and duration. The standard was required to readily volatilise from the loop, thus minimising possible surface diffusion effects etc., but not to be so volatile as to evaporate appreciably before the loop entered the flame. The element to be used as the standard also had to have a spectral line of high transition probability which could be readily excited with the relatively low thermal energy available beyond the p.r.z.; an additional advantage would be gained if this thermal emission were in the visible region of the spectrum, permitting visual correlation with the recorded signal.

The element chosen to meet these requirements was strontium, as the hydrated chloride, $Sr\ Cl_2 . 2H_2O$. The Sr 460.7 nm. line meets the requirements for thermal emission above; the melting and boiling points of $Sr\ Cl_2$ are $873^{\circ}C$ and $1250^{\circ}C$ respectively (83), satisfying volatilisation requirements, and the Sr O and Sr OH band emission in the red part of the visible spectrum provides a sensitive (visual) check on the presence or absence of a sample.

Samples picked up from a I00 p.p.m. strontium solution, in the manner described in section 4:I above, were introduced into a fuel rich C_2H_2/N_2O flame; the flame was burned on a 0.6 cms. diameter burner at a pressure of I00 Torr. The flame was made just sufficiently fuel rich to prevent visible oxidation of the tungsten (see later); the pressure of I00 Torr. was rather arbitrarily selected on the grounds that it was low enough to give a sufficiently thick reaction zone for accurate and reproducible positioning of the loop, but not so low as to give an excessively large flame, which would engulf the whole loop assembly. Under these conditions, it was found that the strontium samples did indeed give a visible pulse of (oxide) emission, showing that the loop was at least carrying the sample as far as the flame, and that the sample was then being atomised; thus it was known that the technique was at least qualitatively operative.

The first possible cause of quantitative error examined was that the tungsten loop might not be picking up a reproducible volume of sample solution. However, visual observation of the solution film as it evaporated from the loop (see above) showed that the evaporation time of successive samples was reasonably constant; furthermore, the visually observed intensity of the red (oxide) emission did not appear to vary sufficiently to account for the inconsistencies of the corresponding electronic response signals. For these reasons therefore subsequent

work was based on the assumption that the causes of error arose at some stage between the evaporation of the solvent film, and the reception of the sample emission pulse by the photomultiplier; an assumption which was subsequently justified experimentally.

Two possible sources of error arising before the loop entered the flame were thought to be a) premature evaporation of the sample, due to overheating of the loop by its exposure to the heated gases within the flame pressure vessel, and b) surface diffusion effects, causing 'trapping' of the sample on the surface of the loop. However, it was found that if the loop were exposed to the hot exhaust gases adjacent to the flame for extended periods of time, before actually being positioned within the flame, sample emission signals could still be obtained, although the non-reproducibility of the system did not permit realistic amplitude comparisons to be made. Hence it was concluded that a finite amount of sample remained on the loop even after such prolonged exposure, and thus if the exposure time of the loop were reduced to a few seconds, then any resultant evaporative sample loss could reasonably be ignored.

If sample trapping on the surface of the loop were occurring to any significant extent, the apparatus would be expected to show some resulting memory effect, which could be detected even with a non-reproducible system. Such a memory effect was not observed in practice, and it was therefore

assumed that surface trapping of the sample did not contribute significantly to the non-reproducible response of the equipment.

The experiments above suggested that a reproducible mass of sample was being introduced into the flame, and that therefore the experimental errors were introduced at some time between the volatilisation of the sample from the surface of the loop, and the detection of the resulting emission signal. The time available for the introduction of error between these two events had already been reduced to a minimum during the experiments above; the equipment was therefore modified, to reduce this time even further, by the addition of a (blackened) collimating tube, mounted within the pressure vessel, which permitted the sample emission to be viewed in even closer proximity to the surface of the loop without the continuum emission of the white hot tungsten causing spectral interference. This arrangement proved to be remarkably effective in improving the performance of the equipment, and hence it then became possible to isolate and examine a number of other experimental parameters whose effect, although individually small, collectively contributed appreciably to the poor reproducibility of the apparatus.

During the course of the examination of these 'secondary parameters', it was found that the reproducibility of the system, as measured by the standard deviation of a set of 10

readings, improved as the sensitivity of the equipment improved, and that these two variables always reached a simultaneous maximum; a phenomenon which in fact suggested the fundamental cause of the original non-reproducibility (see later). Thus it became possible to identify immediately an optimum experimental setting of a given parameter from the average amplitude of a set of results, rather than from their standard deviation; the saving of calculation time thus achieved was invaluable, since it permitted the virtually instantaneous assessement of a set of readings in a situation where both sensitivity and reproducibility were subsequently found to be time dependent (see later). Those 'secondary parameters' which were examined by this technique, and which are known to have some effect on the reproducibility of the equipment, are discussed below.

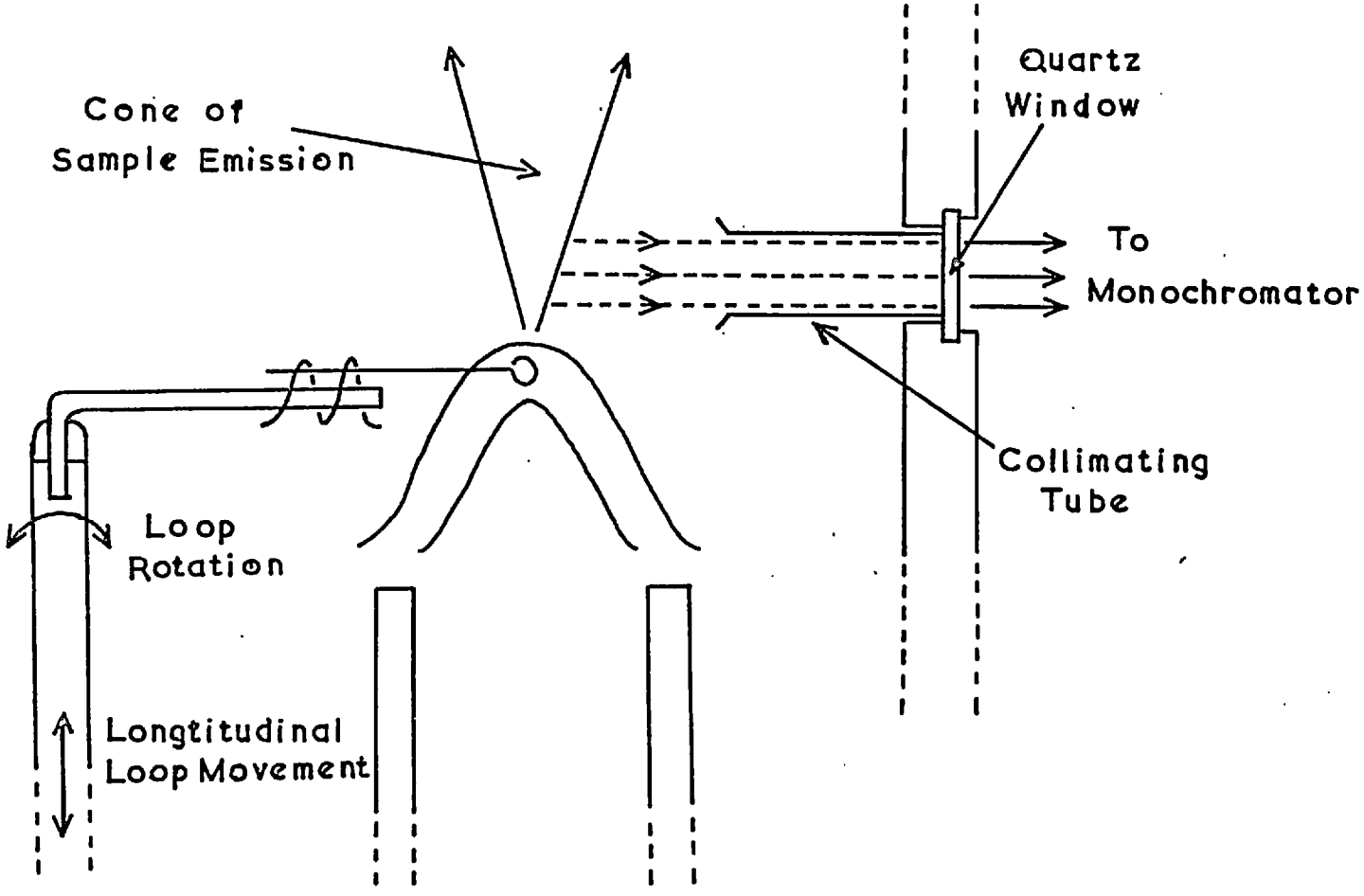
(a) The Depth of Loop Penetration into the P.R.Z.

The optimum position of the loop with respect to the flame was found to be that of maximum symmetry, with the loop completely surrounded by the gases of the p.r.z., at the extreme tip of the flame (see Figure 15).

(b) Speed of Delivery of the Loop into the Flame

Initially, the loop was (manually) delivered into the flame as fast as possible, to minimise premature volatilisation

FIGURE 15


Cone of
Sample Emission
Quartz
Window
To
Monochromator
Collimating
Tube
Loop
Rotation
Longtitudinal
Loop Movement

effects. However, the optimum speed of delivery was later found to correspond to a comparitively slow rotation of the tube supporting the loop assembly, taking 2 or 3 seconds to cover 90^{o}. The reason for this was thought to be the mechanical vibration resulting from the rapid deceleration of the loop after a rapid introduction into the flame; the appropriate speed of delivery under given conditions was something which was gradually learned with increasing experimental experience, and was one of the reasons why the equipment, in the prototype form described, demanded a certain amount of operative skill for its optimum performance, even after the correct alignment of the various experimental parameters now under discussion.

(c) Optical Alignment.

A single lens was used to focus the (collimated) light signal from a sample emission pulse onto the monochromator slit. The best position of this lens was found to be that which gave a maximum D.C. output, using a wide slit width as required, from the continuum emission of the tungsten loop; a result implying that the thermal inertia of the system was sufficient to inhibit sample volatilisation until some finite time after the loop had been brought to rest in the flame.

(d) Orientation of the Loop in the Flame

It was physically possible to align the plane of the tungsten loop either perpendicular or parallel to the axis of the burner head, or at any intermediate position. The requirements of visual observation during solvent evaporation favoured the latter position, and this was fortunately found to also be the optimum position for maximum sensitivity and reproducibility.

As far as possible, the above factors were assessed in decreasing order of importance; thus having discovered this order, and the approximate optimum alignment of the equipment, during a series of preliminary experiments, the work was repeated in the order given above, to obtain the best settings of the various parameters involved.

Minimisation of the critical loop / emission viewing point distance, together with the optimisation of the other less important factors given above, greatly increased the sensitivity of the equipment, and improved its reproducibility to the point where about 50% of all readings taken lay within ± 10 % of the appropriate mean. However, despite further investigation, it was not found possible to improve substantially the performance of the equipment beyond the point already reached; thus it was decided to examine the causes of the non-reproducible effects occurring between the atomisation of a sample from the surface of the loop and the observation of the resulting emission pulse.

The relation between reproducibility and sensitivity, noted above, together with the fact that the effects considered apparently occurred entirely in the vapour phase, suggested that random mass distribution effects, associated with turbulent gas flow, might be occurring. The studies on the A.C. behaviour of the flame, in Chapter 2 above, showed that the significance of time-dependent distribution effects in the flame could not be neglected, although visual observation of the p.r.z. suggested that such effects were associated with regular pumping impulses rather than with turbulent flow of the flame gases.

The hypothesis of turbulent flow beyond the visible edge of the flame was satisfactorily confirmed by increasing the acetylene flow rate until the flame became luminous; when the gas flow had had a few seconds to take up an equilibrium distribution, stable flow patterns were marked out by the lines traced by incandescent carbon particles. These lines showed a linear gas flow from the centre of the burner to the exhaust, surrounded by large, three dimensional eddies across the surface of the pressure vessel. In addition to these large eddies, a region of marked turbulence was apparent beyond the surface of the reaction zone, forming an outer cone beyond the p.r.z. This turbulence was comparatively localised, and did not affect the normally visible part of the flame at all; the degree of turbulence was marginally increased after the introduction of the tungsten loop. The existence of these relatively complex gas flow patterns

within the flame pressure vessel was felt to account for the long-term stability problems of the equipment, mentioned earlier: thus as the pressure vessel heated up with use, the thermal gradients at the vessel surface correspondingly changed, thus altering the large scale flow patterns. This effect was observed in practice to cause a physical extension of the turbulent gas layer surrounding the flame, and to cause new regions of turbulence at the outer corners of the pressure vessel.

The problems caused by this turbulent flow were largely overcome by using the cruciform (absorption) pressure vessel, rather than the cylindrical fluorescence one (see Chapter Two). Investigation with a luminous C_2H_2/N_2O flame revealed the gas flow patterns to be much more stable in the former case; in addition, the larger surface area of the cruciform vessel permitted more efficient external cooling to be applied, thus reducing the time-dependent characteristics of the system.

At this stage of development, the sensitivity of the equipment had shown a further increase, and its reproducibility had improved to the point where 88% of all readings taken lay within $\pm$ I0 % of the appropriate mean. This level of reproducibility was felt to be sufficient for the present purposes, and the equipment was not therefore refined any further beyond this point.

4:3 Summary of Practical Operating Conditions for the Tungsten Loop.

The discussion above describes how a number of semi-empirical parameters were investigated in order to determine the optimum alignment for the equipment. In the present section of work, a brief description is given of the experimental procedure adopted for adjusting these factors during routine experimental work.

When a new tungsten loop had to be fitted, it was fastened by a copper cooling coil to the copper heat sink (see previously). The position of the loop had to be such that, when mounted, it would pass just below the solution reservoir in such a way as to physically move through any liquid drop which might be suspended there. When the loop was fastened in this position, the geometry of the equipment ensured that the loop head would subsequently be delivered into the flame on an arc terminating at the exact centre of any of the burner heads used (Figure I5). The positioning of any new loop was thus a precisely defined operation, and the only variable was the position of the copper cooling coil. In practice, this coil was usually placed so as to leave c.a. $1\frac{1}{2}$ cms. of tungsten wire between the loop head and the point of attachment to the heat sink when used in conjunction with a C_2H_2/N_2O flame; an arrange-

ment which was found in practice to cool the loop sufficiently to give it a lifetime of several minutes of continuous operation. The exact distance between the loop head and the cooling coil was varied according to the operating pressure; e.g. although I½ cms. was suitable at pressures up to about I50 Torr., at higher pressures it was necessary to correspondingly reduce this distance.

The final point to be observed when adjusting the position of a new loop was to ensure that the plane of the loop was parallel to the axis of the burner, both to permit visual observation of the sample carried by the loop, and to obtain the maximum reproducibility from the equipment.

When the loop was thus correctly positioned, the flame was ignited on the appropriate burner head for the pressure required; the flame was then advanced until its (visible) image was focussed against the monochromator slit, and the loop position adjusted to correspond to the configuration shown in Figure I5. The loop was then withdrawn from the flame, the monochromator slit opened to about 25 microns, and the photomultiplier gain increased until the (A.C.) flame noise began to register on the amplifier output. The loop was then replaced in the flame, and the position of the focussing lens adjusted by maximising the D.C. signal from the tungsten continuum emission, increasing the monochromator slit width if required. With the focussing lens

correctly positioned, and the monochromator slit width returned to 25 microns, the loop was repeatedly replaced in the flame, and slight adjustments given to its position so that the continuum emission pulses thus generated just registered over the flame noise.

If this optimum positioning of the loop took the system too far away from the geometry of Figure I5, the flame was repositioned as required, and the whole alignment procedure then repeated.

This procedure enabled the equipment to be set up for maximum reproducibility; its sensitivity could however be improved, at the expense of reproducibility, by slightly withdrawing the flame and loop together, away from the field of vision of the monochromator: a procedure which appreciably diminished background noise levels. The best compromise between sensitivity and reproducibility was something which became easier to judge with practice (as with the actual manipulation of the loop assembly), and thus increasingly improved results were obtained from the equipment as increasing familiarity with its practical operation was acquired.

The exposure of the new loop to the flame during the alignment procedure was invariably sufficient to clean the loop surface of any oxide film, surface contaminants etc., and the loop was, therefore, ready for use after this treatment. Before

picking up any samples on the loop however, the inlet capillary and solution reservoir were washed by pumping a small amount of sample solution through the inlet system (see previously). This ensured that the solid waste formed by evaporation of any previous sample was washed away; a precaution of some importance, in particular as the apparatus aged and the flame shields were gradually burned away.

If an extended run were proposed, a beaker placed below the solution reservoir served to catch the waste solution produced; otherwise, waste was permitted to collect in the cool portion of the pressure vessel by the steel front plate.

During the alignment procedure above, the pressure vessel warmed up sufficiently to permit the time dependent turbulence effects, already mentioned, to be ignored; thus after completing this procedure, the equipment was ready for immediate use. The alignment procedure was repeated whenever the operating pressure of the equipment was changed in order to obtain optimum results, as a consequence of the varying flame dimensions at different pressures.

4:4 Potential Advantages of the Tungsten Loop Technique.

By overcoming the inherent analytical disadvantage of the poor atomisation efficiency of the low pressure flame, the

tungsten loop technique permitted the analytical advantages of such flames to be utilised. A number of such possible advantages were discussed in Chapter One, but of these the most outstanding one was felt at this time to be the chemically reducing properties of the low pressure flame. The theoretical reasons for this reducing ability are discussed later; it was however strikingly empirically illustrated at the present stage of work by the ability of the (fuel rich) low pressure C_2H_2/N_2O flame to support a piece of tungsten at white heat without any tungsten oxide emission being observed, and without visible oxide formation or oxide embrittlement of the tungsten occurring. In practice, oxide formation was only totally suppressed in fuel rich C_2H_2/N_2O flames at pressures below about IOO Torr.; the rate of oxide formation at higher pressures did not however appear sufficient to impair seriously analytical work, apart from the reduction of loop lifetimes which occurred in consequence.

The emission studies in C_2H_2/N_2O flames, described later, were mainly carried out at pressures in excess of IOO Torr., which correspondingly limited the reducing properties of these flames; it was however necessary to work in this pressure range, partly because of the increased thermal excitation energy then available beyond the p.r.z. (see later), and partly because the very large physical size of the flames observed when

C_2H_2/N_2O mixtures are burned below about 70 Torr. appeared to have an adverse effect on both the sensitivity and the reproducibility of the technique. Both of these effects were however subsequently overcome by the use of C_2H_2/O_2 rather than C_2H_2/N_2O flames, and some correspondingly useful preliminary results have thus been obtained using the former flame (see later).

A second important advantage of the tungsten loop technique lies in the very high temperatures which can be attained at the loop surface, thus enabling refractory samples to be volatilised: an effect manifested experimentally in the observed ability of the technique to volatilise samples containing for example such high melting point elements as chromium, vanadium and titanium.

The reason for the high surface temperature of the loop is thought to be associated with the non-equilibrium environment in which the loop is placed; a situation which requires the surface layer of the loop to act as a buffer between the gas phase chemiluminescently excited species discussed in Chapter One, and the comparatively cool loop matrix. Thus the surface layer of the loop is forced to accept the collisionally transferred energies of the excited radicals occurring in the p.r.z., and unless the chemical bonding between the loop surface and and the bulk of the loop is sufficiently strong to permit very

rapid energy transfer, the surface layer must therefore store this energy for a finite period of time: since very few chemical bonds are capable of carrying the excitation energies thus considered, bond rupture and atomic volatilisation can be expected to be observed under these conditions. The strong interatomic forces of metallic tungsten prevent this situation from arising to any significant extent in the surface layers of the tungsten loop itself; however, the forces holding a sample deposited by solvent evaporation on the tungsten surface are very much weaker, and thus permit such energy storage and the subsequent sample atomisation processes to occur.

The final potential advantage of the tungsten loop to be considered here is the (observed) rapidity with which the loop heats up. Thus volatile samples such as $Sr\ Cl_2$ were found to be completely volatilised within a few milliseconds (see Chapter 5); a rapidity creating a correspondingly favourable signal to noise ratio. Such a phenomenon is felt to offer considerable analytical advantages, provided that the associated electrical circuitry is capable of handling such short 'single event' signals (see appendix).

The ability of the tungsten loop technique to atomise refractory samples, together with the reducing properties of the low pressure flame, which inhibit the (gas phase) formation of the refractory oxides with which such samples are commonly

associated, suggests the analysis of such samples to be a potentially very useful analytical application of the tungsten loop technique. Thus at the present stage of the work, it was felt that the application of the tungsten loop technique to the small sample analysis of refractory samples probably represented the most promising direction for its future development. The viability of such an approach was therefore investigated as soon as the implications of the observed chemical behaviour of the tungsten loop within a low pressure flame were fully realised; the results of this investigation are discussed in the following chapter.

CHAPTER FIVE

5:I Preliminary Results.

The initial examination of the analytical potential of the tungsten loop technique was carried out using strontium, for the reasons discussed in Chapter Four. However, as soon as the chemical reducing properties of the low pressure flame were realised, the experiments with strontium were duplicated using aluminium. Aluminium was selected firstly because the thermal stability of its oxide makes conventional flame analysis correspondingly difficult, and should thus render aluminium particularly susceptible to analysis by the tungsten loop technique; secondly, the high oscillator strengths of the transitions giving rise to the 396.I and 394.4 nm. lines make aluminium very suitable for thermal emission studies; finally, the thermal stability of the (solid state) oxide enables previous suppositions concerning the high surface temperature of the loop to be tested.

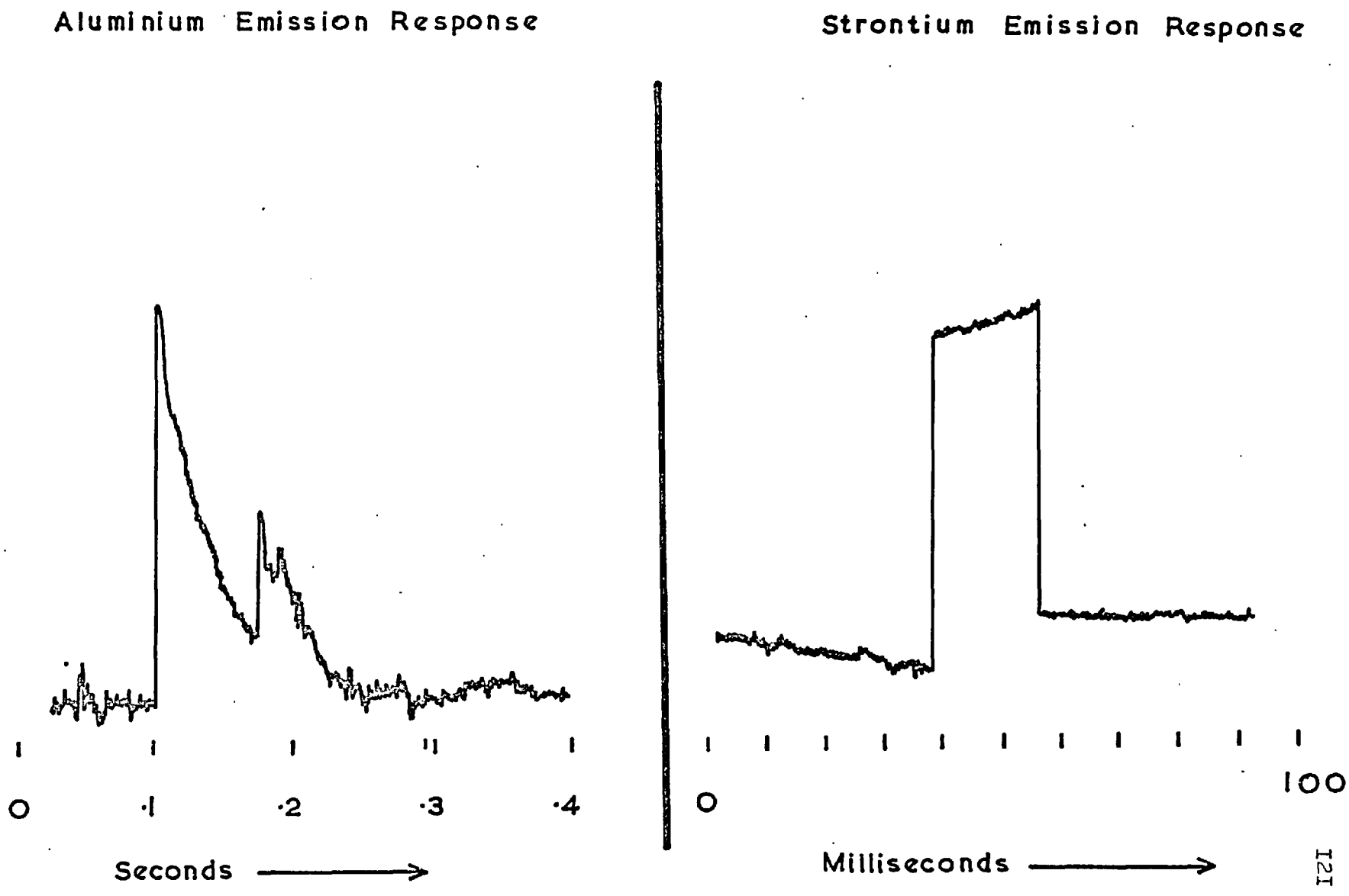
In the present experiments, all samples were made up in aqueous solution; strontium solutions were prepared from 'AnalaR' strontium chloride, $Sr\ Cl_2 . 2\ H_2O$; aluminium solutions

were prepared by dissolving aluminium foil in a minimum of dilute H Cl, and diluting the solution to the required concentration. Sample introduction was effected by the procedure described in Chapter Four. Individual readings, for calibration curves etc., were usually obtained from the average of a set of five results, although this number was increased if the experimental conditions were such as to adversly affect reproducibility.

Figure I6 shows the shapes of the emission pulses, observed on a storage oscilloscope, for samples containing $I \times 10^{-10}$ and 5×10^{-8} respectively of strontium and aluminium. The rapid rise and fall times of the strontium response reflect the low thermal inertia of the tungsten loop, the resulting speed of atomisation of the sample, and the correspondingly good signal to noise ratio thus observed. The profile of the strontium response in fact suggests that square wave filters could be usefully incorporated into the electronics (92), to amplify such signals selectively, and thus improve the sensitivity of the equipment still further.

In the case of aluminium, the situation appears to be rather different. The response can be seen to occur over a much longer time interval than was the case with strontium, and, (at the relatively high concentrations used) to exhibit the two distinctly separate responses shown in Figure I6. It is perhaps

FIGURE 16


Aluminium Emission Response
Strontium Emission Response
0
·1
·2
·3
·4
Seconds
0
100
Milliseconds

tempting to ascribe this phenomena to the partial evaporation of the sample as the (volatile) chloride, followed by a slower reduction of the oxide formed during simultaneous degradation of the hydrated chloride in the solid state. Such an explanation must however over-simplify the evaporative processes occurring on the loop surface, if only because it neglects all the possible chemical interactions between for example the flame gases and the sample, and it is therefore felt that any such association of the two signals with two defined chemical species must be viewed with considerable caution.

The first quantitative work undertaken with aluminium and strontium was the investigation of the emission response with varying pressure. Initial experiments were carried out over the pressure range 70 - I00 Torr., in a C_2H_2/N_2O flame; in accordance with the arguments of Chapter 3:3, and in direct contrast to the results obtained following solution nebulisation, no significant variation in the response was observed under these conditions.

The experiment was then repeated over the pressure range I8 - 250 Torr., again in a C_2H_2/N_2O flame. New burner heads were used for this work (see Chapter 2:2), and each was individually aligned in the manner discussed in Chapter Four; aluminium and strontium sample sizes of $5 \times I0^{-8}$ and $I \times I0^{-I0}$ g. respectively were used during these experiments. The gas flow rates used were determined by the procedure described in

section 5:3 below.

The variations with pressure of the emission signals of aluminium and strontium, thus found, are shown in Figure I7. However, before these results can be interpreted in the more realistic terms of the (relative) vapour phase atomic population of the sample, it is necessary to know the dependence of flame (sample excitation) temperature on pressure.

Experimentally, flame temperatures were measured by the two line method, and for reasons considered elsewhere (93), iron 373.33 and 373.49 nm. lines were chosen for this purpose. The comparatively high intensity of these particular lines was the major reason for their selection, from the various line pairs available, even though this choice involved working outside their optimum applicable temperature range (93). The samples of iron were introduced by the same technique, and under the same conditions, as were used for aluminium and strontium above; the pressure dependence of both C_2H_2/O_2 (see later) and C_2H_2/N_2O flame temperatures, thus determined, are shown in Figure I8. As suggested by the previous experiment, the temperature variations with pressure thus found are relatively small, again providing a direct contrast to the temperature fluctuations apparently demanded by the emission results, following solution aspiration, which were discussed in Chapter Three.

FIGURE 17

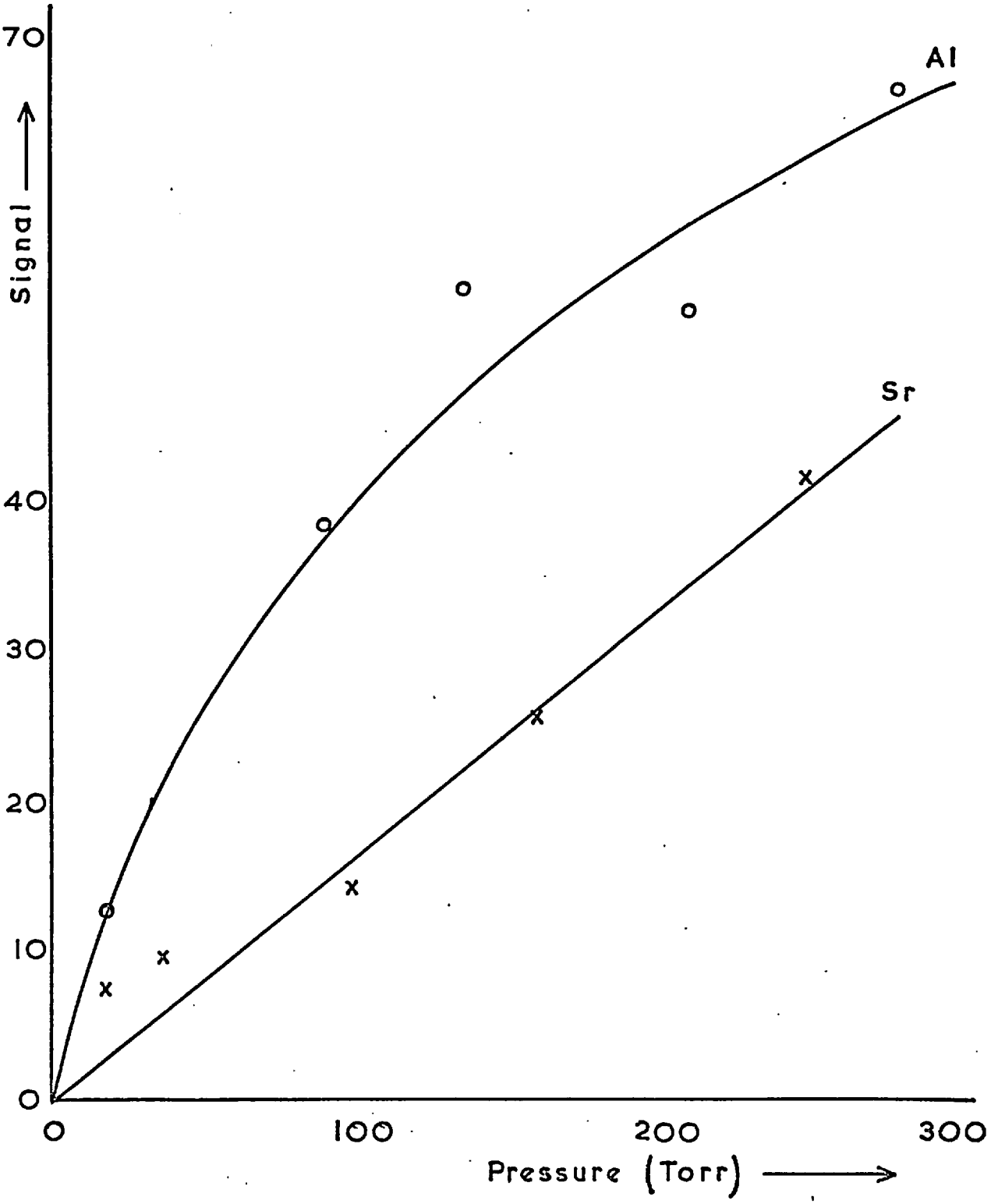
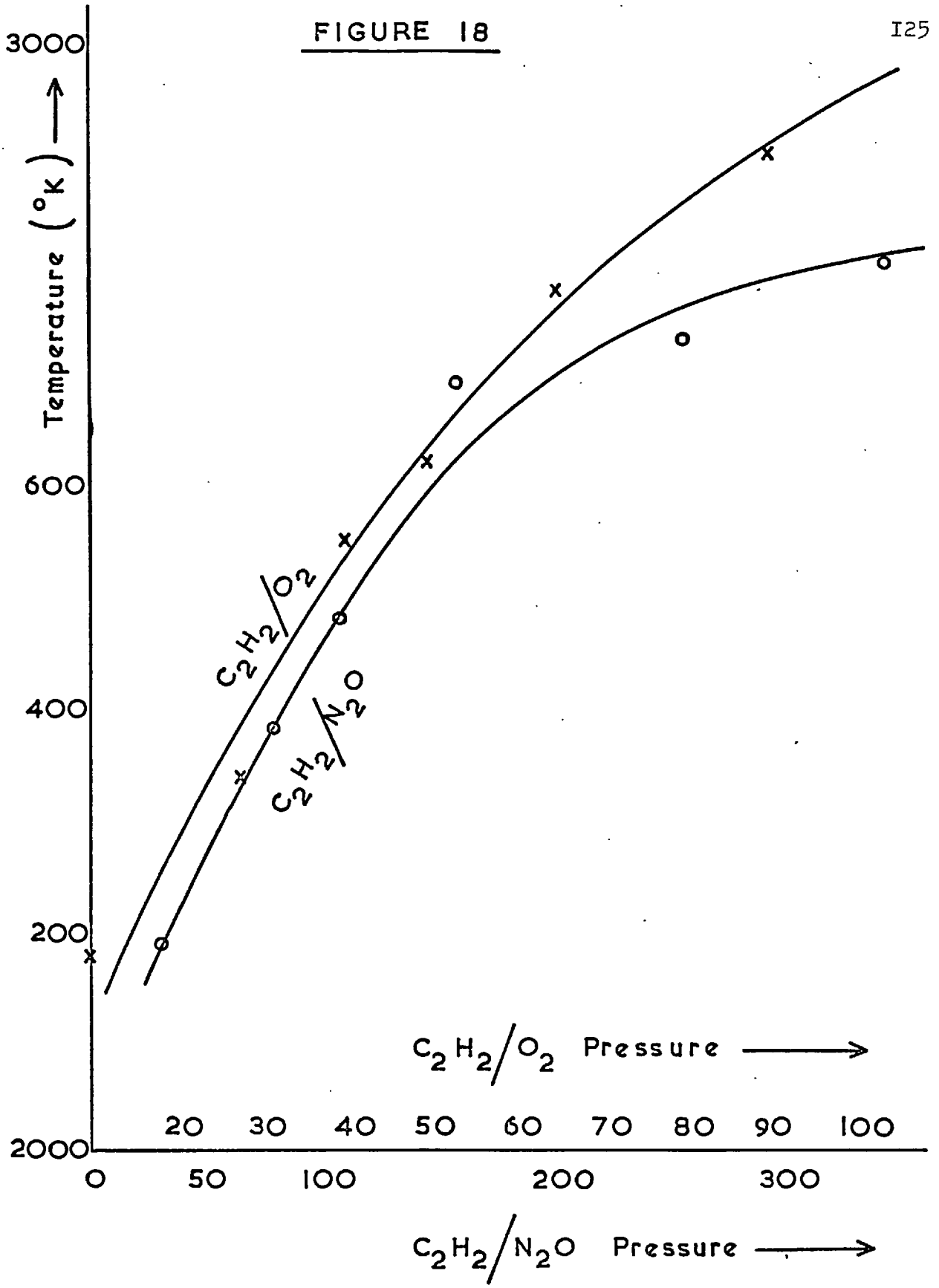


FIGURE 18


3000
Temperature (°K) ⟶
600
400
200
2000
C_2H_2/O_2
C_2H_2/N_2O
C_2H_2/O_2 Pressure ⟶
20 30 40 50 60 70 80 90 100
0 50 100 200 300
C_2H_2/N_2O Pressure ⟶

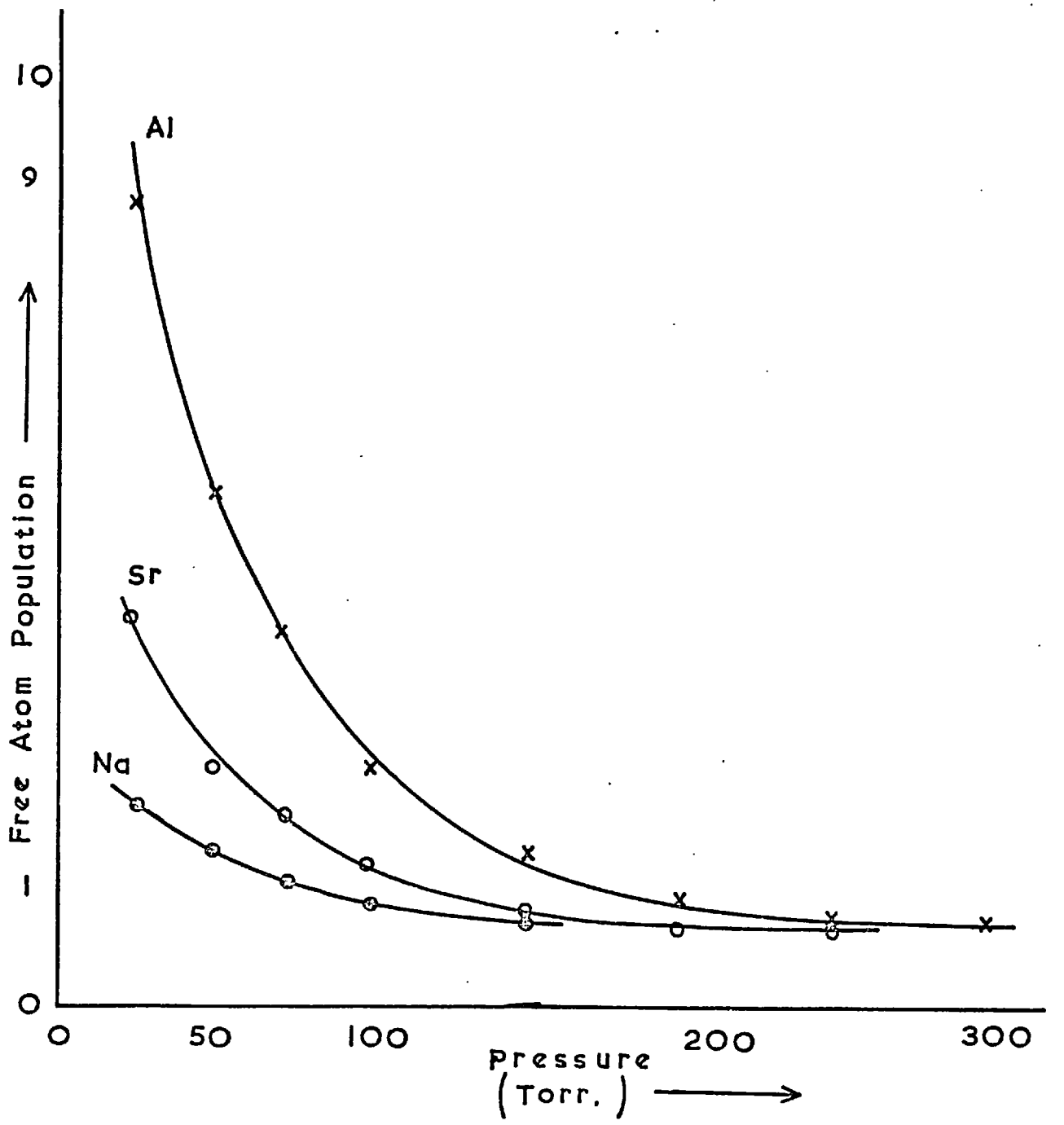
5:2 Atomisation Efficiency of the Low Pressure Flame.

The variations in ground state atomic concentrations with pressure of strontium and aluminium can be estimated from the results given in Figures I7 and I8; hence the (relative) variations of atomisation efficiency of the C_2H_2/N_2O flame with pressure for these elements, shown in Figure I9, can be determined.

The results given in Figure I9 show the concentration of the vapour phase atomic population of aluminium to be highly sensitive to pressure, whereas that of strontium is appreciably less so; the results for sodium, included for the sake of comparison, show only a slight pressure dependence. Qualitatively, this order of pressure dependence can be seen to reflect the relative thermal stabilities of the oxides of these elements, and thus it is suggested that the variations of free atom concentrations shown in Figure I9 arise from the chemically reducing properties of the low pressure flame; a deduction supported by the discrepency between the results shown in Figure I9, and their equivalents, determined elsewhere, observed in an inert atmosphere (94).

The suggested cause of the results of Figure I9; i.e. more effective free atom removal with increasing pressure due to compound (oxide) formation, provides a satisfactory correlation with the deductions made in Chapter 3:4 concerning

FIGURE 19


10
9
0
Al
Sr
Na
Free Atom Population
0
50
100
200
300
Pressure
(Torr.)

the degree of compound formation occurring in the low pressure flame. Furthermore, the rise observed in Figure I9 of free atom concentrations with reduced pressure, in the case of aluminium in particular, suggests that the low pressure flame becomes increasingly chemically reducing at lower pressures; a deduction which is in agreement with the conclusions given in Chapter Four.

Two possible causes of the chemically reducing properties of the low pressure flame can be suggested. Firstly, the decreased pressure must be expected to favour molecular dissociation, quite apart from any chemical factors associated with the flame itself. Secondly, it seems reasonable to suppose that carbon particle formation must be inhibited at low pressure, resulting in an increase in the maximum concentration of free carbon atoms which can be supported within the flame. Such an effect can arise both from the decreased molecular (atomic) collision frequency, leading to a kinetic inhibition of particle growth, as well as from the increased tendency to molecular (atomic aggregate) dissociation already mentioned, thus leading to a corresponding increase in the fuel-rich limit of the flame prior to the onset of luminosity.

5:3 Carbon Formation in the Low Pressure Flame.

The results obtained in the previous section of work suggest that the chemical reducing properties of the low

pressure flame are pressure dependent, and that one possible reason for this lies in the greater population of free atomic carbon which can be supported, prior to particle formation, at reduced pressures.

Measurement of the carbon to oxygen (C:O) ratio of the flame reactant gases is one way of experimentally investigating such an effect, and it is therefore proposed to discuss the problem of carbon formation in the low pressure flame from an observation of the pressure dependence of the C:O ratio. As already mentioned, such an examination is of interest in that it is pertinent to the discussion of the reducing properties of the low pressure flame, but in addition it has been attempted because it is also essential to the consideration of gas flow rate adjustment given in the next section of work.

The pressure dependence of the C:O ratio of a pre-mixed flame at the onset of luminosity has been measured elsewhere (I6,95), and, in agreement with the previous remarks concerning a possible increase in the concentration of free atomic carbon at reduced pressures, was found to increase with decreasing pressure; similar results have also been obtained using low pressure diffusion flames (96). These data however, and particularly that from pre-mixed flame studies, have been the subject of some discussion (I6), and such evidence cannot, therefore, be said to be conclusive at the present time.

FIGURE 20

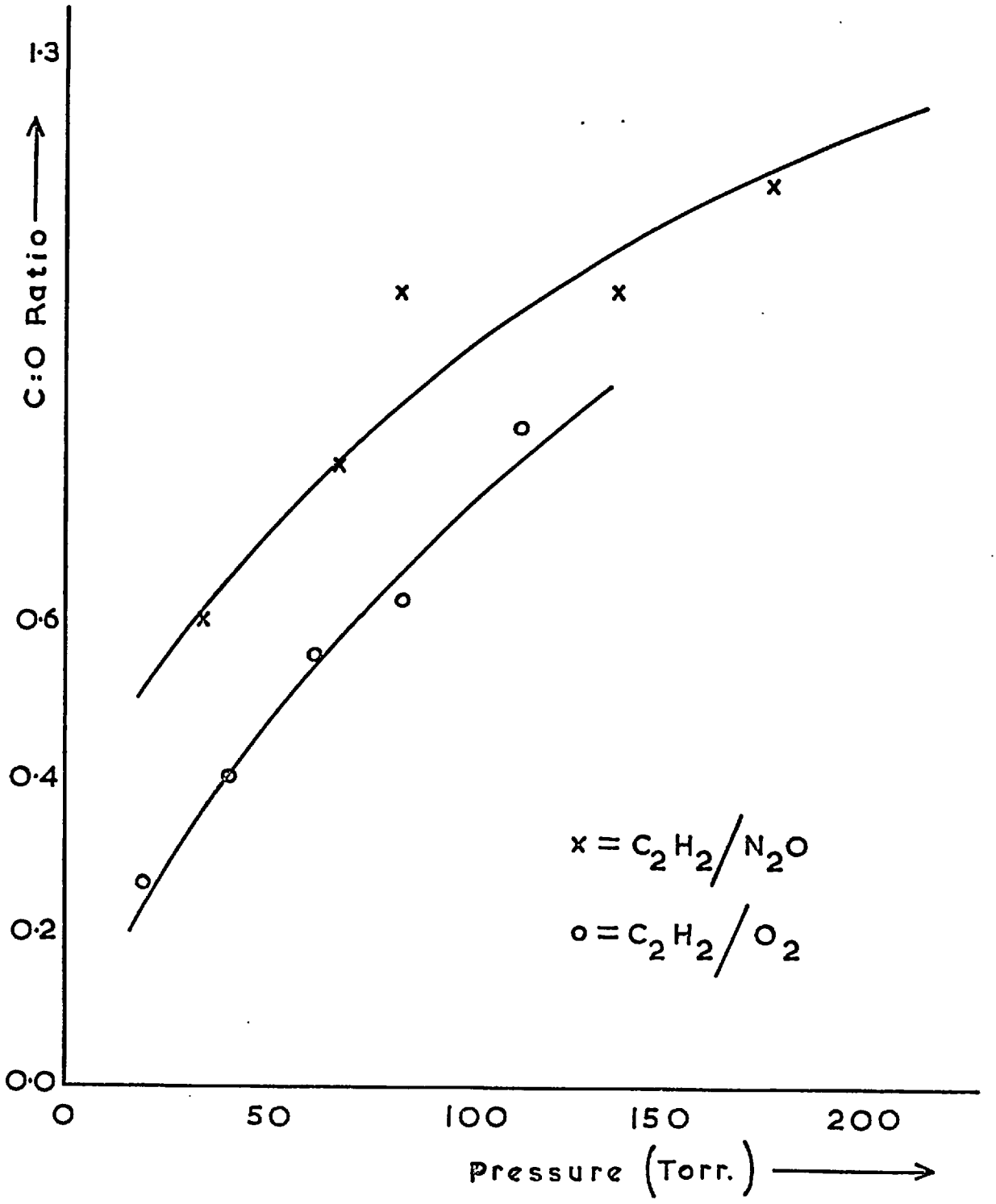

1·3
C:O Ratio
0·6
0·4
0·2
0·0
0
50
100
150
200
Pressure (Torr.)
x = C2H2/N2O
o = C2H2/O2

Figure 20 shows the variations, measured in the present experiments, of the C:O ratios of C_2H_2/O_2 and C_2H_2/N_2O flames with pressure, at the onset of luminosity. In direct contrast to both the data mentioned above, and to previous expectation, these results show a decrease of the C:O ratio with decreasing pressure. No immediate explanation for this discrepancy can be given, except perhaps insofar as Gaydon (I6) has suggested a possible influence of experimental conditions, such as the degree of flame quenching for example, on carbon particle formation in pre-mixed flames. It is, therfore, concluded that the limiting C:O ratio of a given flame appears to be pressure sensitive, at least under the conditions used in the present experiments, but whether this sensitivity is a fundamental property of the flame or is determined by the nature of the apparatus used still remains uncertain.

Although the lack of agreement between the present and published results cannot really be satisfactory reconciled, it is still possible to explain the trend shown by the present results in a manner which permits the (relative) concentration of atomic carbon in the flame to increase with decreasing pressure, as suggested by the arguments of section 5:2 above.

Although the processes actually leading to carbon particle formation in pre-mixed flames are still uncertain (97-I0I), and therefore correspondingly difficult to discuss, it is known with reasonable certainty from the work of Homann

and Wagner (I02), and others (I03 - I06), that saturated polymeric species exist, even in non-luminous flames; species which may be considered to act as nuclei for true carbon particle formation under suitably fuel rich conditions. It is therefore suggested that the observed drop in the C:O ratio in the reactant gases of a (luminous) pre-mixed flame with decreasing pressure can be explained in terms of the greater efficiency of free carbon atom formation from the fuel gas at low pressure; i.e. the loss of carbon as (relatively) chemically inert polymeric species is reduced, and hence a greater concentration of vapour phase atomic carbon can be generated from a given volume of fuel gas, despite the fact that the absolute rate of carbon introduction may be undergoing a simultaneous reduction.

It is concluded from this discussion that the discrepancy between the present and published data supports the suggestion that the C:O ratio is numerically determined, at least in part, by the characteristics of the equipment used, and may not necessarily depend on the nature of the flame. Thus it is a valuable parameter to the extent that experiments such as those decribed may provide useful data relating to e.g. the influence of mechanical design on carbon formation in internal combustion engines; a subject of considerable interest at the present time. The C:O ratio is not however felt to be of particular value in relation to the problem of atomic carbon formation

in the p.r.z., since, even if such results were consistent between different types of equipment, no absolute interpretation could be given; a conclusion illustrated by arguments given previously in this section of work.

5:4 Adjustment of Gas Flow Rates during Experimental Work.

When working at pressures approaching $\frac{1}{2}$ atmosphere it was necessary to use very fuel rich flames, to avoid oxidation of the tungsten loop. However, it can be seen from Figure 20 that once the flame pressure was reduced, such a fuel: support gas ratio could not be maintained without producing a luminous flame; thus if results were to be compared over a wide pressure range, using the tungsten loop for sample introduction, it was necessary to vary the C:O ratio of the reactant gases by reducing the C_2H_2 flow rate; a process which should apparently have made the flame increasingly fuel lean at lower pressures. That this is not in fact the case can be seen from the results of Chapter Four, in which it was pointed out that at lower pressures it was no longer necessary to use very rich flames to avoid oxidation of the tungsten; the reasons by which the flame can become more fuel rich while the C:O ratio of the reactant gases is simultaneously reduced were considered in the previous section of work.

The technique adopted for adjusting gas flow rates

to a reproducible level under the conditions described above is given below.

It was noticed during the experiments discussed in section 5:3 that, prior to the flame becoming luminous, an abrupt breakdown in the sharp, visible edge of the p.r.z, occurred, leading to a blurred, 'feathery' appearance of the flame. Qualitatively, this phenomena was not pressure dependant, although the C:O ratio at which it was observed varied with pressure as shown in Figure 20, and it was considered that this condition represented the point of saturation of the flame with atomic carbon; gas flow rates were, therefore, adjusted to this point for each new burner head during the above investigation of the pressure dependance of the emission intensities of aluminium and strontium in section 5:I above. This procedure was adopted because it permitted apparently reproducible flame conditions to be set up , irrespective of the flame pressure used. In practice, the condition described was achieved by setting the N_2O flow rate to a (constant) value of 3.2 litres/minute[I], and adjusting the C_2H_2 flow rate to the required level by visual observation of the flame. The N_2O flow rate of 3.2 litres / minute was not varied throughout the present series of experiments, except where otherwise stated, and all adjustments of flame composition were achieved by altering the C_2H_2 flow rate.

[I] All flow rate values given are corrected to N.T.P.

The curves of Figure I7 and I9 were thus determined using flames adjusted to the maximum practicable C:O ratio at any given pressure, to try to achieve a comparable flame composition over the wide pressure range examined. Although the p.r.z. does not appear to be chemically sensitive to pressure (Chapter One), its tolerable fuel rich limit does seem to be pressure dependent, in the manner, and for the reasons, already discussed in section 5:3 above. Thus the technique used for adjusting gas flow rates should at all times give a flame which is saturated with atomic carbon; a condition which must, therefore, represent the limit of the reducing properties of that flame. For the reasons given in section 5:3, it is uncertain whether this limit is fundamental to the flame itself, or, as in fact seems more likely, it is influenced by the design of the equipment. In either case however, the adjustment procedure described is at least valid from a practical point of view in that, under the given experimental conditions, the chemical reducing properties of the flame could not be increased further. Thus the method of C_2H_2 flow rate adjustment described provides a viable basis for the (practical) comparisons of Figure I9; an argument which does not apply to alternative methods of defining the flame composition under conditions of varying pressure, and which in particular does not apply to the technique of adjusting the C_2H_2 flow rate for maximum sensitivity of the element concerned; a technique

which was considered as a possible alternative procedure to the one in fact actually adopted.

When working at a defined pressure however, one of the variables affecting flame performance is removed, and the procedure of adjusting the C_2H_2 flow rate for maximum emission sensitivity then becomes quite acceptable. Thus whenever analytical results, such as the measurement of calibration curves etc. were determined at a given pressure, the C_2H_2 flow was set for maximum sensitivity for the element concerned. The onset of oxidation of the tungsten loop itself in fact restricted the range of permissible C:O ratios which could be used at any particular pressure (see above); fortunately however most of the elements examined were themselves very susceptible to oxidation, so that the optimumC:O ratios for those elements generally lay within this permissible range.

The relatively greater reducing power of the lower pressure flames permitted leaner (hotter) flames to be used. The effect of this did not however appear to be great enough to alter the overall increase of emission sensitivity significantly with pressure observed in Figure I7; for this reason, therefore, all of the following analytical results were obtained at the maximum operating pressure of the equipment.

Figures 2I and 22 show the calibration curves obtained for aluminium and strontium in a C_2H_2/N_2O flame at a pressure

FIGURE 21

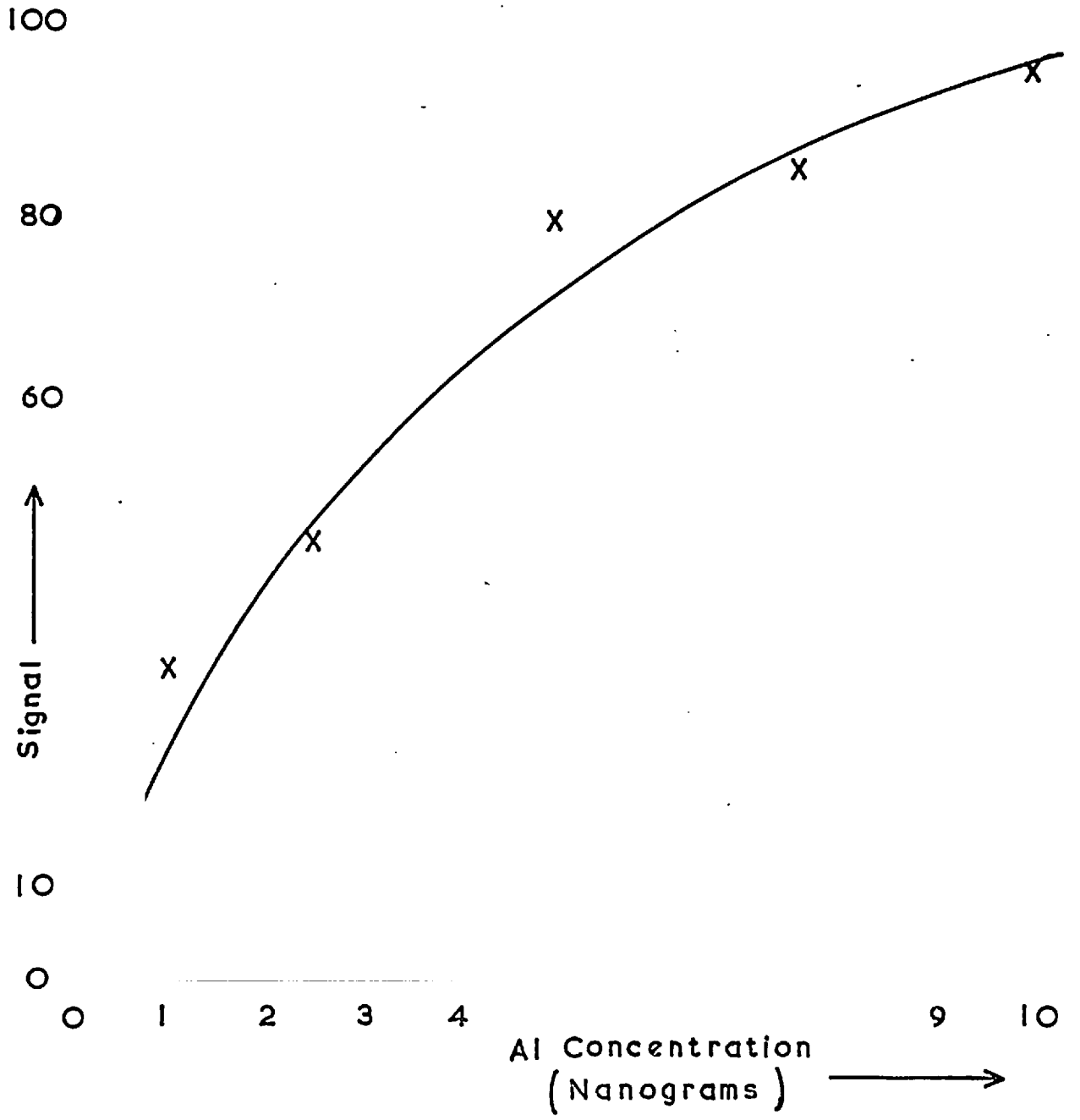
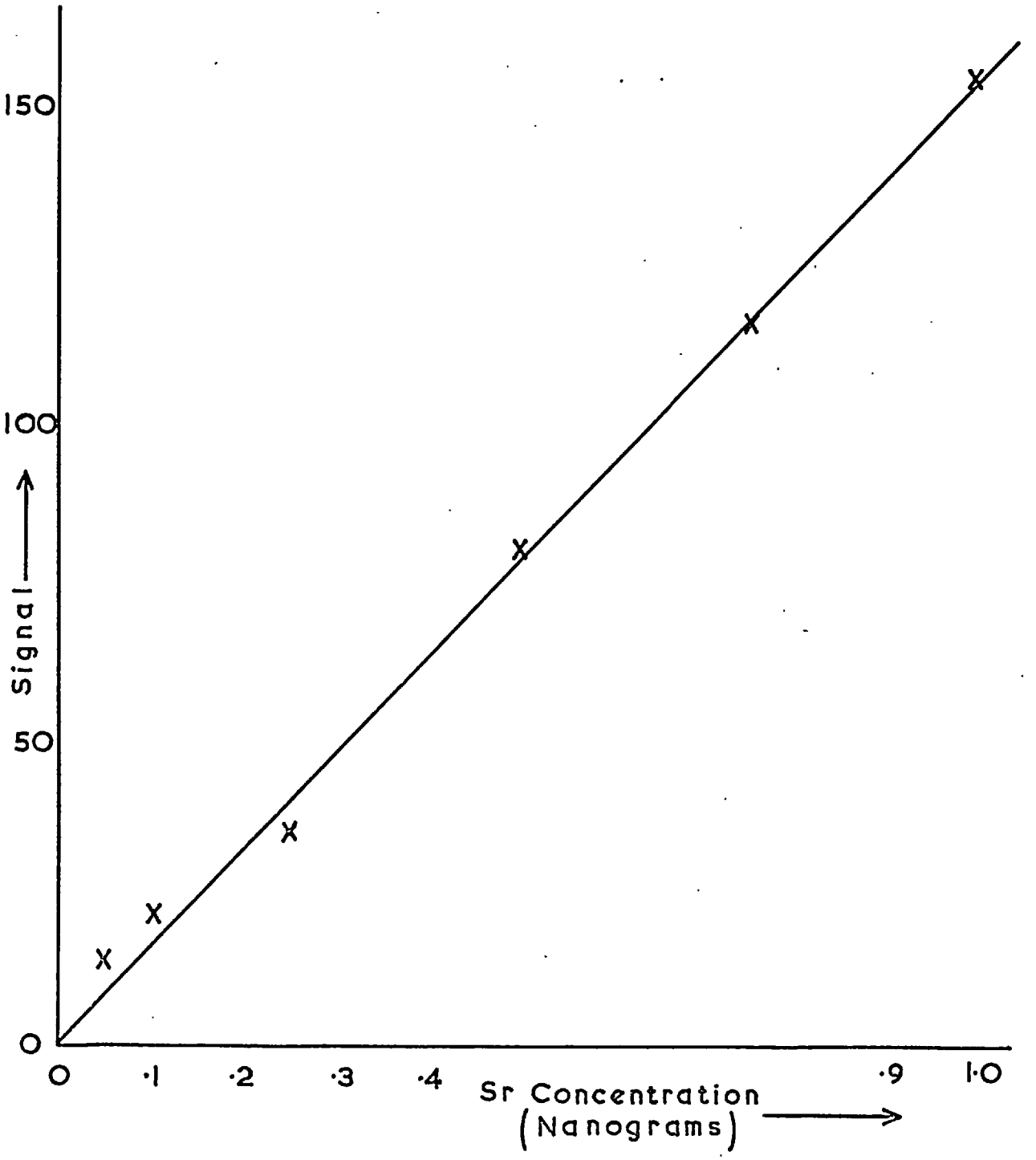


FIGURE 22



of 250 Torr. (the maximum safe upper pressure limit of the equipment for sustained operation). C_2H_2 and N_2O flow rates of I.3 and 3.2 litres / minute respectively were used during both of these determinations. The convex calibration curve observed for aluminium does not appear to be in any way remarkable; indeed, the characteristics of the integrator required it to give a non-linear output for sufficiently prolonged signals, which thus made such a response curve virtually essential (see appendix). The linearity of the strontium calibration curve is however more unusual, suggesting perhaps that self-absorption effects in the low pressure flame are of less significance than is the case with their more conventional atmospheric counterparts; an effect presumably resulting from the reduced optical density of the low pressure flame (57).

The analytical detection limits determined for aluminium and strontium from their calibration curves are given in Table 5 below. The values of the detection limits in Table 5 are given in grams, and to permit calculation of these absolute values from known solution concentrations, it was necessary to know the mass of the solution film picked up by the tungsten loop. This was determined by weighing a number of individual loops on a microbalance before and after picking up a film of water; I0 loops were examined in this way, and it was hence found that the average mass of water picked up was I3 micrograms,

with a standard error of ± 9%, (although this figure contains an undetermined weighing error).

5:5 Some Elements of the First Transition Series.

The success of the tungsten loop technique when applied to aluminium and strontium prompted the analytical investigation of a number of other elements to be undertaken. This work concentrated on the members of the first transition series, partly because of their relatively high melting points, and partly because of the ability of a number of these elements to form refractory oxides, thus rendering their analysis by conventional means correspondingly difficult. The elements initially selected were limited by the requirements of thermal emission, although a number of the other elements were subsequently examined by chemiluminescent emission within the p.r.z. (see later).. The results of the initial thermal studies are summarised in Table 5 below.

All the results given in Table 5 were determined under the same experimental conditions. These were with C_2H_2 and N_2O flow rates set at I.3 and 3.2 litres / minute respectively, and at a flame pressure of 250 Torr.

TABLE 5

Element	Detection Limit (g)	Wavelength (nm.)	Standard Error ± (%)
Sr	4×10^{-12}	460.7	6
Al	1×10^{-10}	396.1	9
Cr	4×10^{-9}	357.9	9
Cu	3×10^{-10}	324.8	7
Ti	3×10^{-7}	364.3	16
V	5×10^{-9}	318.4	11

Note:- 1) Detection limits were determined at a signal to noise ratio of 2:1 on the integrator output.

2) Standard errors were determined from a set of 5 readings measured at the detection limit.

5:6 Summary of Experimental Results.

1) The ability of the tungsten loop technique to atomise aluminium from hydrated samples provides some experimental confirmation for the high surface temperature of the tungsten loop, deduced in Chapter 4. Further evidence to this effect is

provided by the ability of the technique to atomise samples of chromium, vanadium, and in particular of titanium, which shows that the surface energy available is sufficient to cause rupture of even such thermally stable bonds as those formed between titanium and oxygen.

2) The analytical detection limits which were obtained are felt to be fairly satisfactory, comparing quite well with those given by other flame-heated atom reservoirs hitherto reported (I07-I09). The analytical potential of the tungsten loop technique is further emphasised by the comparative scarcity of other small sample techniques, involving either flame-heated or non-flame cells, which are also capable of handling refractory samples such as those examined here (II0-II4). However, the analytical detection limits obtained, because of the prototype nature of the equipment, are in fact considered to be of less immediate significance than the results which are shown in Figure I9; results which indicate that the free atom population generated from a vapourised sample, and in particular from samples prone to forming refractory oxides, increases as the flame pressure is reduced. This effect has been related above to the chemically reducing properties of the low pressure flame, and results in a corresponding increase in the atomisation efficiency of the flame. Thus when considering refractory samples in particular, and provided that a sample introduction system

such as the tungsten loop method used here is acceptable, it is considered from the present work that the low pressure C_2H_2/N_2O flame can be justifiably regarded as a system of practical analytical applicability.

CHAPTER SIX

6:I Low Pressure Diffusion Flames.

The results discussed in the previous Chapter showed the emission sensitivity of the low pressure C_2H_2/N_2O flame to be increased by working at higher pressures, despite the inherantly lower atomisation efficiency of the flame under such conditions. Since this effect was attributed to the increased excitation temperature of the flame at higher pressures, it was decided to try to increase the flame temperature while still keeping the flame pressure to a minimum, in order simultaneously to gain the benefits of good atomisation efficiency together with a high level of thermal excitation. The required temperature increase was obtained by providing a supporting atmosphere within the pressure vessel, permitting a diffusion flame to be maintained around the (normally observed) interconal zone; thus thermal shielding of the interconal zone could be provided, to at least reduce the pressure dependence of the flame excitation temperature. No difficulty was found in maintaining the flame pressure when the supporting gas was fed into the pressure vessel; the equipment in fact proved to have a sufficient reserve of pumping capacity to maintain diffusion flames down to press-

ures of about I5 Torr.

When this technique was applied to a fuel rich C_2H_2/N_2O flame, burning at a pressure of I00 Torr., at C_2H_2 and N_2O flow rates of 0.9 and 2.8 litres/minute, and maintaining a nitrous oxide supporting atmosphere, the emission signals given by $5 \times I0^{-8}$g. samples of aluminium were found to increase by a factor of 3x in comparison with the 'separated' counterpart of the same flame. However, it was now found that the outer regions of the flame were so oxidising that the tungsten loop lifetimes were seriously reduced; furthermore, severe overheating of the pressure vessel also occured, to the extent that sodium, driven from the surface of the glass, began to cause spectral interference by its continuum emission. Thus it was decided that, despite the enhanced emission sensitivity given by the diffusion flame, the accompanying disadvantages prevented the general adoption, or even any extended examination, of the technique at the present time.

One result of interest which was however obtained during the course of this work was the observation that the enhancement of aluminium emission, using an air-supported diffusion flame under the same conditions as those described above, only occurred to the extent of about 50%, compared to the 300% enhancement observed with a nitrous oxide supported diffusion flame. The reasons for this discrepency are not clear; the result does however imply that conventional atmospheric flames could be

usefully supported in gaseous atmospheres other than that which is provided by air alone (see later).

6:2 Sample Atomisation Rate Control.

It was pointed out in Chapter 4:5 above that the faster a given sample could be made to volatilise, the better the inherent signal to noise ratio of the system should be. In the case of volatile samples such as $Sr\,Cl_2$, the rate of atomisation was already so high naturally that any further increase would have taken the speed of the emission pulse beyond the useful frequency response of the integrator. However, more refractory samples, such as the aluminium salts also investigated, volatilised at a considerably lower rate, and thus any increase in the atomisation rate of such samples could be expected to be correspondingly analytically beneficial.

The technique adopted to try to achieve this effect required the refractory sample to be held in a volatile crystal matrix. Thus on immersion in the flame, it was hoped that the rapid evaporation of the matrix would carry the sample quickly away from the loop surface; a process followed (if necessary) by molecular decomposition of the vaporised sample during its passage through the p.r.z., to give free vapour phase sample atoms.

An intial investigation of this technique did not however prove to be encouraging. Experimentally, the required matrix salt was added to normal, aqueous sample solutions, which were then introduced into the flame in the usual way. The resulting emission signals, measured in a fuel rich C_2H_2/N_2O flame at a pressure of I00 Torr., were displayed on a storage oscilloscope, which thus permitted both the pulse length and the maximum pulse amplitude to be determined. The effects of a number of possible matrix salts were examined, at a variety of concentrations, on the emission pulses given by 5×10^{-8} g. samples of aluminium; the greatest attention however was paid to the halides of the alkali and alkaline earth elements, and of copper, zinc and cadmium, on the grounds of their volatility. Unfortunately, none of these salts appeared to give rise to the desired result, although a number of other interference effects were noted during the course of this work; for example, fluorides in particular appeared to exert a strongly depressing effect on the amplitude of aluminium emission.

However, by carring the samples of aluminium into the flame on a loop made from 38 gauge copper wire, the emission pulse length was reduced from I20 to about 20 milliseconds (the time required for the flame to cause total volatilisation of the loop).

The above result thus suggests the technique of pulse length control, to be valid, at least in principle. However,it

is felt that considerably more work is needed, beyond the rather cursory examination so far attempted, before the potential applicability of the system can be evaluated.

6:3 The Low Pressure C_2H_2/O_2 Flame.

In Chapter 4:5, it was mentioned that the very low pressure operation, and hence the reducing capacity, of the C_2H_2/N_2O flame were restricted by the very large physical size, and low excitation temperature, of the resulting flame. Both of these difficulties were successfully overcome by the use of pre-mixed C_2H_2/O_2 flames, which could be usefully burned at pressures down to about 5 Torr.

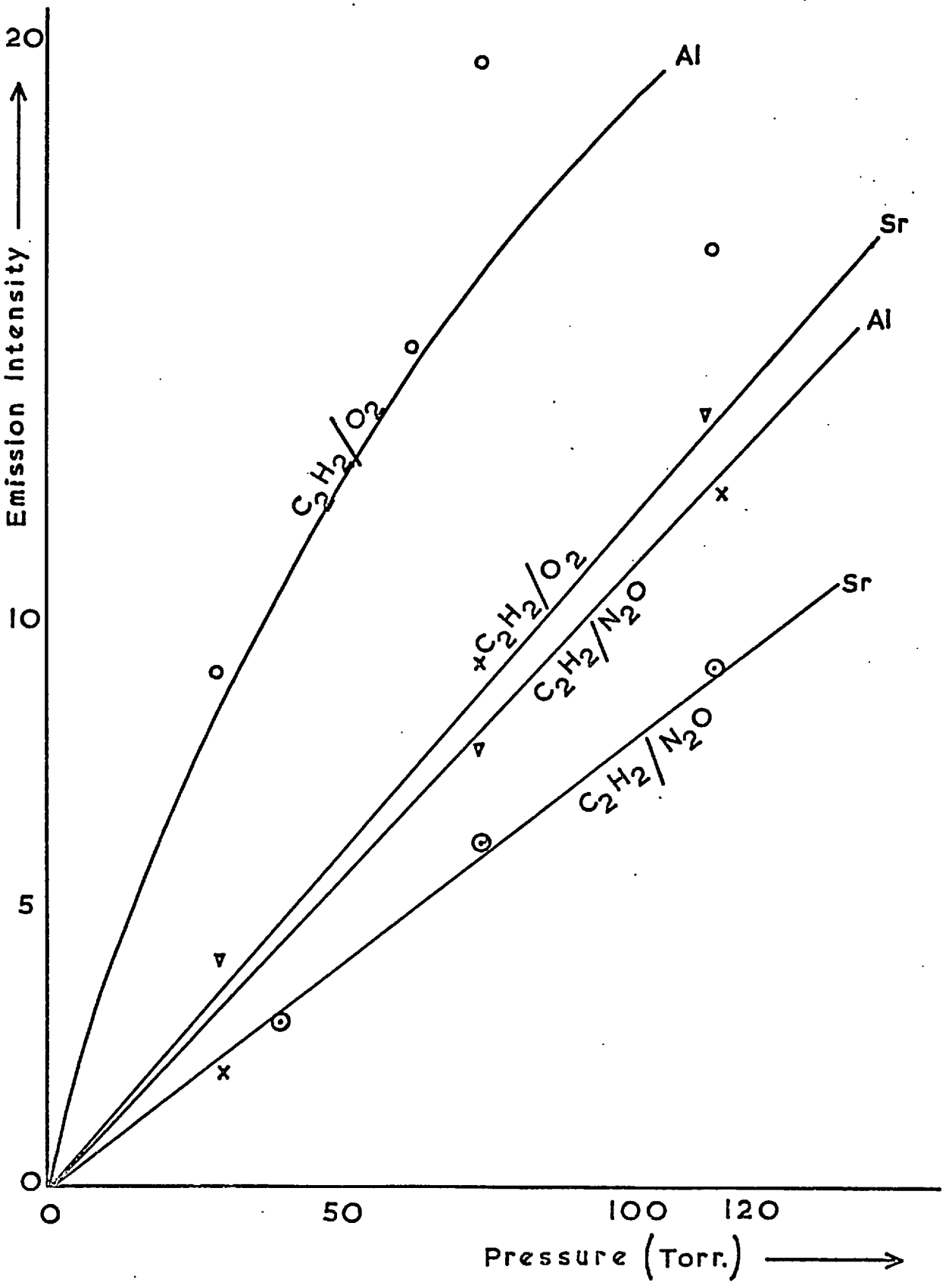
The same burner heads were used for C_2H_2/O_2 as for C_2H_2/N_2O flames, although their operating pressures were reduced to the values given in Table 2, Chapter 2. The same sample introduction technique was used for C_2H_2/O_2 flames as was described in Chapter 4 for C_2H_2/N_2O; it was however found that the higher temperature of the oxygen-supported flame required greater cooling of the tungsten loop at any given pressure; for this reason, studies with the C_2H_2/O_2 flame were restricted by an upper pressure limit of about I20 Torr., at which point the heat output of the flame became sufficient to melt both the tungsten loop and the cooling assembly together.

The ability of the low pressure C_2H_2/O_2 flame to melt the tungsten loop, rather than simply burn it away as vapour phase oxide particles, suggested the low pressure C_2H_2/O_2 flame to have a comparable, and possibly even a greater, chemical reducing capability than the equivalent C_2H_2/N_2O flame (II5,II6). Direct quantitative comparison of the two systems was not however attempted in the present work, for reasons which are discussed below.

The variations of emission intensity with pressure for aluminium and strontium in both C_2H_2/O and C_2H_2/N_2O flames are shown in Figure 23. Experimentally, the equipment was set up for both types of flame in the manner described in Chapter Four; aluminium and strontium sample sizes of 5×10^{-8} and 1×10^{-10} g. respectively were used. Oxygen and nitrous oxide flow rates were set at 4.0 and 3.2 litres/minute, and the acetylene flow rate adjusted for the maximum emission signal of the element concerned; a procedure necessitated by the weak emission signals obtained in the C_2H_2/N_2O flame over the pressure range examined. For the reasons discussed in Chapter 5:3 above, this method of flow rate adjustment precluded any realistic comparison of the relative atomisation efficiencies of C_2H_2/O_2 and C_2H_2/N_2O flames; a comparison in any case complicated by the experimental difficulty found in measuring C_2H_2/N_2O flame excitation temperatures at very low pressures.

The (relative) pressure dependence of the atomisation

FIGURE 23

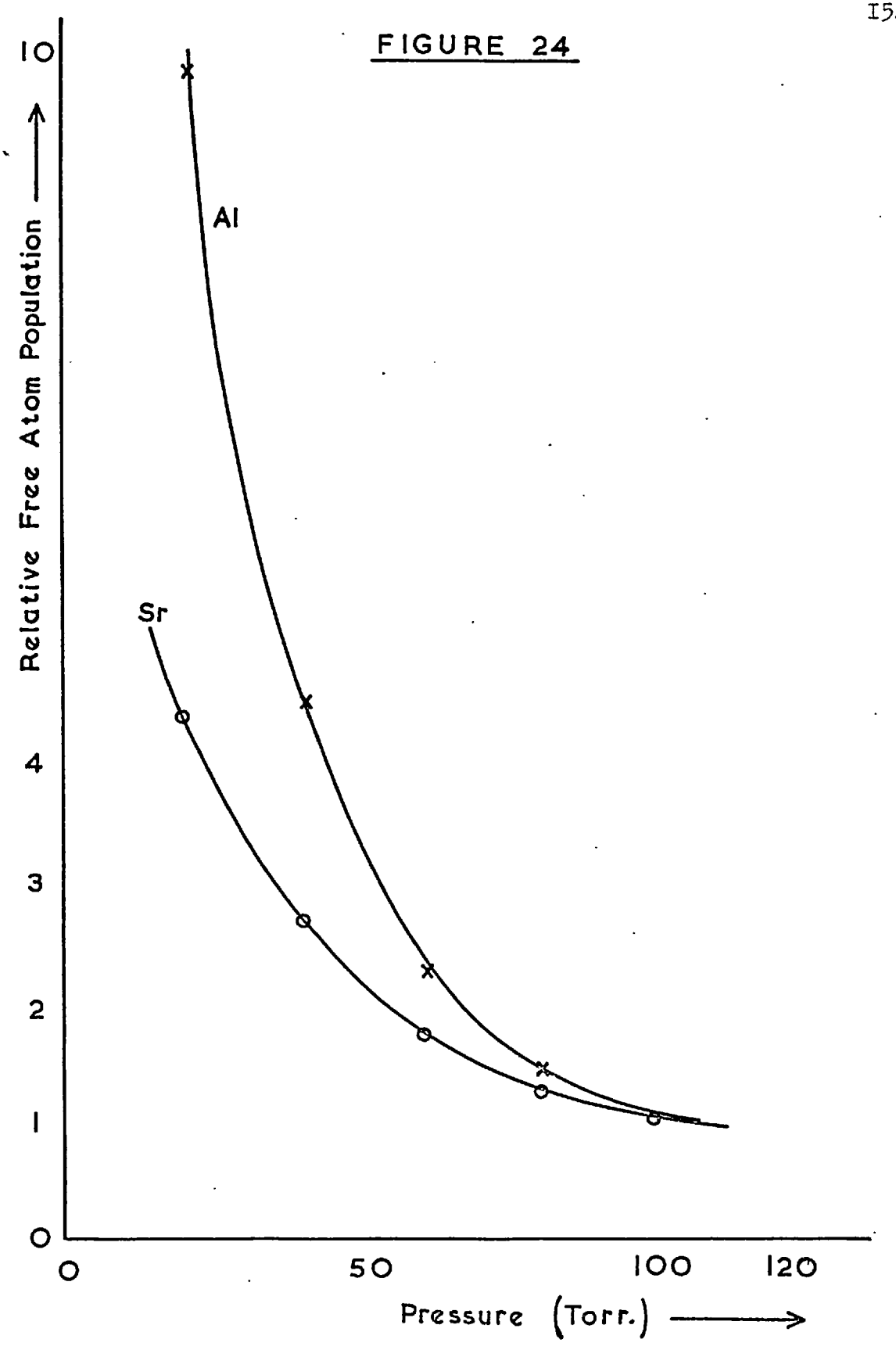

20
10
5
0
Emission Intensity
Al
Sr
Al
Sr
C_2H_2/O_2
$+C_2H_2/O_2$
C_2H_2/N_2O
C_2H_2/N_2O
0
50
100
120
Pressure (Torr.)

efficiency of a 'saturated' fuel rich C_2H_2/O_2 flame, for aluminium and strontium, was determined over the pressure range 15 to 110 Torr. by exactly the same procedure as that used previously for C_2H_2/N_2O flames (Chapter 5:2). The results thus obtained are shown in Figure 24; as observed with the C_2H_2/N_2O flame, an abrupt rise in the flame atomisation efficiency with decreasing pressure again appears to occur, suggesting that the factors responsible for the chemically reducing characteristics of the low pressure C_2H_2/N_2O flame, discussed in Chapter 5, are also operative in the low pressure C_2H_2/O_2 flame.

The results of Figure 24 thus show the chemically reducing properties of the low pressure C_2H_2/O_2 flame to increase with decreasing pressure; an effect presumably still further enhanced by the very low pressures at which C_2H_2/O_2 flames can usefully be maintained; arguments which suggest that, in practical terms, such very low pressure C_2H_2/O_2 flames may prove to be among the most chemically reducing flames available for analytical work at the present time.

In addition to its reducing properties, the results of Figure 23 suggest the low pressure C_2H_2/O_2 flame to be inherently more suitable for emission studies than the equivalent nitrous oxide supported flame, presumably because the former system, despite its low mass density, can still exhibit a high excitation temperature (Figure 18).

FIGURE 24


Relative Free Atom Population
10
4
3
2
1
0
Al
Sr
0
50
100
120
Pressure (Torr.)

An attempt was made to apply the properties of high temperature, low (mass) density, and chemically reducing environment provided by a very low pressure C_2H_2/O_2 flame to the analysis of even more refractory oxides than those already examined. It was hoped that the high surface temperature of the loop (Chapter 4) would permit such samples to be volatilised, and that by sufficiently lowering the pressure, the flame could be made to reduce the vaporised samples thus produced to free sample atoms. The possibility of achieving such a result was examined using samples of uranium, made up in aqueous solution from the nitrate, $UO_2(NO_3)_2$. Approximately 0.I microgram samples of this salt were introduced into a fuel rich C_2H_2/O_2 flame, burning at a pressure of 5 Torr.; however, despite the low excitation energy of the uranium resonance lines (I7), no thermal emission could be detected under the conditions described.

The initial failure of this approach was attributed firstly to an uncertainty of the exact pressure which would provide the best compromise between the requirements of atomisation efficiency and of thermal excitation for atomic uranium in a C_2H_2/O_2 flame, and secondly to the fact that at the very low pressures used, local quenching of the flame by the (relatively) large mass of the loop could cause a reduction, or even a total suppression, of sample volatilisation from the

loop surface. Such quenching of the flame could in fact be seen to occur under suitable conditions, showing up as a visibly darkened region separating the loop from the strongly radiating gases of the p.r.z.

No further work relating to this effect will be considered at the present time; however, some of the possible techniques by which it could perhaps be satisfactorily overcome, thus enabling the analysis of very refractory samples such as uranium salts to be attempted, are discussed in Chapter 8.

6:4 Some Chemiluminescence Studies in Low Pressure Flames.

The experiments below examine some aspects of the chemiluminescent excitation of foreign atoms introduced into the p.r.z. of a low pressure flame; a phenomenon of some analytical interest in the present work, since the greater excitation energy thus made available permits the range of elements hitherto examined by atomic emission to be correspondingly extended.

An initial spectroscopic examination of the p.r.z. of a low pressure C_2H_2/O_2 flame showed strong 'fourth positive' CO band emission, under a variety of conditions of flame composition and pressure. The examination was carried out between 200.0 and 210.0 nm., using the conventional Techtron AA4

monochromator and amplifier, in conjunction with an RCA IP 28 A photomultiplier.

No such CO emission could be detected, under the conditions described, from the equivalent nitrous oxide supported flame; thus since the intensity of the chemiluminescent excitation of foreign atoms within the p.r.z. has already been related elsewhere to the simultaneous occurrence of CO^{*} (53 , 54), it was considered that the nitrous oxide supported flame was the less suitable for chemiluminescence studies, and the present experiments were accordingly carried out entirely in low pressure C_2H_2/O_2 flames. As far as possible, these experiments were carried out at the lowest practicable flame pressures, at which the thickening of the p.r.z., mentioned in Chapter One, permitted easier spectroscopic examination.

The wavelengths examined during the present experiments generally lie within the ultra-violet regions of the spectrum, at which it was possible to ignore the spectral existence of the tungsten loop, and hence to examine samples at the the moment they volatilised from the loop surface; an important attribute in a system in which a reaction zone perhaps no more than one millimetre thick had to both heat the loop and cause sample excitation at the same time.

During these experiments, it was found that extremely poor reproducibility was observed for samples of Zn, Cd and Pb; indeed, Zn and Cd samples failed on occasion to give any

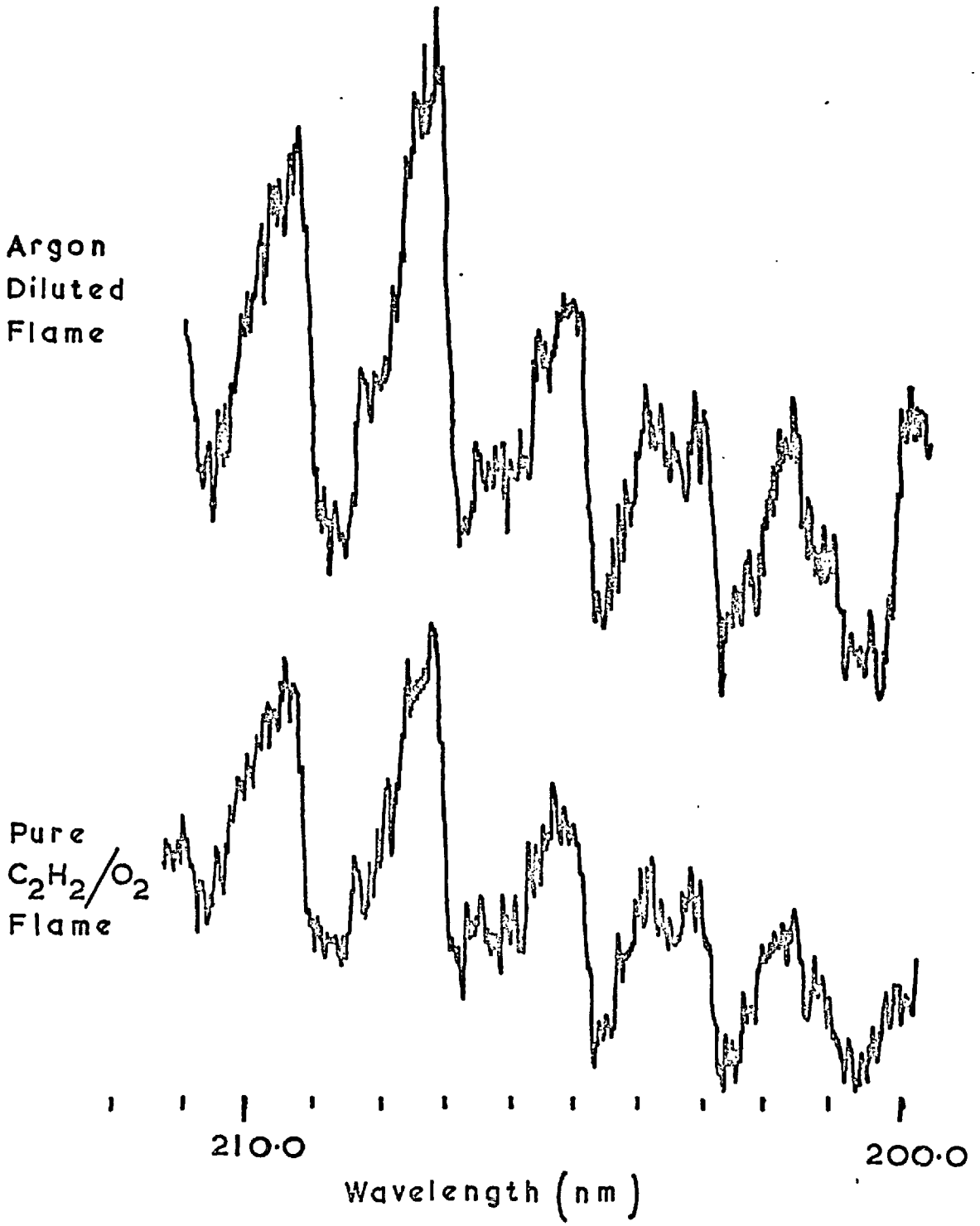
detectable signal at all. Such behaviour was attributed to premature sample evaporation before the loop had entered the p.r.z., and was the first evidence so far encountered to suggest that premature sample evaporation could be a significant effect; a result illustrating the defects of the existing equipment, and which correspondingly limited the scope of the present experiments.

As mentioned above, the present experiments are of some analytical interest in that they permit an extended range of elements to be studied by atomic emission. However, the major objective of these experiments was not the investigation of the analytical properties of the p.r.z., but was rather concerned with establishing the chemical role played by argon within the p.r.z.; the analytical potential of the p.r.z. in fact emerged as a secondary result from this work. The role of argon in the p.r.z., in view of some phenomena observed in the low pressure flame, is discussed below.

Argon has been used as a flame diluent in a number of studies of chemiluminescent excitation (52 - 54), in which its effect has been assumed to be that of a chemically inert additive. It was however considered possible that under the conditions encountered within the p.r.z., argon might be forced to take an active chemical part, by participation in the energy transfer reactions occurring in this region of a flame.

Evidence supporting this supposition was initially obtained by the examination of the CO fourth positive spectrum between 200.0 and 210.0 nm., shown in Figure 25. The lower

FIGURE 25


Argon
Diluted
Flame
Pure
C_2H_2/O_2
Flame
210·0
200·0
Wavelength (nm)

intensity spectrum was obtained in a pure C_2H_2/O_2 flame, using C_2H_2 and O_2 flow rates of 0.65 and 3.5 litres/minute respectively, and burning at a pressure of I5 Torr.; the higher intensity spectrum was obtained in a flame burning on the same head and at the same C_2H_2 and O_2 flow rates as before, but diluted with I.5 litres/minute of argon. The dimensions of both the pure and diluted flames were matched as closely as possible by increasing the flame pressure of the latter; the increase in flame dimensions caused by dilution was thus offset by the effect of the greater flame pressure. To achieve exact matching, the burner positions for both maximum and half maximum emission intensity were noted for the two flames, and the pressure of the diluted flame was increased until the two sets of values coincided. Both of the spectra shown in Figure 25 were recorded following this procedure, and with the burner position subsequently adjusted for maximum emission intensity during spectral measurement.

Further quantitative evidence relating to possible chemical participation of argon in the p.r.z. was obtained in the following experiments.

Chemiluminescent emission signals given by 0.I microgram samples of Mg, at wavelengths of 285.2 and 278.0 nm., were examined in the p.r.z. of a C_2H_2/O_2 flame, again at C_2H_2 and O_2 flow rates of 0.65 and 3.5 litres/minute; as far as possible, flame dimensions were kept constant by simultaneously increasing

the flame pressure with argon flow rate, using the same technique as that described above. An initial flame pressure of 20 Torr. was used, increasing linearly with the argon flow to 37 Torr. at the maximum argon flow rate of 4.0 litres/minute.

The results thus obtained are given in Figure 26, which shows a small, approximately linear increase of emission intensity with argon flow rate, reaching a maximum, and then falling off rapidly. This effect is emphasised in Figure 27, in which the ratio of Mg emission intensity at 278.0 nm. to the flame background at the same wavelength is plotted against argon flow rate. The results of Figure 27 are thus sufficient to at least suggest that the flame becomes considerably more efficient at exciting (chemiluminescent) Mg emission after increasing dilution by argon; unfortunately, the very low background at 285.2 nm. precluded calculation of the signal to background ratio at this wavelength, for the purposes of comparison with the results of Figure 27.

In presenting the results shown in Figures 26 and 27, no account has been taken of the pressure dependence of vapour phase sample diffusion rates; an effect ignored on the grounds that the sample was viewed at a distance from the loop which was small in comparison with the width of the field of vision of the monochromator. In any case, errors arising from such a cause must be expected to be offset by the fact that no account has been taken of the increased mass flow rate through the

FIGURE 26

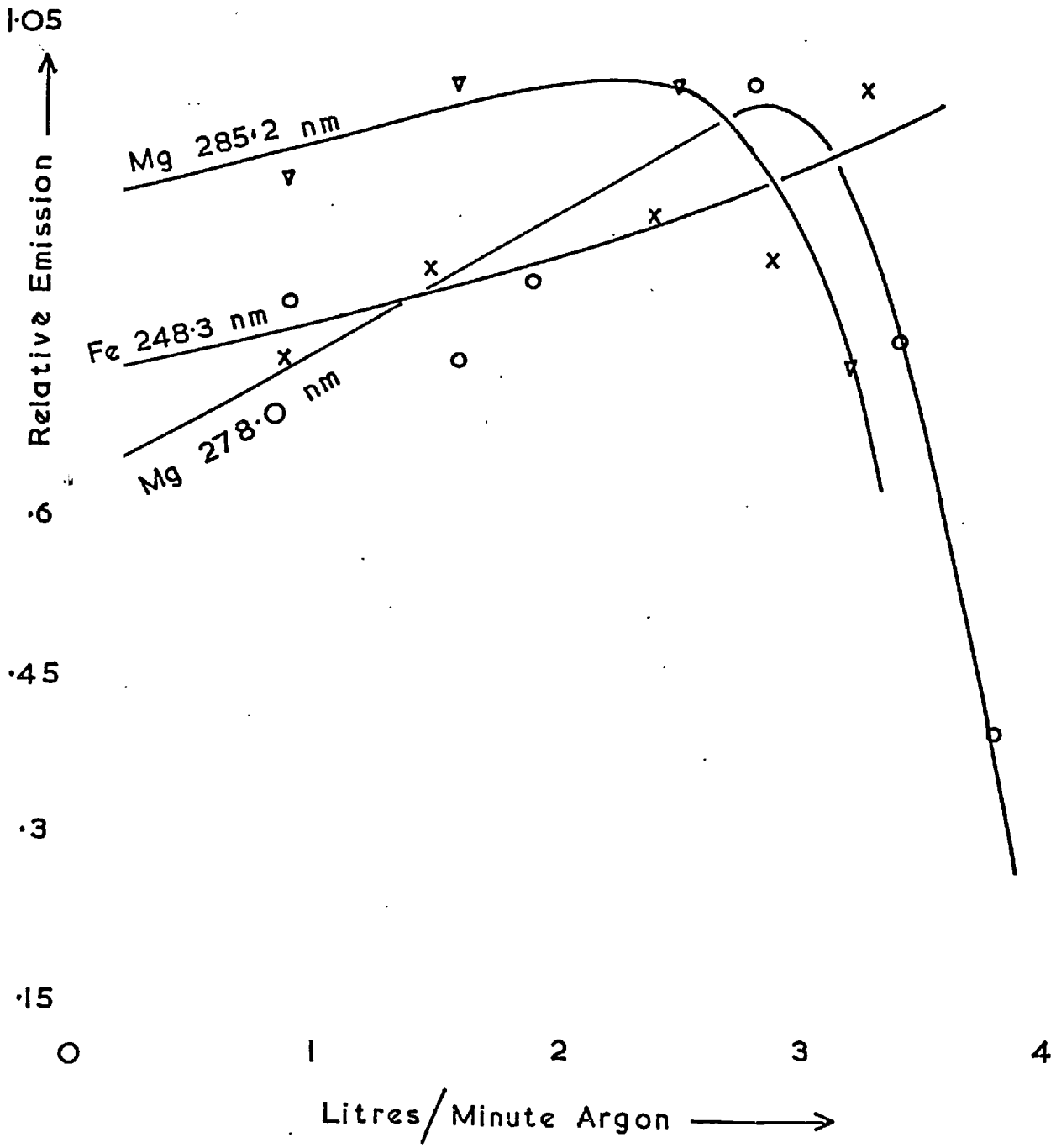
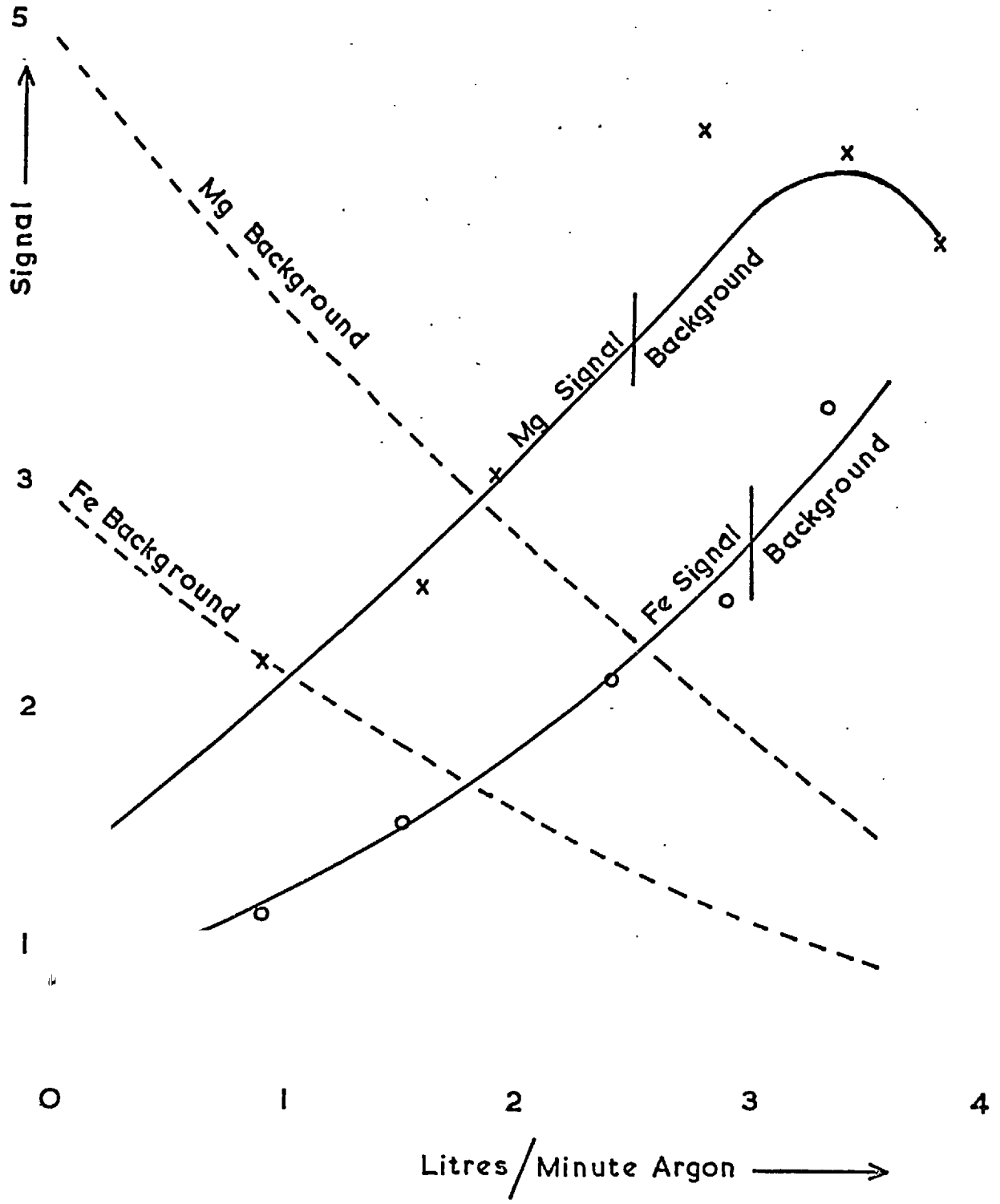

1·05
Relative Emission
Mg 285·2 nm
Fe 248·3 nm
Mg 278·0 nm
·6
·45
·3
·15
0
1
2
3
4
Litres/Minute Argon

FIGURE 27

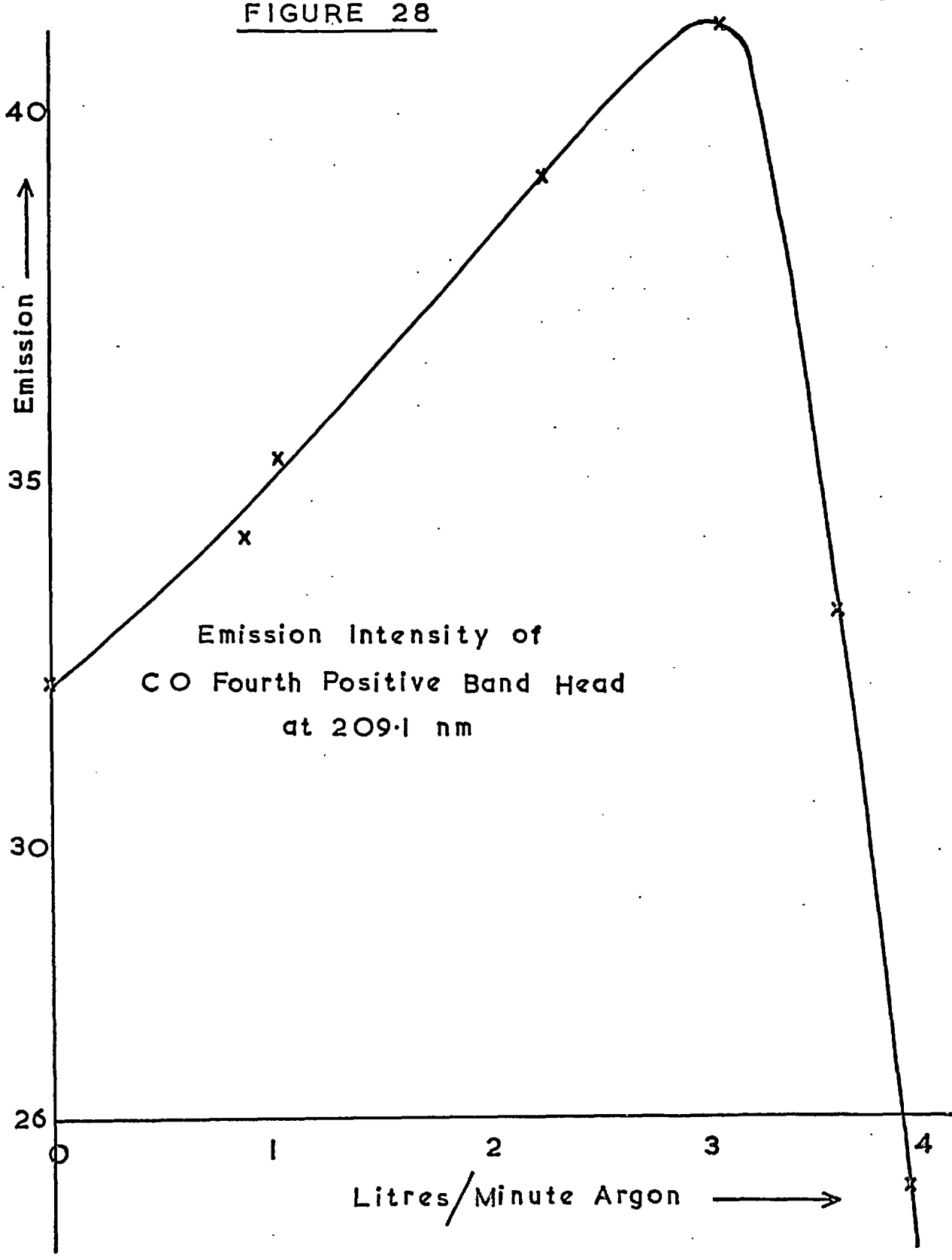

5
3
2
1
Signal
Mg Background
Mg Signal
Background
Fe Background
Fe Signal
Background
0
1
2
3
4
Litres / Minute Argon

burner following dilution of the flame; an effect which must be expected to decrease the observed emission intensity below its true value due to the consequently faster dissipation of the sample. Thus it is felt that, under the conditions described, the results given above undoubtedly show argon to behave in a manner other than that which would be expected of an inert diluent.

The results which were thus obtained for Mg received support from a further series of experiments, the results of which are shown in Figures 26-28. These figures show the variations of the emission intensity and signal to background ratio of the iron 248.3 nm. line, and the emission intensity of the CO fourth positive band head at 209.I nm., with increasing argon flow; these results were all obtained under the same conditions as were described above for Mg. The emission intensities of all the CO fourth positive band heads observed were found to behave in a similar manner during this experiment (see Figure 25); thus the curves of Figure 28 were assumed to be quite general for the purposes of the argument which is discussed in section 6:5 below.

Figure 27 shows the flame background at the Mg 278.0 and Fe 248.3 nm. lines to fall with increasing dilution, in direct contrast to the emission behaviour of the CO fourth positive system. It has not however proved possible to satis-

FIGURE 28


40
35
30
26
Emission
0
1
2
3
4
Litres/Minute Argon
Emission Intensity of
CO Fourth Positive Band Head
at 209·1 nm

factorily account for this observation with the information at present available, and it is not therefore proposed to comment further on this apparent anomaly at the present time.

6:5 Conclusions Drawn from the Chemiluminescence Studies.

The results of Figures 26-28 show the emission intensities of both CO* and M* to depend similarly on the argon flow rate. Such an effect might be reasonably explained in terms of the low quenching cross-section of argon causing a reduction in the rate of collisional de-excitation of CO*; against such an argument, however, is the fact that, in the absence of any (absolute) pressure dependent reaction(s) within the p.r.z., the experimental procedure adopted should require the collision frequencies of the various species within the p.r.z. to be (at least approximately) invarient; thus any collisional de-excitation processes affecting CO* would be expected to be correspondingly unimportant. In addition, it must also be pointed out that such an explanation of the curves of Figures 26-28 would require these curves to follow a Stern-Volmer plot (55), particularly since the low pressures used here virtually ensure the validity of the Stern-Volmer approximation. Inspection of Figures 26-28 suggests this not to be the case, and thus it is concluded that any explanation of these curves in terms of coll-

isional deactivation effects must be regarded as being correspondingly unlikely.

That the results observed are indeed due to chemiluminescence, and are not confused by simultaneous thermal emission, is shown by the high energy levels of the observed transitions (II7); i.e. at Mg 285.2nm. (ground state to 4.35 eV) and Fe 248.3 nm. (ground state to 4.99 eV), in comparison with the Mg 278.0 nm. line (2.72 to 7.I7 eV).

In view of these arguments, it is suggested that the above results may be plausibly explained by assuming that M^* and CO^* both derive their excitation energy from some common source, which may thus account for their apparent mutual dependence, and that this common source is itself sensitive to the presence of an 'inert' diluent such as argon.

The formation of unstable, excited transition state complexes during initiation of the chain reactions occurring in the p.r.z. was discussed in Chapter One, where it was pointed out that such species should have a very high excitation energy available; furthermore, they must excercise considerable control over the reaction sequences occurring in the p.r.z., and hence over the relative concentrations of the species existing there. It is therefore proposed to identify such transition state intermediates with the (chemiluminescent) excitation source, common to M^* and CO^*, mentioned above.

The origin of the sensitivity of the common excitation

source to argon can perhaps be explained in the following terms. Firstly, argon is assumed to have the capacity to act as a third body during, or immediately after, the formation of the transition state complex, in a similar manner to that suggested by the shock tube experiments of Givens and Willard, and others (II8, II9). Whether the interactions involved under the present conditions can justifiably be considered in terms of the 'energy transfer' and 'atom chaperone' models (I20) derived to describe the shock tube data is uncertain; however, no matter what form of interaction is in fact ultimately considered, it seems reasonable to suppose that at least some of the internal energy of the transition state complex can be removed by such a mechanism, thus leading to a corresponding increase in its chemical lifetime; a process which, in view of the stability of the C-O bond, can then be expected to favour the formation of (relatively stable) CO* as a subsequent reaction product. Thus by acting as a third body, argon may offer an alternative energy sink to those already naturally existing in the p.r.z.; a process then leading to an increase in the efficiency of the flame in generating CO*.

Such an explanation can simultaneously explain the sensitivity of chemiluminescent emission from the p.r.z. to the presence of argon, as well as the occurrence of the linear

regions of Figures 26 - 28, and is at the same time in accordance with the observations of other workers who have related the occurrence of CO^* in the flame to the intensity of the chemiluminescent emission of foreign atoms also present (53, 54). It must, however, be pointed out that the mechanism of the actual subsequent excitation of foreign atoms cannot hence be deduced, since it may involve direct excitation by the transition state complex, or may occur through the agency of the argon diluent, or <u>via</u> CO^* as already suggested (53, 54), or, as seems most reasonable, by a combination of these processes; the nature of the actual mechanism does not alter the form of the correlations between Ar, M^* and CO^* already noted, and cannot therefore be immediately determined.

Although the above suggestions provide a plausible explanation to account for the effect of argon on chemiluminescent emission from the p.r.z., a number of defects are also apparent in the argument. Firstly, although the linear portions of the curves of Figures 26 - 28 can be explained, no certain reason can be given for the occurrence of the maxima, and subsequent sharp fall, shown by these curves. Secondly, and perhaps even more seriously, a monatomic species such as argon can only accept either translational or electronic energy; thus, since the conversion of electronic or vibrational to translational energy is an extremely inefficient process, at least over the

limited time intervals available here, it might be assumed that the process of acting as a third body would lead to electronic excitation of the argon; a deduction suggesting that argon emission should be observed from the p.r.z. of the diluted flame. Such emission has not been observed in practice, although observation was experimentally restricted by the spectral characteristics of the IP 28 A photomultiplier, which permitted only an examination of those regions of the argon spectrum which were inherently obscured by the background radiation due to species such as CH, C_2, OH etc.

The discussion given above clearly touches only lightly on what is considered to be a relatively complex phenomenon. Incomplete though the conclusions are however, the work is nevertheless of considerable interest in that it illustrates the unique potential of the low pressure flame when combined with the tungsten loop technique for the investigation of chemiluminescent excitation within the p.r.z. For instance, investigations carried out in conventional atmospheric flames are severely limited by the small physical size of the p.r.z., making its spectroscopic examination correspondingly difficult. Furthermore, the results of Chapter 3 show that chemiluminescence studies carried out in such atmospheric flames following sample introduction by the usual method of solution nebulisation must give results which are seriously biased by the variable atomisa-

tion efficiency of the p.r.z.

The use of low pressure flames can overcome the difficulties of spectroscopic examination experienced at atmospheric pressure, as well as reducing the quantitative significance of e.g. collisional de-excitation processes. However, the examination of the chemiluminescent excitation of foreign atoms within the p.r.z. of low pressure flames has hitherto been restricted by the necessity of introducing such atoms as vapour phase samples (Chapter 3), in order to overcome the low atomisation efficiency of such systems.

For these reasons therefore it is considered that the experiments described above, although far from complete in terms of both the results obtained and of their interpretation, are of value in that they lead to a general technique permitting the chemiluminescent excitation of foreign atoms within the p.r.z. of any pre-mixed flame to be studied without suffering the experimental difficulties, characteristic to this region of the flame, which have hitherto been encountered.

CHAPTER SEVEN

7:I A Self-Contained Low Pressure Burner.

It was considered that the results discussed in the preceding chapters were sufficient to demonstrate the potential analytical advantages to be gained by the use of low pressure flames, and hence to suggest that some practical application of such systems might ultimately be envisaged. It was however also felt that the existing equipment was rather impractical, involving as it did a number of highly specialised componants, both for the construction of the pressure vessel, and in the form of the two high capacity rotary pumps required to maintain the vacuum. The pumps in particular are expensive items; a point of some importance, since the corrosive nature of the flame exhaust gases must result in a severely restricted pump life. For these reasons therefore an attempt was made to develop a burner which could support a low pressure flame without the aid of external, mechanical pumps, and which would if possible be sufficiently compact to enable it to be used in conjunction with any conventional spectroscopic equipment.

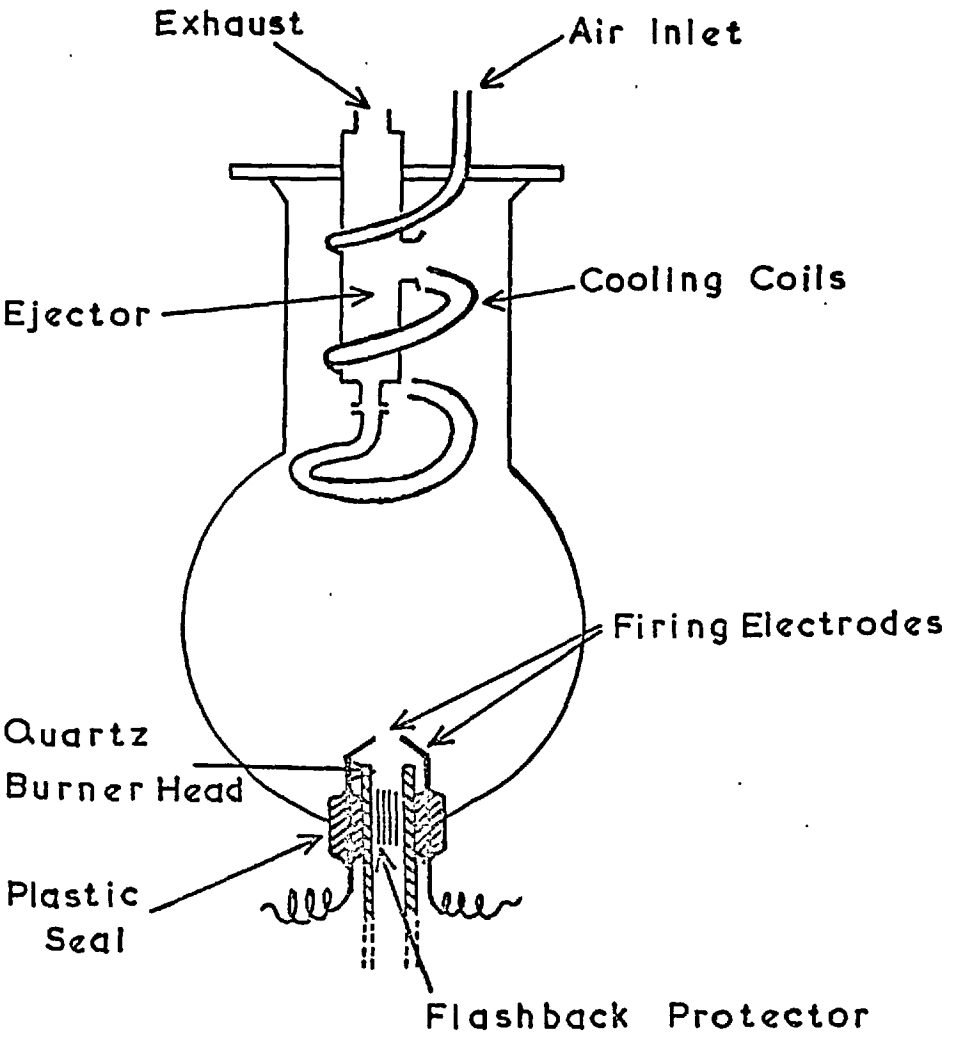
A number of possible techniques for achieving such an effect were examined, of which the most promising was considered

to be the use of an ejector, to pump out a small pyrex pressure vessel. The ejector used was an IM2 / 32 / 24, manufactured by W.S.A. Engineering Ltd.; this was mounted in the neck of an ordinary 2 litre pyrex flask, which acted as the flame pressure vessel. Air was fed to the ejector inlet through a series of copper coils mounted within the neck of the flask (see Figure 29); these coils also served as a heat exchanger, to cool the flame exhaust gases and prevent damage to the venturi surfaces of the ejector.

A suitable burner head was tested on the conventional low pressure flame equipment, and then sealed into the base of the flask; at the same time, two electrodes were sealed alongside the burner head, to permit ignition by means of an electrical discharge in the usual way. An initial series of experiments showed that the new burner could be expected to reach a pressure of a little under 300 Torr. while pumping flame exhaust gases, and the original equipment was then used to determine the ideal C_2H_2 and N_2O flow rates for immediate ignition at this pressure; a necessary precaution, since the very low reserve of pumping capacity of the ejector, together with the high operating pressure of the burner, represented a dangerous combination in the event of delayed ignition of the flame.

The new burner was found to operate quite successfully, and proved capable of maintaining a C_2H_2 / N_2O flame at an

FIGURE 29


Exhaust
Air Inlet
Ejector
Cooling Coils
Firing Electrodes
Quartz
Burner Head
Plastic
Seal
Flashback Protector

absolute pressure of 290 Torr. No serious overheating problems were apparent, despite the comparatively restricted physical size of the pressure vessel, presumably due to its relatively thin walls, which permitted correspondingly efficient convective cooling to occur.

It was found that the continuous pumping action of the ejector gave a very stable flame, in comparison to its rather (mechanically) noisy counterpart observed in the conventional equipment (see Chapter 2). One disadvantage of the new system however was that it vented appreciable quantities of both HCN and NO_2 straight into the atmosphere (a problem avoided with the original equipment by attaching a fume extractor to the pump exhausts).

The main purpose of this experiment was to determine whether the flame could be made to heat the ejector pumping gas (air) to the point where an appreciable improvement of the pumping efficiency of the system could be obtained by passing the effluent gas through a condenser, as is done for example with commercial steam ejectors. Such a modification did not however appear to be practicable, since the low efficiency of the ejector demanded a correspondingly large volumetric flow rate of the pumping gas; thus the temperature of the effluent gas was only slightly greater than room temperature. It was therefore concluded that the lowest pressure which could be

attained by a system such as that described would be governed by the performance of the ejector used, and could not be enhanced by making use of the extra heat energy available from the flame.

The best ejectors at present available can maintain a minimum pressure of about 250 Torr. when venting against atmospheric pressure[I], due mainly to jet saturation effects, leading to 'choking' of the venturis, beyond a certain limiting flow rate of the pumping gas; a limitation which would appear to restrict the applicability of the design of low pressure burner discussed above. However, in a further series of experiments, it proved possible to construct an ejector which could maintain a high pressure gradient while operating with a very low pumping gas flow rate; an effect achieved by introducing a suitably varying degree of curvature to the venturi surfaces. By strapping this ejector to the conventional W.S.A. IM2/32/24, an absolute pressure of I20 Torr. was attained, although only at the expense of a severe reduction in the pumping capacity of the system.

Thus it is concluded from the experiments described above that the somewhat cumbersome and expensive apparatus hitherto used to maintain a low pressure flame is not an obligatory feature of the technique, and that, provided it is not required to work at very low pressures, a burner such as that described in this section of work can provide a viable alternat-

[I] Courtesy of W.S.A. Engineering Ltd.

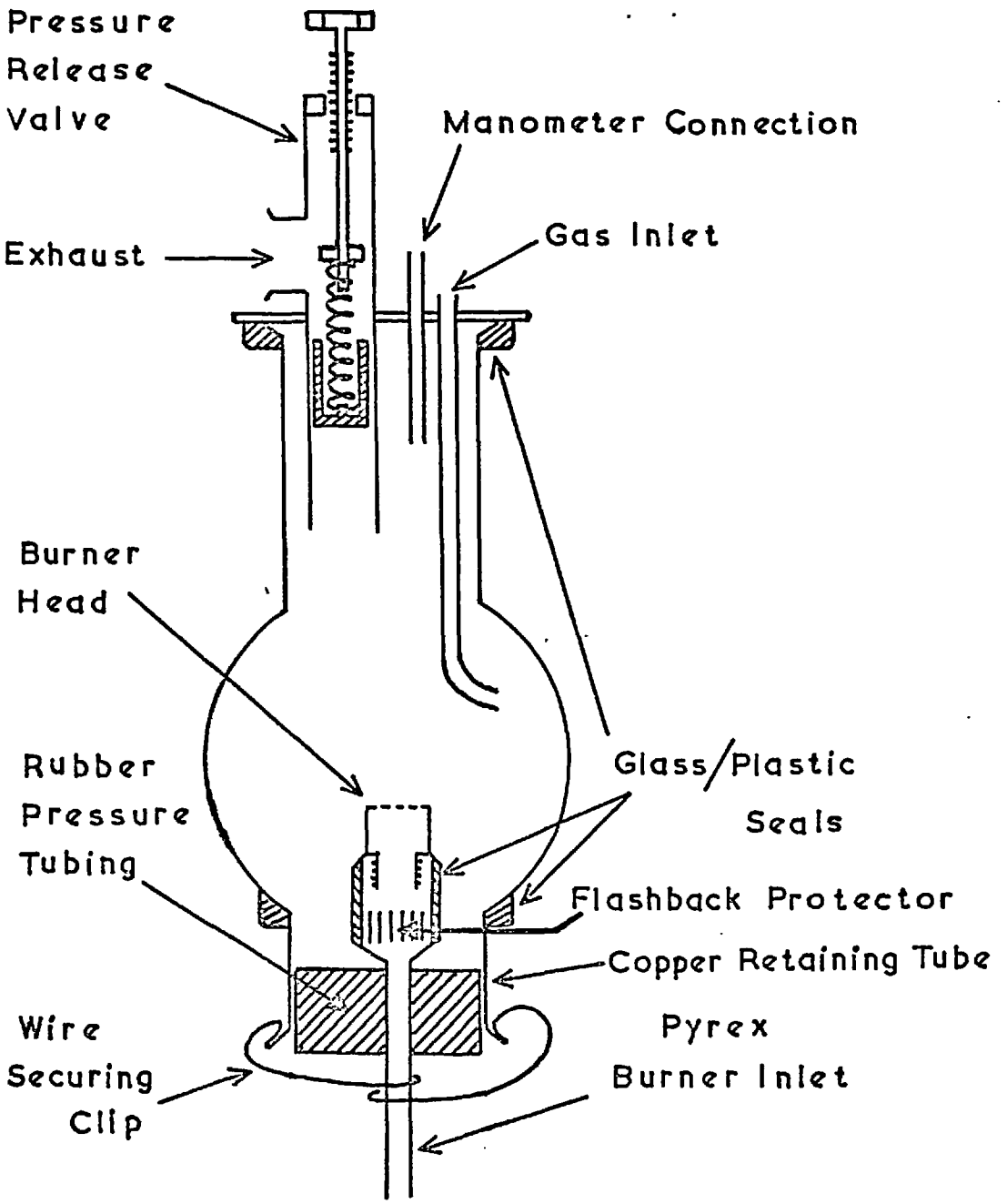
ive to the conventional equipment used upto the present time.

7:2 The High Pressure Burner.

The work discussed in Chapter 2 suggested that sample atomisation efficiency at the base of a flame, following sample introduction by solution nebulisation, was strongly affected by the molecular collision frequency, and hence by the pressure, of the flame, and it was therefore decided to examine the practicability of nebulising a sample solution into a flame burning at a pressure greater than atmospheric. Analytically, high pressure flames have never received any serious attention, although, as mentioned in Chapter One, a certain amount of work has been carried out on such systems by engineers interested in the problems associated with internal combustion engines; thus an examination of the possible analytical uses of high pressure flames represents an unexplored, and correspondingly interesting, field of study.

The equipment used for these experiments is shown in Figure 30; the burner consisted of a conventional air-acetylene head, which was mounted in the base of a 5 litre pyrex flask as shown. The neck of the flask was fitted with a gas inlet, to both cool the vessel and also to provide a controlled flame atmosphere, and a pressure release valve (Figure 30). The burner

FIGURE 30


Pressure
Release
Valve
Manometer Connection
Exhaust
Gas Inlet
Burner
Head
Rubber
Pressure
Tubing
Glass/Plastic
Seals
Flashback Protector
Copper Retaining Tube
Wire
Securing
Clip
Pyrex
Burner Inlet

was operated by lighting a pre-mixed air-acetylene flame within the atmosphere, in the usual way, and then pushing the burner firmly into position in its housing at the base of the flask; the atmosphere within the flask was maintained during this procedure by pumping air down the gas inlet. The burner head was then fastened in position with wire clips, and the flame pressure increased as required by gradually closing the pressure release valve.

Solution nebulisation was carried out by the use of a conventional Techtron nebuliser, but in order to balance out the effect of the varying burner pressure the sample solution was placed within a tube connecting the waste outlet of the nebuliser to the capillary inlet. The solution was thus held in a sealed system, in which the pressure across the capillary was maintained at a constant value governed by the normal venturi action of the support gas flow; thus violent fluctions in solution aspiration rates with varying flame pressure were avoided.

Using this equipment, it was found that a fuel rich air-acetylene flame could be satisfactorily maintained up to a pressure of about IO p.s.i. above atmospheric. A normal diffusion flame could be sustained by passing air down the gas inlet, or alternatively the flame could be readily separated by substituting nitrogen for the air. If required, the atmosphere within

the flask could be enriched with oxygen, or any other supporting gas (e.g. the experiments of Chapter 6:I suggest N_2O might be used with advantage).

The only experiment carried out with this equipment was the measurement of the variations of sodium emission intensity, at 589.0nm., with pressure. It was found following aspiration of a 50 p.p.m. sodium solution that over the pressure range 0-8 p.s.i. above atmospheric, an increase in the emission intensity occurred, in accordance with expectation. This increase was attributed to a temperature effect (I7), since the emission was viewed at a point sufficiently high in the flame to permit the variable atomisation effects mentioned in Chapter 2 to be neglected; the magnitude of the increase of emission intensity corresponded to a total increase in the flame temperature of about $60^{o}C$.

No further work has been attempted with this burner, largely because of the flame turbulence, caused by the flow of the gas controlling the flame atmosphere, which was experienced. This effect caused a number of difficulties in the prolonged operation of the burner, and the system was accordingly redesigned, in the manner mentioned below, to permit the difficulties which were encountered during the operation of this prototype to be overcome.

7:3 The Variable Pressure Burner.

The similarity in the design of the two previous burners suggested their combination, to give a single burner whose pressure could be varied between e.g. I/3 and 2 atmospheres. A variable pressure burner of this type is accordingly under construction at the present time, although it has not yet reached completion. In the proposed design of this combined unit, the cooling gas for high pressure operation is passed in a laminar flow down the walls of the pressure vessel; thus by also placing the pressure release valve immediately above the burner head, it is hoped to avoid the region of turbulence around the flame, observed with the original design.

The new burner is designed to be fitted with a tungsten loop attachment, for use at the low pressure end of the range if small sample operation were to be required. However, the main application of such a system is envisaged as lying in its capacity to provide an optimum flame pressure for analytical work following conventional solution nebulisation, and perhaps also in the degree of flame atmosphere control which could also thus be provided.

CHAPTER EIGHT

The work considered in the previous seven chapters is felt to lead to the following conclusions.

Firstly, low pressure flames have been found to be inherently inefficient in generating a vapour phase atomic population from a solid sample, due to the low energy density of the flame, and in order to overcome this effect it is necessary to use a correspondingly efficient means of sample introduction. The method of carrying the sample into the flame on a metal loop, adopted in the present work, is considered to be the only practicable general technique available for atomising a solid sample into a low pressure flame, even though this method automatically carries with it the disadvantage that only a very short time interval is then available for the examination of individual samples.

Secondly, low pressure flames have been found to have the analytical advantage that they offer a very chemically reducing environment, which is an attribute of considerable value when dealing with those elements which are normally susceptible to the formation of refractory oxides. This advantage is enhanced by the apparently high surface temperature acquired by a metal

loop placed within a low pressure flame, which permits the volatilisation of solid refractory oxide samples into the reducing environment of the flame to occur in the first place. The technique described thus leads to an analytical method suitable for handling small amounts of refractory samples; a development which is considered to be of particular value in view of the scarcity and the limitations of comparable existing techniques.

Thirdly, the development of a burner capable of supporting a low pressure flame without the use of external, mechanical pumps, and which is in consequence small enough to be used in conjunction with the standard instruments available for analytical flame spectroscopy, increases the practicability of the tungsten loop technique, to the point where it might reasonably be advanced as a viable analytical method.

Finally, the work of Chapter 6 has shown the effectiveness of using pressure as an extra variable, to control the physical parameters of a flame. This effect was utilised during the present experiments both to expand the flame, to permit easier spectroscopic examination, and to counteract the physical effects of diluting a flame with an inert gas; this permitted some observations of chemiluminescent excitation to be made without encountering the difficulties which have tended to handicap such work when carried out within the confines of the

atmosphere.

Although the work discussed has been sufficient to show some of the potential advantages of low pressure flames, the experiments are far from complete. A number of ways in which the work might usefully be extended further are discussed below.

Chapter 6:3 briefly mentioned the possibilities of using a very low pressure C_2H_2 / O_2 flame for the analysis of highly refractory samples, such as uranium salts. Experiments in this direction are felt to be worth pursuing, e.g. by making use of chemical effects on the loop surface, also mentioned in Chapter 6 in connection with the control of sample pulse length. One possible chemical interaction which might be worth investigating in this context is that of iodine, which, by analogy with the van Arkel process of extraction metallurgy, might be expected to promote the atomisation of uranium and similar elements.

The experiments discussed in this work were restricted by the limitations inherent in atomic emission spectroscopy, and thus it is felt that there is considerable scope for extending the present observations by using other methods of spectroscopic analysis. In particular, the potential of atomic fluorescence spectroscopy (A.F.S.) in combination with the present techniques might be worth investigation; A.F.S. could eliminate

the effects of flame temperature on sample emission and of flame background on instrumental response, which proved to be rather troublesome in the present work, without suffering from the reduced optical density of the low pressure flame to the same extent as atomic absorption spectroscopy.

The chemiluminescence studies of Chapter 6 do no more than commence the study of the processes occurring in the reaction zone of a diluted flame, and further work could perhaps be usefully continued in the same direction. In particular, the effect of other inert diluent gases, with both higher and lower first excited states than argon could be studied, perhaps together with the effect of molecular diluents, offering a wider range of lower energy levels. Such experiments would be expected to clarify the nature of some of the processes occurring in the p.r.z. of a diluted flame, representing knowledge of value to both low pressure and atmospheric flame studies.

Finally, a few suggestions will be given on the possible analytical future of the recently developed variable pressure burner. It is felt that, in order to make full use of this unit, it would be useful to develop a burner head capable of maintaining a given flame over a very wide pressure range; even if this did not prove practicable however, the use of the variable pressure burner must in any case permit experiments to be carried out to determine the optimum pressure for analytical work following

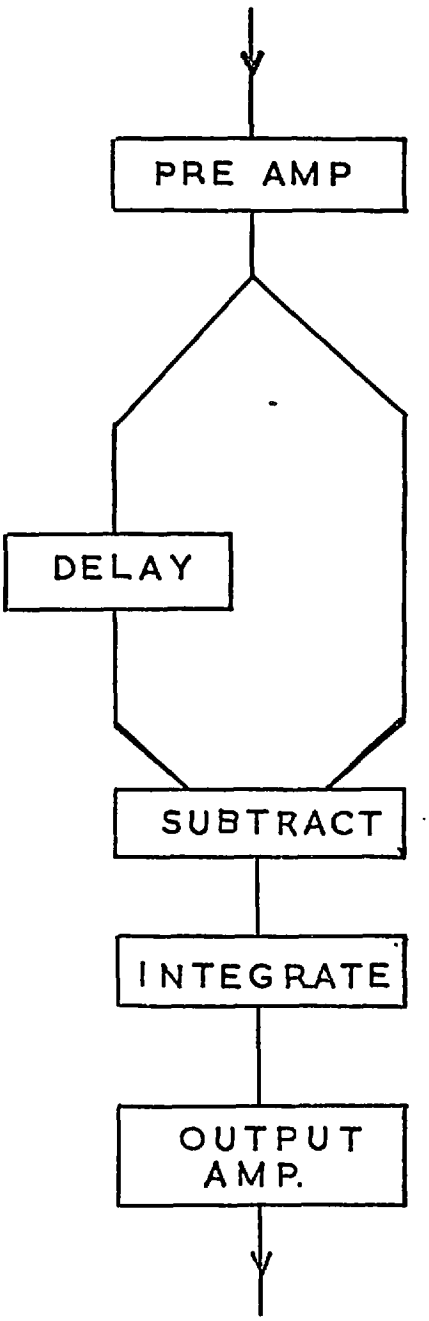
conventional solution nebulisation; a determination which has hitherto never been attempted. In addition, and by permitting pre-mixed flames to be supported at pressures in excess of atmospheric, the variable pressure burner opens up a new and completely unexplored field of analytical flame spectroscopy; a field of study which must therefore be expected to ultimately yield results of corresponding analytical significance.

APPENDIX

The use of the tungsten loop technique entailed measurement of sample emission signals with pulse lengths down to a few milliseconds duration; a requirement which lead to two immediate problems in handling the associated electrical signals. Firstly, an integrator was needed which could operate in the presence of a D.C. background, due to the flame; thus it was considered necessary to use a circuit which would reject the 'D.C.' component of the photomultiplier output, to prevent immediate grounding of the amplifier due to integration of the flame background. Secondly, in order to integrate the emission pulses over their lifetime without suffering an unduly poor signal to noise ratio, it was necessary to use an amplifier with a correspondingly short integration time; a difficult demand to meet, since it requires a circuit which can automatically recognise a 'single event' transient without external control.

The operating principles of the circuit built to meet the above requirements can be understood from the block diagram of Figure 3I . The output from the pre-amplifier is fed into two identical channels, one of which goes through an electrical delay circuit. The voltages on the two channels are then subtra-

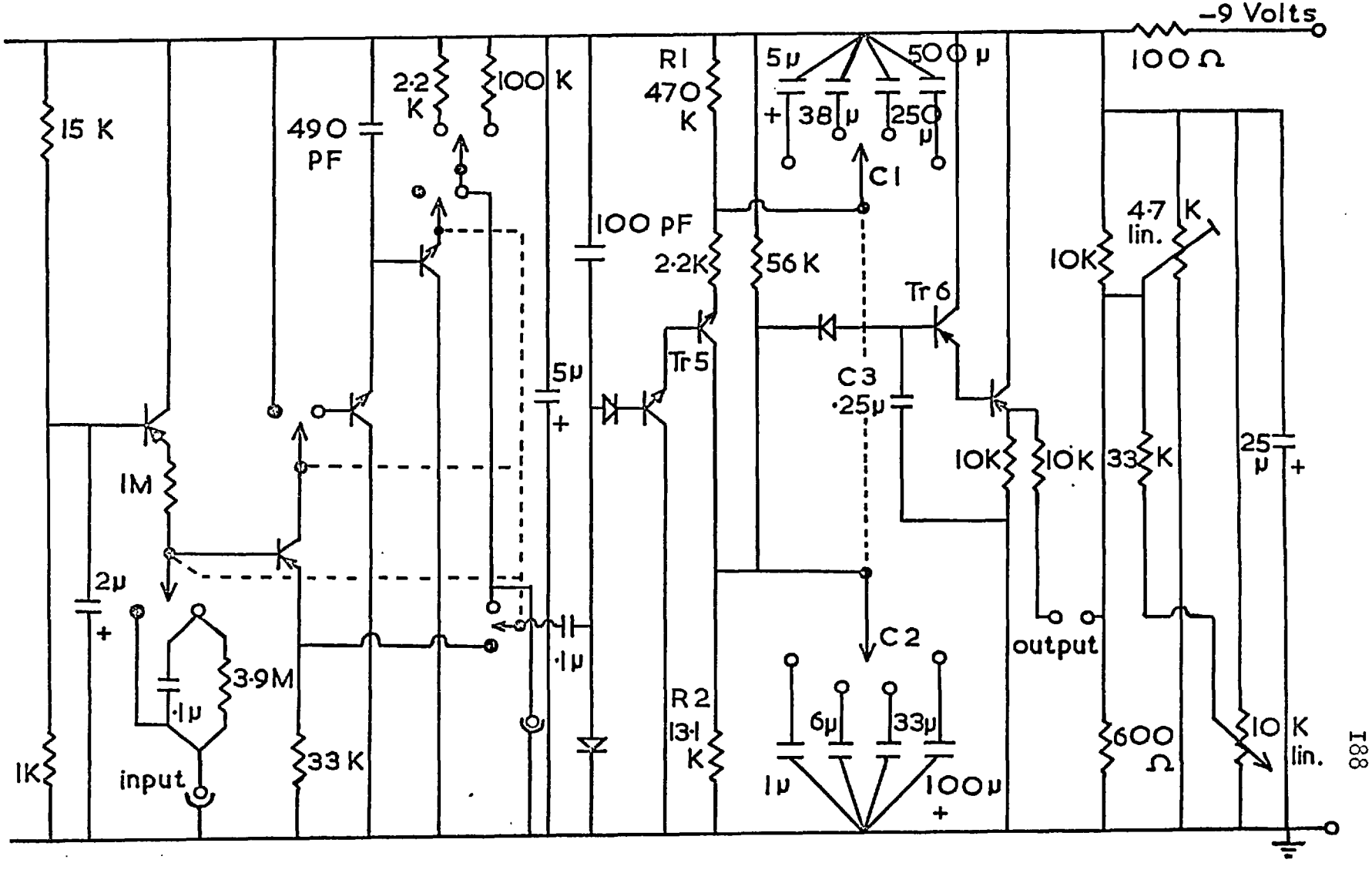
FIGURE 31



cted, integrated and fed to the output amplifier. For a D.C. signal, the delay circuit makes no difference, and the voltage across the integrator is thus automatically adjusted to zero independently of the magnitude of any D.C. background which might be present. In practice, by using a suitably small delay time, the circuit can similarly be made to cancel out both long-term drift in the D.C. background, and also low frequency A.C. noise; a useful attribute in the present work, in view of the noise characteristics of the low pressure flame mentioned in Chapter 2. However, a fast transient signal, no matter when it arrives, throws the two inputs to the 'subtract' unit out of balance; thus such a transient can be passed on to the integrator, and the integrated output displayed as required without the necessity of using external control of the integrator.

The equivalent circuit to the block diagram of Figure 3I is shown in Figure 32. The first stages simply act as a pre-amplifier, feeding the integrating stage formed by C2 and Tr5. In the presence of a background signal, CI charges up to a voltage governed by the amplitude, frequency and rate of arrival of the background pulses at the base of Tr5, and by its rate of discharge through RI. Thus by trying to hold the emitter voltage of Tr5 at the background level, CI correspondingly reduces the background current through Tr5, and hence the current fed to the integrating capacitor C2; thus CI acts as the 'delay', and

FIGURE 32


-9 Volts
100 Ω
15 K
490 PF
2·2 K
100 K
R1 470 K
5μ
500 μ
+ 38 μ
250 μ
C1
100 pF
2·2K
56 K
4·7 K lin.
10K
Tr 6
Tr 5
5μ
C3 ·25μ
10K
10K
33K
25 μ
1M
2μ
3·9M
·1μ
·1μ
input
33 K
1K
R2 13·1 K
C2
6μ
33μ
1μ
100μ
output
600 Ω
10 K lin.
I88

and Tr5 as the 'subtract', stages of Figure 3I .

By acting as the collector load of Tr5, C2 integrates the total collector current over a time interval governed by the values of R2 and the input impedance offered by Tr6; thus C2 corresponds to the integrator of Figure 3I . The integrated output across C2 is fed to the peak height measuring circuit formed by C3 and Tr6,7; a procedure necessitated by the fact that, ideally, C2 goes through its charge / discharge cycle in a time interval comparable to the signal duration time; i.e. considerably faster than the response time of conventional recording equipment.

C2 can eventually discharge through R2 and Tr6, so that after handling one transient signal the circuit will automatically re-set itself. The D.C. compensation given by Tr5 / CI means that the D.C. output of the integrator is invariant, and thus provides an unchanging baseline when fed to a recorder. Thus once set up, the integrator requires no adjustment at all during actual operation.

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