

SAMPLE PRESENTATION IN ANALYTICAL
SPECTROSCOPY

by

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ABSTRACT

The design and evaluation of some sample presentation systems for analytical optical spectroscopy are described in this thesis.

The potential of photoacoustic spectroscopy (PAS) for the direct examination of materials in the solid phase is assessed for the rapid quantitative determination of the β -adrenergic receptor blocker drug, propranolol, and for the determination of fat in spray dried milk powders. Significant improvements in sample preparation time may be expected in relation to more traditional methods of analysis.

Studies have been carried out for the improvement of sample introduction systems for inductively coupled plasma optical emission spectroscopy (ICPOES). A novel electrochemical method was investigated for on-stream pre-concentration of trace analyte species by electro-reduction onto a glassy carbon wall-jet electrode prior to nebulisation. The feasibility for simultaneous multi-element analysis is discussed.

The performance of dry-aerosol electrothermal vaporisation techniques are reported for the introduction of microlitre samples into the ICP. Filament in furnace vaporisation (FIFV) is critically examined and a preliminary study indicates that severe prevaporisation losses of analyte may occur. A graphite rod vaporiser (GRV) has been adapted for the direct assay of slurries of mineral components in some pharmaceutical preparations.

Modification of the plasma discharge properties when employing dry-aerosol sample introduction is investigated. The electron density in the plasma was determined in relation to the amount of water entering the discharge, by monitoring the Stark half width of the 486.13nm. $H\beta$ line. Analyte excitation phenomena are discussed for both conventional and miniature plasma discharges.

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'Alright,' said Deep Thought. 'The Answer to the Great Question...'

'Yes.....!'

'Of Life, the Universe and Everything...' said Deep Thought.

'Yes....!'

'Is...' said Deep Thought, and paused.

'Yes....!'

'Is...'

'Yes....!!!!....?'

'Forty-two,' said Deep Thought, with infinite majesty and calm.

THE HITCH-HIKERS
GUIDE TO THE GALAXY
DOUGLAS ADAMS

CHAPTER 1
SAMPLING, SAMPLE PREPARATION
AND INTRODUCTION TECHNIQUES.

1.1 Introduction.

The emergence of spectroscopy as a science is generally considered to have started in 1666, when Newton first experimented with the solar radiation spectrum. Since then it has played an important part in the scientific and technological advances of man and has been of particular benefit to our understanding of solar and astrophysics, plasma physics, spectrochemistry and the structure of matter.

Spectroscopy has also played a crucial role in the development of analytical chemistry, possessing the following desirable characteristics of analytical techniques :-

- (a) Applicable to qualitative and quantitative analysis.
- (b) Specific for many materials.
- (c) Extremely rapid : capability for multiplexed analysis.
- (d) Wide dynamic ranges of calibration obtainable.
- (e) Structural and conformational information obtainable.
- (f) Excellent stability, accuracy and precision.

The disadvantages of spectroscopic techniques are,

- (a) High initial equipment cost.
- (b) Analysis is rarely accomplished on an absolute basis.

It has long been the analytical chemist's objective to be able to analyse any sample in any form. The excellent spectrochemical techniques which are becoming available may allow this objective to be realised, but their full potential has not yet been exploited because efficient, rapid and reproducible sample preparation and introduction systems have still to be developed. This is now recognised by analytical chemists as an area which requires urgent attention.

The term sample presentation as pertaining to spectroscopic analysis is used to connote the processes involved from the selection of sample for analysis, to the final introduction of sample in suitable form into the analytical instrument and each stage is of crucial importance if an accurate and representative analysis is to be performed. Thus sampling procedures must provide the analyst with a representative sample from the bulk material to be analysed and measures taken to ensure that no deterioration occurs during storage. After the sample has been selected, it must be converted into a form compatible for direct measurement with the particular technique selected. The final process is the mechanical introduction of sample into the instrument.

In all stages of sample presentation, attention must be directed to the significance of sample and standards contamination, especially in relation to the information required from the sample. The criteria which determine the amount of attention that needs to be directed to each aspect of sample presentation will be dependent on the type of analytical technique used. All the techniques used for analytical spectroscopic analysis may be classified into one of two types depending on the physical characteristics of the sample cell. If the sample cell (the site where spectroscopic perturbation of the sample

occurs) is physically compatible with the ambient external environment, the cell can be considered as passive, whilst if the cell is physically remote from the ambient environment, the cell can be regarded as active.

For the passive cell, typified by molecular absorption and fluorescence techniques, no physical conversion of the sample is required after introduction into the instrument before spectroscopic perturbation and measurement, and therefore sample introduction is rarely a problem. However, because no conversion takes place, sample preparation procedures become relatively important.

In contrast, the active cell represents a case where the sample has to be converted into a form far removed from local physical conditions. Examples of active cells are encountered in atomic absorption, emission and fluorescence spectroscopy, where the production of a free population of atoms, usually at high temperatures, is necessary before any spectroscopic perturbation can take place. Therefore the most crucial step in the sample presentation process is usually the sample introduction stage, because the sample introduction system essentially represents the interface between the passive and the active environment. Careful design of the sample introduction system is required if accurate and reproducible data is to be obtained.

1.2 Sampling and Sample Preparation.

1.2.1 Sampling.

Sampling may be defined as "that process by which a

representative portion of the material to be tested is selected for analysis by the laboratory." Unfortunately this has frequently been an area which has received little attention on the part of the analytical chemist. Sampling is, moreover, just as important as the final analytical measurement, because the final result can only reflect the constitution of the sample and if this is not representative, misleading data will be obtained which is difficult to interpret in relation to the bulk material. A comprehensive discussion of sampling will not be presented here because the subject is treated adequately in specialist texts (1,2), and has recently been the subject of a review article (3).

There are four main areas to consider in producing a sample for analysis.

- (1) Identification of the information required from the material and the statistical population required to produce a representative sample.
- (2) Selection and collection of the sample from the bulk material within the constraints offered in (1).
- (3) Reduction of the sample to a size convenient for the laboratory to handle.
- (4) Measures taken to protect the sample from degradation in transit or storage before analysis.

If the sample is to be selected from a large population, it is usually inconvenient to sample every element of that population. Two approaches can be followed in order to obtain a suitable sample. Firstly, a random selection process can be used in which samples are extracted from arbitrary elements of the population. This approach is

not particularly scientific and can lead to distinct bias in the selection process. The second approach is to select samples according to a defined protocol or by using random tables, and selecting the minimum number of samples from the population which will produce reliable information about that population.

Samples are often required for studies in which chemical reactions are followed or are concerned with the dependence of one variable on another. This is called systematic sampling and the same rules apply here as for other types of sampling. Care must also be taken to ensure that any random events or physical disturbances do not affect the composition of the samples, and the timing of the sampling protocol becomes important.

Sampling of material is routinely required from all physical phases, gases, liquids and solids, and standards exist (4) which define how this should be done. Gases rarely present problems in sampling because homogeneity is quickly established and they can be easily collected or transported by pumping. Sampling of liquids is similarly without problems as they can be stirred or mixed rapidly. Homogeneity of the bulk material is extremely important and sedimentation or phase separation effects must always be recognized. The sampling of solids is usually difficult because the extent of homogeneity is often unclear. Solids cannot easily be stirred or mixed and the only way to achieve this is normally to select small batches from spatial locations in the material and to mix these by coning and quartering techniques. If the material is not in powdered or granular form, then it must be crushed or ground before a sample is selected.

After the sample has been selected, it may have to be protected against deterioration in storage or transit before analysis can begin.

This is of most importance where trace species are analysed because deposition of analyte on the walls of the container can occur. To minimise interferences from these effects or from other types of deterioration such as oxidation, steps must be taken to ensure that the sample is stabilised, by adding special stabilising agents or sampling in special containers.

1.2.2 Sample Preparation.

After a representative sample has been supplied to the laboratory, and is ready for analysis, it must be converted to a form which will suit the analytical technique that has been selected. This stage is termed sample preparation. If the sample is a solid, it is usual practice to remove surplus moisture. The method used to achieve this depends on the characteristics of the sample. The most common method is to dry the sample in an oven at 60-105°C, but if the sample is thermally sensitive, alternative techniques must be used such as freeze drying or drying under vacuum in a pistol or desiccator.

Ideally, the next stage of the process would be the introduction of the sample in its natural phase into the analytical instrument. This is usually not possible for solids because sample introduction methods have not been able to compete with the reproducibility and accuracy afforded by the introduction of solutions. The dissolution of solid materials is very time consuming and tedious and allows an opportunity for the contamination of the sample. Another disadvantage is that the concentration of the analyte will be lowered in proportion to the amount of solvent added, which may be unacceptable if trace constituents are being examined.

Solid dissolution may be accomplished by the simple addition of solvent if the solid displays good solubility characteristics in that medium. If this is not the case, dissolution can be achieved by fusion with fluxes such as lithium metaborate, by dry ashing or by wet ashing. Dry ashing requires little operator attention and few reagents, but some materials take a long time to ash and there is also the possibility of losing analyte by vaporisation. It has recently been reported (5) that no less than 25 elements can be lost by dry ashing at 600°C. Alternatively wet ashing in acid, under pressure, requires a minimum of apparatus and is less prone to volatilisation and retention losses. However, large amounts of reagents are required and there is a danger from explosion from certain acid / sample combinations which therefore demands constant operator supervision.

If the sample is a liquid, the amount of time that needs to be spent on sample preparation is minimised, but attention must be directed to the removal of any species if these would interfere with the analytical measurement. This rule will also apply to solutions prepared from solids.

In common with the simplicity of sampling, the preparation of gases rarely produces significant problems owing to the ease of mixing and delivering material in the gaseous state. Consequently sample preparation, as far as gases are concerned, is fairly rapid, although relatively few materials can be conveniently obtained or converted to the gaseous phase.

1.2.3 Preconcentration.

For many determinations, the concentration of the analyte in the

sample is below the detection limit of the technique selected for the analysis. If this is the case, and if no alternative technique is available, the concentration of the analyte must be increased until it is above the detection limit of the analytical technique employed for determination. The process by which the concentration of the species is raised is termed preconcentration and can be considered as a part of sample preparation. In many cases other benefits will also accrue from the selective enrichment of the analyte, such as elimination of interfering matrix and stabilisation of the chemical species. Preconcentration has recently been reviewed for trace element determination in aqueous samples (6,7).

The simplest method of preconcentration of material in solution is to remove substantial quantities of the solvent (8). This particular method is slow and all matrix constituents will also be concentrated. This can lead to severe matrix effects later in the determination.

The most popular method for preconcentration of samples has been the selective removal of the species by the addition of a suitable complexing agent, which will either precipitate the species or enables extraction into another solvent. This method can facilitate removal of the matrix and can often be accomplished at the site of sampling. The most common chelating agents for metals are 8-hydroxyquinoline (9), diethyldithiocarbamate (10) and β -diketones (11).

Ion-exchange substrates may also be used for the selective concentration of trace species. Operator attention is minimised, but the preconcentration times are usually very long. Species may be extracted back into small volumes of solution after collection on the exchanger. Direct determination of ion-exchange resins by flameless

atomic absorption spectrometry has also been reported (12,13).

Numerous other methods have been developed for the selective concentration of trace species. Surface adsorption of metals onto tungsten wire (14,15) or activated carbon (16) has been reported and enables detection limits by graphite furnace atomic absorption spectrometry, for many metals of environmental interest, to be usefully extended down to 0.001 parts per billion levels. Torsi et al. (17) have reported the electrostatic accumulation of mercury in a furnace followed by graphite furnace atomic absorption spectrometry, which enabled them to measure mercury vapour concentrations down to 50ng./m³. Michalik and Stephens (18) preconcentrated 33 elements by electrostatic preconcentration of aerosol on a water electrode. Deposition on graphite substrates electrochemically is also being actively investigated (19,20). In this approach species are deposited on graphite, constituting one part of an electrochemical cell. After deposition has been completed, the graphite is electrothermally heated and the species determined by atomic absorption spectroscopy.

1.3 Contamination.

Contamination effects are as important in spectrochemical analysis as in all other branches of analytical chemistry, and may occur at any stage of the analysis, from the sampling process to the final introduction of the sample into the instrument. It is often the case that the extent or type of contamination is completely unknown and can only be detected by rigorous checking with analytical blanks. Problems with contamination of samples or standards are of most significance when the species to be determined is at the trace or

ultratrace level and any reagents used have to be specifically screened for excessive quantities of these species.

Contamination can occur from a variety of sources (5) :-

- (a) The environment in which sampling or analysis is performed.
- (b) From the container used for storage of the sample.
- (c) From any apparatus in direct contact with the sample at any stage of the analytical determination.
- (d) From reagents used in the analysis.
- (e) From the person performing the analysis.

Careful design of the total analytical procedure to reduce the opportunity for contamination is usually necessary. Reagents should be tested for the species to be determined to ensure that no significant contamination can occur. Much use has been made of the ultra high-purity reagents which have appeared commercially in recent years. The possibility of contamination from borosilicate glassware has been known for a long time and all serious work is best conducted using alternative apparatus made from polythene or polytetrafluoroethylene (teflon). Significant contamination from plastics may however still be possible, as has been pointed out (21) in a study of memory effects from polythene micropipette tips. Minimisation of contamination may also be achieved by conducting analytical work in stringently clean conditions, in cleanrooms and by filtering the air. The last route for contamination is from the person performing the analysis and can occur from the most unexpected sources. Cigarette smoke contains large concentrations of nickel, and substantial amounts of zinc are added to some shampoos. Wedding rings contain proportions of gold, iridium and

platinum and numerous contaminants are present in the polishes used for cleaning benches.

Protection against the possibilities of sample contamination is an integral responsibility for the analytical chemist planning or performing quantitative or qualitative determinations. Without such protection, the results of the determination become totally meaningless and therefore a general awareness of the principles of contamination is of much use.

1.4 Sample Introduction Techniques.

1.4.1 Introduction.

Sample introduction is the process of transporting the sample for determination, into the measurement cell of the analytical instrument. For most of the traditional molecular techniques this has rarely been a problem, because only the macro-optical properties of the sample are required. For atomic spectroscopy this has not been the case as these techniques are concerned with the interaction of radiation with atoms. Efficient methods for the formation of an "atom cell" are therefore necessary and considerable attention has to be given to the design of suitable systems to interface the atom cell to the laboratory environment.

1.4.2 Sample Introduction for Atomic Spectrometry.

The first reported attempt (22) at the introduction of a sample into a spectrochemical atom cell was in 1859 when Kirchhoff and Bunsen

inserted samples melted on platinum wire, into a flame. The following year this procedure was modified (23) by dissolving the sample in acid and inserting a zinc rod into the solution. The sample was released in the effervescent reaction and was transported into the flame in the fuel gas supply. In 1862, Mitscherlich (24) used capillary action to supply samples to the flame by placing one end of a bunch of platinum wires in the sample solution and the other in the flame. The crudity of these methods did not allow the constant or reproducible supply of material to the flame and were therefore of little use for quantitative investigations. The first serious attempt to solve this problem was made by Gouy (25) who developed a pneumatic nebuliser based on an earlier exposition by Morton (26). Such was the success of nebulisation, that it is still the most popular method for sample introduction in atomic spectroscopy.

Nebulisation.

A pneumatic nebuliser is a simple device for converting a liquid into a suspension of fine droplets in a gas stream. This is achieved by positioning two capillary tubes close to each other, one for the gas stream and the other for the solution uptake. The conversion of the liquid into an aerosol is by the so called venturi effect where a pressure drop is created, forcing liquid through the uptake tube, and the liquid stream is then shattered into small droplets by impinging into a high velocity gas stream. The resultant aerosol consists of a dispersion of different droplet sizes. The larger droplets in the stream which cannot be efficiently vaporised, are separated out by passing the aerosol through an expansion or spray chamber. The

mechanism for the production of aerosol is extremely complex and involves both primary and secondary nebulisation effects. The treatment by Nukiyama and Tanasawa (27) in 1939 was the first rigorous mechanistic explanation for the production of aerosol, but some excellent studies by Browner et al. (28,29) are currently being reported, which represent significant improvements to the understanding of the nebulisation process.

Pneumatic nebulisers are basically of two types. When the tubes are placed at right angles to each other, a crossflow nebuliser is formed (30). The tubes may also be aligned one inside the other creating a concentric nebuliser (31). The popularity of nebulisation devices has stemmed from the simplicity of construction and operation, low cost and good uniformity in operation. However the efficiency of sample transport is low (2-10 %) and tube alignment can present problems. Another problem is that the uptake rate of the nebuliser is dependent on the physical properties of the liquid and it is intolerant to solutions of high dissolved solids which tend to block the uptake tube.

The poor efficiency of pneumatic nebulisation stimulated the appearance of ultrasonic nebulisers. These work on a principle proposed by McCubbin in 1953 (32), in which the liquid is exposed to an oscillating transducer plate driven at ultrasonic frequencies. The efficiency of production of aerosol (ca. 20%) is higher than for pneumatic nebulisation and the droplet diameter can be controlled by varying the ultrasonic frequency. However, problems can be encountered with plate fracture, and where desolvation of the aerosol stream is required such as for sample introduction into the inductively coupled plasma, memory effects can be observed, caused by the deposition of

analyte onto the apparatus at the temperatures employed.

Numerous attempts have been made to design alternative nebulisation systems. The breakup of liquids by the direct action of an electric spark was reported as early as 1928 (33) and an electric field has also been employed recently by Savage and Hieftje (34) to improve secondary droplet breakdown of the aerosol stream. Nebulisers have also been designed in which the sample solution is brought into contact with a spinning disc (35) and converted into aerosol by centrifugal action. The most recent and most notable design of nebuliser has been reported by Babington (36). In his design, the effects of sample viscosity and dissolved solids are minimised by allowing solution to flow over the surface of a sphere into which is cut a groove. Nebulisation is effected by passing gas, at high pressure, through a hole in the groove. No clogging effects are observed because the solution does not pass through a narrow capillary, and Babington claimed to be able to nebulise most liquids, including fuel oil and tomato soup. The Babington design has been adapted for use in flame atomic absorption spectrometry by Fry and Denton (37) and for the inductively coupled plasma source by Suddendorf and Boyer (38).

Electrothermal Sample Introduction.

The poor efficiency of nebulisation devices and the limitations of flame spectrometry led to competitive developments in non-flame cells. The sample is commonly atomised by dispensation onto a graphite or metallic surface which is electrically heated to a high temperature. This results in a transient plume of atoms on which

quantitative measurements are made. The heated surface can attain a temperature of ca. 2800K and is usually protected from oxidation by passing an inert sheathing gas over the surface. A graphite furnace was first used by King (39) for the study of transition probabilities, and was developed for use in atomic spectrometry by L'vov (40) and later by Massmann(41). The graphite furnace is an extremely effective atomiser for use in atomic absorption and atomic fluorescence spectrometry (GFAAS, GFAFS). The advantages of furnaces compared with flame cells are :-

- (a) Small amounts ($-\mu\text{l}$) of solution required.
- (b) Vaporisation occurs under reducing conditions, often precluding the formation of refractory oxides.
- (c) The formation of a discrete pulse of atoms allows improvement in detection limits up to two orders of magnitude compared with flame cells.
- (d) Selective separation of the sample from the matrix can be effected by the control of the furnace heating rate.

Graphite is a good medium for electrothermal atomisation as it can be heated to high temperatures (2000 - 3000K), with no degradation in strength and little dimensional change. Graphite atomisers have appeared in a variety of forms including strips (42), braids (43) and discs (44). West and Williams (45) also designed a graphite rod device which could be heated at a faster rate than a furnace and had lower power requirements.

The major disadvantages of graphite are the tendency to form refractory carbides with some elements, and the high porosity which is

especially characteristic of the higher purity grades. These problems have been overcome (46) by pyrolytic graphite coatings (by heating in a hydrocarbon atmosphere), and by using glassy carbon materials. These result in atomisers which have very low porosity, low gas permeability, high sublimation temperature and long lifetimes. Carbide formation has also been reduced by lining the graphite with "inert" metal coatings of tantalum (47) or tungsten (48), or deliberately forming a protective carbide coating prior to use (49).

The early L'vov design of furnace and one proposed later by Woodriff (50), were both characterised by the atomisation into hot gas, and were essentially isothermally operated. In the simpler Massmann design, atomisation was effected soon after the furnace walls had reached the necessary temperature and there was not enough time for the gases to approach equilibrium. This gave rise to interference effects. To retain the simplicity of the Massmann design yet operate it isothermally, L'vov proposed (51) that the sample be placed on a small curved platform which was slightly raised from the walls of the furnace tube. Atomisation from the platform was only achieved when the surrounding gases were fairly hot and resulted in much reduced interference phenomena.

Popularly, electrothermal atomisation has been achieved by resistive heating of the furnace material. However Headridge and Smith (52), used induction heating for the determination of volatile elements by atomic absorption spectrometry. Electrothermal techniques have also been used in atomic emission spectrometry either for direct emission (53) or for introduction of samples into an inductively coupled plasma (54).

The atomisation from graphite surfaces is not without problems,

and most have been discussed. It has also been proposed recently (55) that the graphite can adsorb oxygen which interferes with the atomisation thermodynamics. These problems have led to the appearance of devices enabling atomisation from metallic surfaces. Tantalum (mpt. 2996 °C), molybdenum (mpt. 2620 °C), and tungsten (mpt. 3380 °C) have all been used and have appeared in the form of loops (56), filaments (57), boats (58), wires (59), coils (60) and tubes (61). In all cases these materials have low permeability and the formation of refractory carbides is reduced. Interference effects are observed, however, because these metallic surfaces are not completely inert. Thus McIntyre et al. (62), observed interference in determination of cobalt, nickel and copper when tantalum was used for atomisation. Generally, metallic atomisers have not been as successful as graphite because they cannot be heated to such high temperatures, and the metallic surface soon becomes pitted and brittle. For this reason, atomisation from metals has usually been confined to certain specialised applications. The combination of graphite and metallic atomisers has lately been attempted by Garnys and Smythe (63). Their device, which they termed filament in furnace atomisation (FIFA), consisted of a tungsten wire containing several small coils which were sequentially passed through small holes in the graphite furnace. This device allowed semi-automated operation and permitted ashing and desolvation outside the furnace. It was successfully used for the determination of lead in blood and hair samples with claimed analysis rates three times faster than conventionally operated furnaces.

Hydride Generation.

The generation of volatile hydrides of some elements which exhibit poor sensitivity in flame spectrometry, is now commonly used. The method was first used for the determination of arsenic and selenium in 1971, the hydrides being generated from a zinc-hydrochloric acid reduction couple (64). Since then, acid reduction has largely been displaced in favour of sodium borohydride which produces more rapid reduction. Antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin have all been determined by this means, in most cases with dramatically improved detection limits. Hydride generation techniques have also been reported for sample introduction for atomic fluorescence spectrometry and inductively coupled plasmas (65) and has recently been reviewed (66).

The advantages of hydride generation compared with traditional methods of sample introduction, such as nebulisation are that the elements may be determined more sensitively (up to two orders of magnitude), because the sample introduction stage is very efficient. Additionally, the formation of hydride allows the element of interest to be almost totally separated from the matrix. However, some inter-element interference has been found, by the reduction of other elements (copper, silver, gold, nickel) present, and because a chemical medium is used, reagent contamination of the sample becomes a problem.

Introduction of solids.

The direct introduction of solids or slurries is extremely desirable, because this is the natural phase of many materials and

dissolution procedures are laborious and lead to loss of sensitivity. Unfortunately the direct analysis of solids has never been very successful because the attainable precision is poor, a factor which is exacerbated by the difficulty in accurately dispensing solid samples, and by inhomogeneity problems. Several ingenious methods have been described which attempt to resolve these problems. The most obvious route was to vaporise the solid from a graphite atomiser and was used for the determination of copper in fingernails (67) and lead in leaves, seaweed and mussels (68). The direct introduction of trace elements in metals, using furnaces, for atomic absorption spectrometry has been reviewed by Headridge (69) and the direct analysis of geological and industrial materials has also been discussed by Langmyhr (70). The introduction of solids by vaporisation with a laser has been extensively reported and has been used for the introduction of solids in atomic absorption (71,72), in microwave plasmas (73) and in inductively coupled plasmas (74). The introduction of slurries, which are suspensions of solids in liquid media is somewhat easier to accomplish. The determination of trace elements in titanium dioxide slurries by atomic absorption spectrometry has been discussed by Fuller et al. (75). Ebdon et al. (76) were able to analyse coal slurries by using a modified Babington nebuliser.

The inductively coupled plasma is an excellent excitation source for introduction of solid samples, because the temperatures are high enough to reduce interferences from the matrix. Methods for the introduction of solid samples into this source would therefore appear to be particularly promising.

1.4.3 Hybrid Techniques.

The interfacing of two or more analytical techniques will often produce a system where the advantages of one technique will complement the other. The cost of such systems is usually high but are always worth considering in terms of analytical performance.

Multiple techniques have been used for the introduction of samples for spectrochemical analysis, where one technique is used for the introduction of sample into another. Perhaps the most documented is the linking of chromatography systems with spectroscopic systems, which have been used for separation and introduction of components prior to analysis by atomic absorption (77), microwave plasma (78) and inductively coupled plasma (79) spectrometry. The versatility and high temperature of the inductively coupled plasma have made this source a convenient atom cell for atomic fluorescence (80) and atomic absorption (81), and the ease of ion formation has led to the use of the inductively coupled plasma as a source for mass spectroscopy (82).

1.4.4 Sample Introduction in Molecular Spectroscopy.

Introduction of samples for molecular spectrometry has never been a significant problem and the limitations met have largely been a function of the technique. Molecular techniques rely on the transmission through, or emission from, the bulk sample, and therefore sample preparation is of more significance to the reliability and reproducibility attainable, particularly because liquids and solutions are the most common media for analysis. The direct analysis of solids is not easy by molecular spectrometry. Solids may be investigated by

fusing with alkali halides (83), for infra red spectrometry, or by using reflectance methods, but both of these approaches are poor for quantitative applications. The recent emergence of photoacoustic spectroscopy of solids may represent a significant advance for sample presentation in this field of application.

1.5 Scope of this work.

The research work which is presented in this thesis has been concerned with some investigations of sample presentation for two of the newer analytical spectrometric techniques. Both of these novel techniques have had a dramatic impact in their respective areas of application in molecular and atomic spectroscopy.

The first is photoacoustic spectroscopy (PAS), an example of a passive technique, which may be used for molecular studies. One of the advantages of PAS is that it has been specifically adapted for the study of materials in the solid phase, and complex sample preparation procedures for many materials are not required. The elimination of extensive sample preparation also means that analysis may be achieved without the destruction of the sample. In PAS, the detector is only responsive to the radiation absorbed by the sample. For this reason the effects of scattered and reflected radiation are minimised. PAS therefore represents the unusual situation where the technique has simplified the problems of sample presentation rather than the other way round. It has remained necessary to demonstrate that PAS is suitable for quantitative studies of solids and relevant studies which may show this to be true are presented in chapters 2 and 3.

Another technique that has earned great popularity, is

inductively coupled plasma atomic emission spectroscopy (ICPAES). This technique which makes use of an active sample cell, may be used for the quantitative determination of nearly every element in the periodic table. The ICP is created by coupling high frequency power into a vortex controlled stream of partially ionised gas. The stable plasma which is formed has a temperature of between 5000 - 10000K. These high temperatures enable extremely low detection limits to be obtained with almost total freedom from matrix interference. Additionally, calibration linearity is possible up to five or six orders of magnitude, because the plasma is effectively optically thin for many species. These characteristics have meant that ICPAES may solve many of the problems encountered in atomic spectroscopy, but has been restricted because satisfactory sample introduction systems are still not available.

The results exhibited in the second part of this thesis have been concerned with investigations of new and more efficient methods of sample preparation and introduction for use with ICPAES which it is hoped will make a significant contribution to the development and exploitation of this technique.

1.6 Note on Units.

The units used in the work presented in this thesis do not always rigidly comply with the SI convention. This approach has been adopted to ensure concordance with units popularly in use at the time of writing and to minimise any confusion on the part of the reader when consulting similar work. The SI system has, however, been used wherever practicable.

For the studies in atomic spectrometry the units of concentration are given in ppm and ppb which may be interpreted as parts per million (w/v) and parts per billion (w/v) respectively. As an example, 1ppm would therefore represent 1mg. of species in 1000cm³. of solvent and 1ppb would represent 1 µg. of species in 1000cm³. of solvent.

CHAPTER 2

THEORY AND PRACTICE OF PHOTOACOUSTIC SPECTROSCOPY

2.1 The Photoacoustic Effect.

2.1.1 Historical Development.

During experiments conducted in 1880, Alexander Graham Bell noted that an acoustic wave could be produced when certain materials were illuminated by an amplitude modulated solar beam of radiation. Bell's observations were expounded in a publication (84) the following year in which he concluded that this effect was observable for any physical state of matter, but was more successful for highly coloured or spongy materials. This discovery which Bell called the optoacoustic effect (OA), was further investigated by other workers including Tyndall, (85) but was not subsequently developed for another fifty years.

Further interest in the phenomenon was created following studies by Veingerov (86,87), which were limited exclusively to gases. This latent period in the history of the optoacoustic effect was almost certainly caused by the absence of a reliable transducer. The introduction of the sensitive microphone transducer early in the twentieth century was to allow optoacoustic spectroscopy to be more than just a scientific curiosity.

In 1973, experiments with condensed phase materials were carried out at the Bell Laboratories in the United States (88,89). Since then OAS has enjoyed a relatively high growth rate and appears to have an extremely promising future in certain selected applications. In 1979, the optoacoustic effect was renamed as the photoacoustic effect (PA)

so that confusion with acousto-optical spectroscopy, an entirely different technique, could be avoided.

2.1.2 Principles of Photoacoustic Spectroscopy (PAS).

The interaction of electromagnetic radiation with a molecule may result in transitions from the ground state to one of a number of excited states. This perturbation normally results in the formation of an unstable or metastable condition, and excitation is therefore followed by de-excitation via a number of possible pathways. These pathways are shown in figure 2.1. This representation is referred to as a Jablonski diagram and is a schematic view of the electronic ground and first excited singlet (S_1) and triplet (T_1) spin states of a molecule, together with some of the associated vibrational levels. For simplicity, the molecule is assumed to undergo simple harmonic oscillations only. Following excitation, the ground vibrational state of the S_1 level rapidly becomes populated through a non-radiative process known as internal conversion (half life 10^{-12} s). De-population of the S_1 state can then occur by processes such as fluorescence (half life 10^{-8} s) an optical transition, or by the non-radiative process of vibrational relaxation. Alternatively, the T_1 state can become populated by a process of intersystem crossing in which the energy is transferred from the S_1 state by vibrational coupling. De-population of the T_1 state results in phosphorescence (half life 10^{-2} s) and again vibrational relaxation provides an alternative non-radiative pathway.

The rapidity with which vibrational relaxation can occur usually means this is the dominant de-excitational pathway and the net result is that on a macro scale, the temperature of the sample will rise.

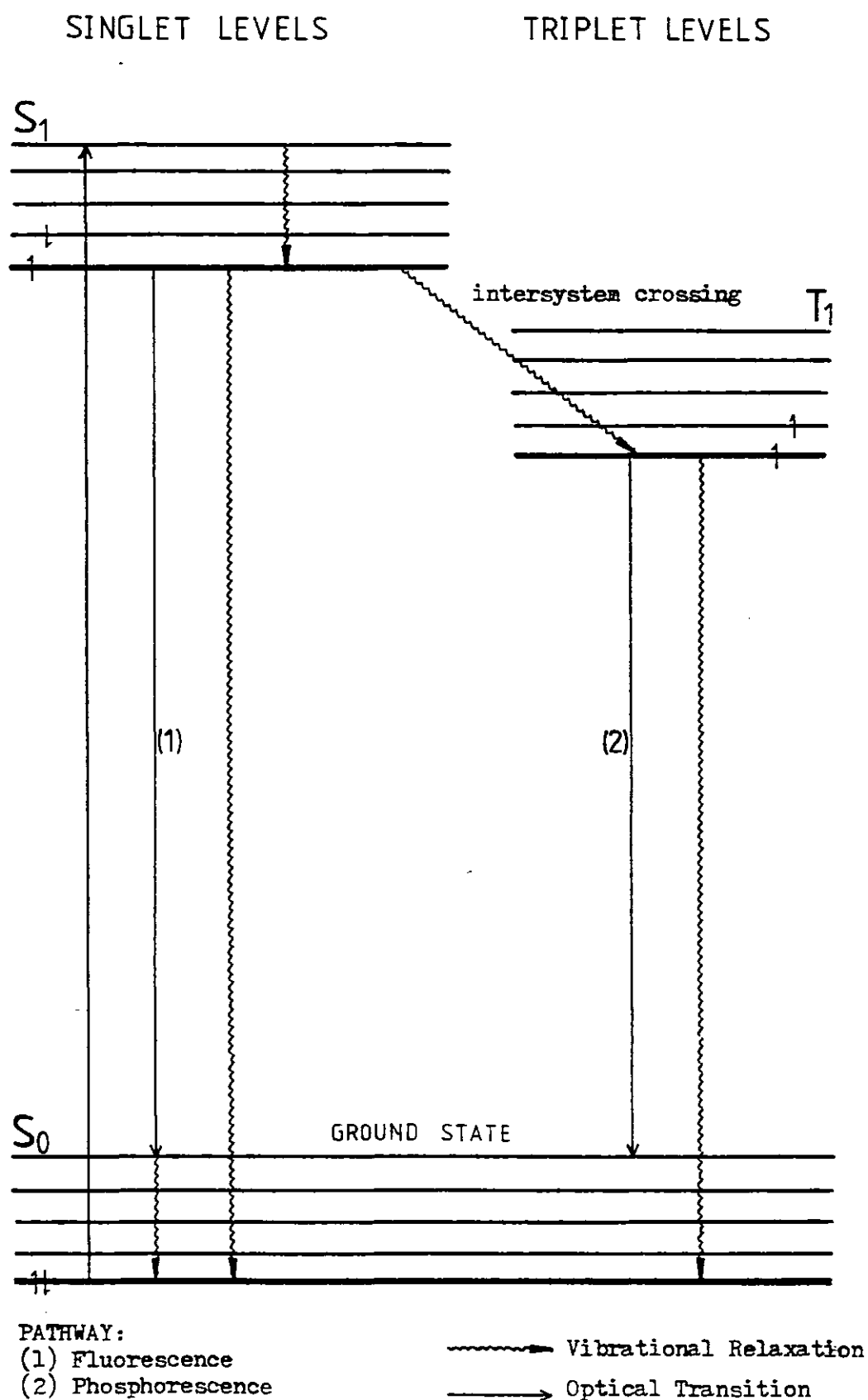


Figure 2-1 — Jablonski Diagram for hypothetical molecule

This could be used as the basis of a calorimetric method for measuring the absorption profile of the particular compound, but unfortunately the increase in temperature (10^{-3} K) is too small for this to be a viable practical method, and, moreover, a D.C. measurement system would be necessary as thermal equilibrium would have to be established at each point on the absorption profile.

In PAS, these disadvantages are overcome by using an A.C. measurement system in which the exciting source of radiation is modulated at low frequencies (10-1000Hz.). The modulated radiation is allowed to impinge upon the sample enclosed in a special "cell" and thermal energy is released in the sample by non-radiative de-excitation. This thermal energy is converted into a thermal wave which diffuses to the surface of the sample and is transmitted to the layer of gas adjacent to this surface. According to current theory (90), this layer of gas, under modulated excitational conditions, acts as an acoustic piston and if the gas is isometrically confined, a pressure wave will be produced, with a fixed phase relationship to the modulated incident radiation. A pressure transducer, commonly a microphone, comprising part of the cell can then be used to measure this thermal wave indirectly and allows the complete absorption profile of the specimen to be measured in any phase.

Bell's original hypothesis for the phenomenon which has been described was that the audible disturbance was caused by the periodic expulsion and reabsorption of pockets of gas in contact with the surface of the sample. This became the subject of severe controversy among his contemporaries and several other mechanisms were proposed. Modern theory suggests that this is not the case, although Bell's original contention that the signal was produced via an optical

absorptive process was completely correct.

2.1.3 Theory of PAS- Rosencwaig-Gersho (RG) Theory.

The popularity of gas phase PAS naturally led to comprehensive developments in the associated theory (91). In contrast, the latent development of solid phase PAS has meant that advances in the theory are still being published. This situation has not been aided by the intrinsic complexity of processes occurring in the solid phase, particularly with respect to the effects of homogeneity of sample packing and surface characteristics.

The first attempt to derive a basic theory to explain the photoacoustic effect for solids was made by Rosencwaig and Gersho (90,92) in 1975 and remains to date the best overall mathematical description. The RG model may be interpreted with reference to figure 2.2 which represents a uni-dimensional treatment of a sample in a simple cylindrical cell of length L and diameter D . The length of the cell is assumed small compared with the wavelength of the acoustic wave (typically 10m.). The sample, in the form of a disc of thickness l , is mounted such that the rear surface is in contact with a backing material, thickness l_b , of poor thermal conductivity. The front surface of the sample is in contact with a length l_g of the gaseous column filling the cell. It is further assumed that the solid sample is isotropic, and that the filling gas and backing material do not absorb any of the incident light flux.

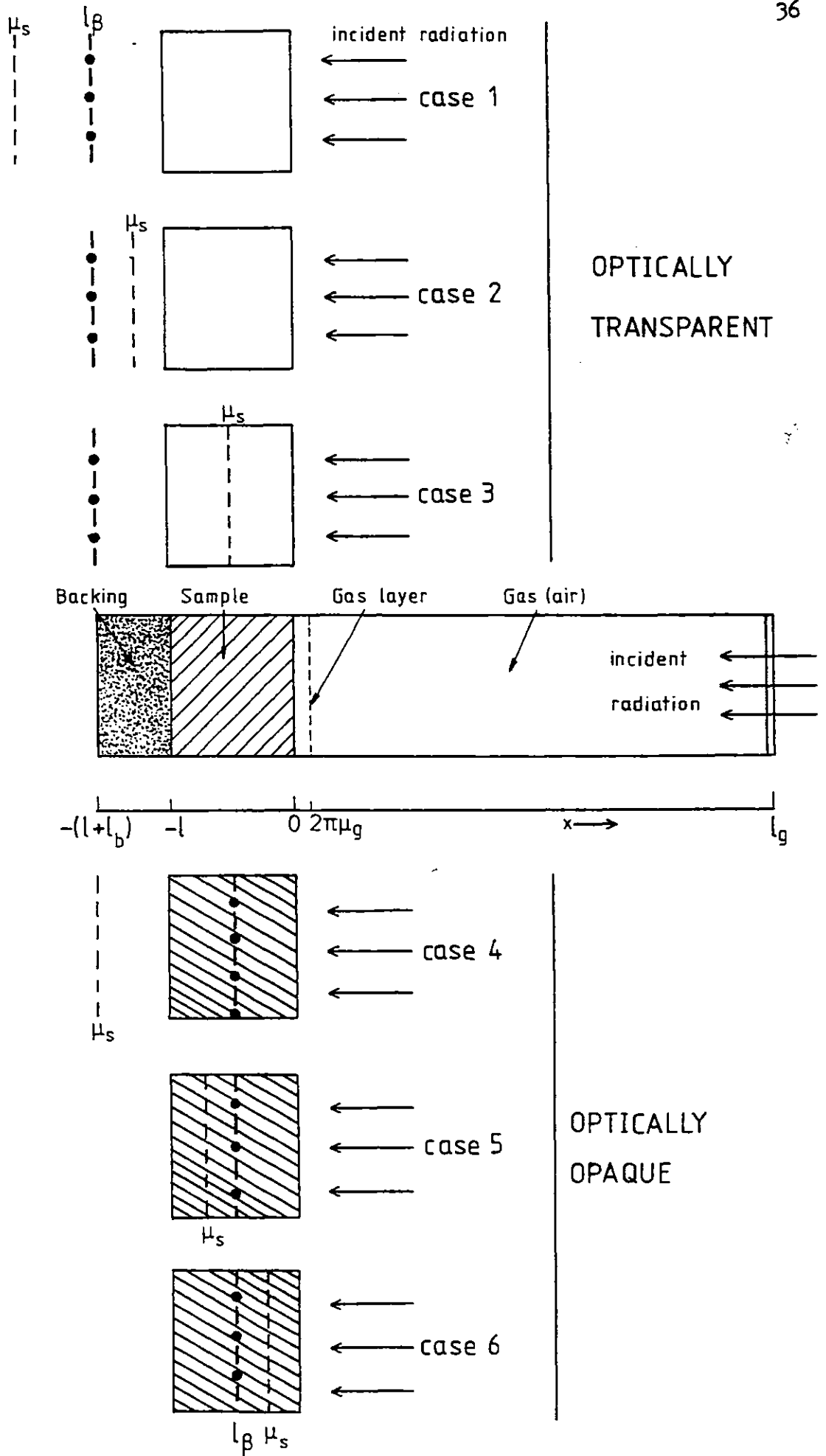


Figure 2-2 - The RG Model and six special cases.

It is now appropriate to define the following parameters:

k_f - Thermal conductivity of material f.

ρ_f - Density of material f.

C_f - Specific heat of material f.

$\alpha_f = k_f / \rho_f C_f$ - Thermal diffusivity of material f.

ω - Modulation frequency of incident radiation.

$\mu_f = \sqrt{(2\alpha_f/\omega)}$ - Thermal diffusion length of material f.

$a_f = 1/\mu_f$ - Thermal diffusion coefficient of material f.

$l_\beta = 1/\beta$ - Optical penetration depth of material.

β - Optical absorption coefficient.

The subscripts g (filler gas), s (sample) and b (backing material) may be substituted for f where relevant.

If the front surface of the sample is now evenly illuminated with monochromatic sinusoidally modulated radiation of wavelength λ , and incident intensity I_0 , a thermal wave may be produced at the surface of the sample producing a complementary wave at the gas boundary layer. This wave is effectively damped after a distance $2\pi\mu_g$, creating a simple gas piston. If continuity of temperature and heat flux is assumed at all boundaries, the pressure Q, detected by the microphone may, by applying the simple adiabatic gas law, be represented by,

$$Q = \frac{\beta I_0 \gamma P_0}{2\sqrt{2}k_s l_g \alpha_g T_0 (\beta^2 - \sigma^2)} \cdot A \dots\dots\dots (2.1)$$

$$\text{where } A = \frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)}$$

$$\text{and } r = (1-i)\beta/2\alpha_s ; b = k_b \alpha_b / k_s \alpha_s ; g = k_g \alpha_g / k_s \alpha_s$$

$\gamma = C_p/C_v$, ratio of specific heats of gas at constant pressure and volume.

$\sigma = (1+i)\alpha$. .

P_0 = ambient pressure.

T_0 = ambient temperature. $i = \sqrt{-1}$

The complex expression for the sinusoidal pressure oscillation cannot readily be physically interpreted. Fortunately it is possible to resolve six special cases where the expression may be simplified and which may be identified from diagram 2.2. These cases may be grouped into two subsections, determined by the relationship of the optical absorption length l_β to the thickness l of the solid.

(a) optically transparent, $l_\beta > l$ cases 1,2,3.

(b) optically opaque, $l_\beta < l$ cases 4,5,6.

For each subsection, there are three cases where the thermal diffusion length μ_s varies from being greater than to less than the optical absorption length l_β . For mathematical simplification, it is assumed that $g < b$ and $b = 1$ and if Y is defined as:

$$Y = \frac{\gamma P_0 I_0}{2\sqrt{2} T_0 l g} \dots\dots\dots(2.2)$$

the six special cases can be summarised as follows:

(a) optically transparent ($l_\beta > l$)

(1) $\mu_s \gg l$; $\mu_s > l_\beta$... "thermally thin"

$$Q = \frac{(1-i) \beta l}{2\alpha_g} \cdot \frac{\mu_b}{k_b} \cdot Y \dots\dots\dots(2.3)$$

The acoustic signal is proportional to βl and μ/k , the signal will therefore depend on ω^{-1} , from the definition of μ ; k . The thermal properties of the backing material will contribute to the effective

signal.

(2) $\mu_s > 1; \mu_s < l\beta \dots$ "thermally thin"

$$Q = \frac{(1-i)\beta l}{2\alpha_g} \cdot \frac{\mu_b}{k_b} \cdot Y \dots \dots \dots (2.4)$$

(3) $\mu_s < 1; \mu_s \ll l\beta \dots$ "thermally thick"

$$Q = \frac{-i\beta\mu_s}{2\alpha_g} \cdot \frac{\mu_s}{k_s} \cdot Y \dots \dots \dots (2.5)$$

The signal for this case is proportional to $\beta\mu_s$ and only light absorbed within the first thermal diffusion length will contribute to the signal. Additionally, the μ^2/k factor results in a $\omega^{-3/2}$ dependence.

(b) optically opaque ($l\beta \ll 1$)

(4) $\mu_s \gg 1; \mu_s \gg l\beta \dots$ "thermally thin"

$$Q = \frac{(1-i)}{2\alpha_g} \cdot \frac{\mu_b}{k_b} \cdot Y \dots \dots \dots (2.6)$$

The pressure dependence now becomes independent of β because all incident radiation is absorbed by the sample within one thermal depth. This situation can be described as photoacoustic "opaqueness" and is generally referred to as photoacoustic saturation. The thermal properties of the backing material will again contribute to the acoustic signal, which has a dependence on ω^{-1} .

(5) $\mu_s < 1; \mu_s > l\beta \dots$ "thermally thick"

$$Q = \frac{(1-i)}{2\alpha_g} \cdot \frac{\mu_s}{k_s} \cdot Y \dots \dots \dots (2.7)$$

(6) $\mu_s \ll 1; \mu_s < l\beta \dots$ "thermally thick"

$$Q = \frac{-i\beta\mu_s}{2\alpha_g} \cdot \frac{\mu_s}{k_s} \cdot Y \dots \dots \dots (2.8)$$

For this case, although the solid is optically opaque, it is not photoacoustically opaque and only light absorbed within the first thermal diffusion length will contribute to the signal. The pressure dependence will therefore be proportional to β , and a dependence of $\omega^{-3/2}$ is also predicted.

It is apparent from cases 1,2,3 and 6 that Q is proportional to β and therefore in principle, quantitative data can be obtained for samples with these optical and thermal characteristics. Cases 4 and 5 would not be expected to generate quantitative optical data since the pressure function is independent of β . Quantitative data can, however, be obtained on such samples if these can be converted to case 6 analogues by increasing the modulation frequency (ω) in which case the dependence on β can often be restored, but with the penalty of deteriorating signal-to-noise (S/N) ratios resulting from the use of such high modulation frequencies.

Cases 1, 2 and 3 represent samples which are optically transparent. Information from different depths in the specimen can therefore be obtained by varying the magnitude of the thermal diffusion depth via manipulation of the modulation frequency. By such means a complete depth profile of the specimen can be obtained.

The simplified RG theory that has been presented here has been validated by various experimental studies (93,94,95) but has not been readily applied to quantitative investigations of real samples. The reason for this is that particulate solids do not possess the ideal physical and optical properties of the RG model and the pressure dependence of the signal becomes distorted by the influence of particle size, scattering effects and inhomogeneity of the solid. The

principles of quantitative PAS will be discussed more fully in section 2.2.

2.1.4 Developments in the Theory of PAS.

Numerous attempts have been published which have sought to improve upon the limitations of the RG theory. In particular, the one dimensional treatment for heat flow of the RG model has been further developed to predict the pressure function for the three dimensional case (96,97) and experimental evidence suggests that the pressure function is identical to that of the uni-dimensional case, except when the radius of the sample chamber is of a similar magnitude or greater than the thermal diffusion length in the gas filling the cell.

The basic RG theory does not take into account the effects of mechanical vibration of the sample. Clearly this could occur because the release of a thermal wave in the sample will cause a periodic expansion-contraction cycle to be set up. McDonald and Wetsel (98), in a more rigorous extension of the theory of the photoacoustic process, made allowance for this contribution by considering a "composite piston" model. They showed that the mechanical vibration of the sample could significantly affect the PA signal and demonstrated the validity of the model for thermally thick samples. They also concluded that acoustic coupling would not become significant for thermally thin samples for which the RG "pressure piston" model would be adequate.

The mechanism of heat transfer into the gas across the solid-gas interface has also attracted considerable attention. Cesar et al. (99) proposed that the heat was transferred by a radiative process, and that the resistance to heat transfer could be included in the general

theory by adding an additional variable, H , the coefficient of heat transfer. This mechanism has since been disputed by Quimby and Yen (100), who maintain that the dominant process for heat transfer across the interface is by a collisional effect of the gas molecules on the solid surface.

2.2 The Role of PAS in Quantitative Analysis.

2.2.1 Introduction.

Quantitative analysis by PAS can be conveniently classified into two distinct areas. Firstly, magnitude and phase information can be interpreted to provide estimates of absolute parameters of selected species, such as the optical absorption coefficient, β , and thermal diffusivity. By monitoring phase data of the signal vector relative to the reference modulation, information on the sample thickness can be obtained and depth profile measurements can readily be accomplished. Numerous such studies have been carried out recently (101, 102). Additionally, PAS has been used to follow the path of chemical reactions. Thus Diebold (103) monitored the evolution of heat produced by exothermic chain propagation involving photodissociated halogen, and Iwasaki (104) followed the photochemical reaction of sensitising dyes adsorbed on ZnO semiconductor powder.

The second main area involves the application of PAS to quantitative analysis, a role which is considered to be of most significance to the analytical chemist. However, this is an area which has not received much attention until recently. One of the first reported attempts at quantitative analysis was made by Oda et al.

(105), who determined cadmium in the metal tolerant fungus, *penicillium ochrochloron* by laser induced PAS, in solution, and found a detection limit of 0.014ppb Cd. Much of the initial work in quantitative PAS was carried out at Imperial College, London. Thus, in 1979, Castleden et al. (106) reported a technique for the quantitative determination of materials on thin layer chromatography (tlc) plates, with a detection limit of 20ng. for fluorescein in 4.5mg. silica, and an rsd of 0.08-0.1. This particular application of PAS would be superior to other instrumental techniques, such as diffuse reflectance, because it would be fairly immune to reflection and scattering from the silica surface. This study was followed by an application to food dye analysis (107), and a study by Lochmuller and Wilder (108) who presented quantitative spectra of coverage on chemically modified silica surfaces. Recently a special cell (109) has been designed for the remote detection of adsorbed species on TLC plates.

PAS studies have been reported for the determination of copper phthalocyanine on glass (110), water content in single cell protein (111), for micro amounts of Hg-diphenylcarbazone complexes (112) and for determination of combined acetate in vinyl acetate/vinyl chloride copolymers (113). PAS has also been shown (114) to have potential for solving problems in dermatology and for routine moisture determinations (115).

2.2.2 Extension of Theory for Quantitative Work.

The theory proposed by Rosencwaig and Gersho is sufficient to predict the simplistic pressure response from an ideal sample. Unfortunately, many samples which face the analytical chemist are far

from ideal and new theories are therefore necessary to predict the pressure functions for real samples, especially powders or particulates, on an absolute basis. Early attempts to relate the theory to predict quantitative behaviour (110, 112) concentrated on derivations modelled on the Beer-Lambert law, in which the molar absorptivity coefficient, ϵ , was used. These expressions were used to predict a linear relation between the PA response and the concentration of the chromophore.

Monohan and Nolle (116) investigated the quantitative response for powdered samples, but found that the particle size of the powder had to be controlled, and inhibited the establishment of reliable calibration curves. Several other workers (117, 118), have attempted to produce quantitative data by utilising phase studies in place of pressure amplitude measurements and found that the range of the calibration function could be extended. The only successful attempt to date, to predict theoretically the behaviour for particulate samples, has been made by Burgraaf and Leyden (119). These authors concluded that the RG theory was useful for predicting the dependence of the PA response but for some of the special cases was as much an oversimplification as the general solution was overcomplex. Consequently, they developed an extension to the theory with which the behaviour of intensely light scattering, thermally thick samples could be predicted, and this was supported by experimental results on chemically modified, fumed, silica. This theory was based on phase angle measurements and introduced a scattering coefficient, S , assuming that the radiation was perfectly diffused throughout the sample.

2.2.3 PAS- Analytical Methodology.

The complicated response function for many samples has precluded the successful derivation of an absolute theory for PAS, and the amplitude observed experimentally will be a weighted mean of all the temperature fluctuations from particles in the sample. At present this means that empirical techniques must be used to derive analytical calibration systems. A number of additional problems arise when solid samples are considered:-

(a) For the analysis of solid samples no diluent species has normally been added. Any variation of the concentration of the analyte in the solid mixture is therefore accompanied by a proportionate variation in the rest of the sample matrix. If these components absorb radiation near to the frequency selected for measurement of the analyte, interference may result from superimposed background shifts.

(b) Unlike liquids, which will homogeneously fill the container used for carrying the sample, solids will adopt a different packing conformation each time they are placed in the sample container. Strict uniformity in sample insertion is normally required.

(c) The proportionate variation of analyte and matrix components means that multicomponent analysis is difficult to achieve. Additionally, interaction of the components constituting the solid will be higher than for the case in solution.

The physical form of particulate solids will profoundly influence the final pressure perturbation detected by the transducer. It is appropriate therefore to consider some of the variables which will affect the absolute magnitude of the PA signal.

Particle Inhomogeneity.

Modification of the PA signal response will ensue if the solid material is not physically and chemically homogeneous, because the signal detected will only reflect the distribution of the absorbing material in the sample. Careful control of sampling and sample preparation is advisable. A recent study (120) has also indicated that the observed signal is affected by the degree of adsorption of the analyte material on other matrix components. This situation may arise if the analyte is vigorously coground with the rest of the matrix or a diluent species, and this should be avoided if possible.

Particle Size.

Particle size is the most critical variable affecting the PA signal amplitude. If the distribution in particle size is diverse, each individual particle can, depending on the thermal properties of the material, be either optically thick or optically thin, since this property is determined in part by the thickness of the particle. A situation may then arise where some of the particles will exhibit different RG behaviour to others in the same sample. A narrow distribution in particle sizes would appear to be advisable for analytical control.

The particle size will also modify the effective surface area of the sample and may reasonably be expected to increase the total area of sample illuminated by the incident radiation. The PA signal magnitude would therefore increase as the particle size decreases. This effect has been disputed by Ashworth (121) who invoked a simplified packing model to show that the total area would remain independent of particle size and that this is not the reason for the

generally observed effect of increased signal magnitudes with decreasing particle sizes.

A wide distribution in particle size will produce gas pockets of different sizes in the sample. These will modify the progress of the thermal wave in the sample which ultimately gives rise to the observed signal. If a particular gas pocket has dimensions of less than the thermal diffusion length of the gas, then the thermal wave will be severely attenuated. If the dimensions of the gas pockets are too large however, attenuation of the wave will again result, because the transfer of the wave from the gas back to the solid particles is not efficient.

Close control of the particle size is needed if interferences are to be avoided in the practical exploitation of the PA effect, a conclusion similarly reached by Kirkbright and Menon (113) when they analysed copolymer mixtures by PAS.

Scattering Effects.

Interferences can arise if any of the radiation is scattered by the sample. If the particle size is small, the scattering effect will become more important, and according to Burgraaf and Leyden (119), this can produce a situation where there is a higher photon density in the upper layers of the sample. The signal amplitude would be expected to increase as the particle size decreases. On this basis, measurements made in the IR region of the spectrum would be less susceptible to the effects of scattering than those made in the UV-vis. region because of the difference in the wavelengths of the radiation.

The variables which have been presented and discussed here must be considered when using PAS to make quantitative measurements. The sample must be produced with care and the particle size controlled such that the combined effects of scattering and thermal wave modification are minimised. If these strictures are adhered to, PAS may be shown to have important advantages for quantitative analytical applications.

2.3 Characteristics of the Spectral Region Studied.

2.3.1 Excitation Processes in the Ultra-Violet-visible Region (UV-vis.).

Historically, the UV-vis. region has played an important part in the development of molecular spectroscopy. This region may be defined as extending from 120nm., the vacuum UV, through to 800nm., the limit of the visible region, and is characterised by the interaction of photons with the outer electrons in the bonding or non-bonding orbitals of molecules. Four different types of excitation are possible, which may be identified from figure 2.3.

$\sigma \longrightarrow \sigma^*$ Excitation from the bonding orbital, formed from a linear combination of atomic orbitals, to the corresponding antibonding orbital.

$\pi \longrightarrow \pi^*$ Excitation from the bonding orbital symmetrically displaced about the axis, to the corresponding antibonding orbital.

$n \longrightarrow \sigma^*$ Excitation from an orbital containing electrons not involved in bonding, to the σ antibonding orbital.

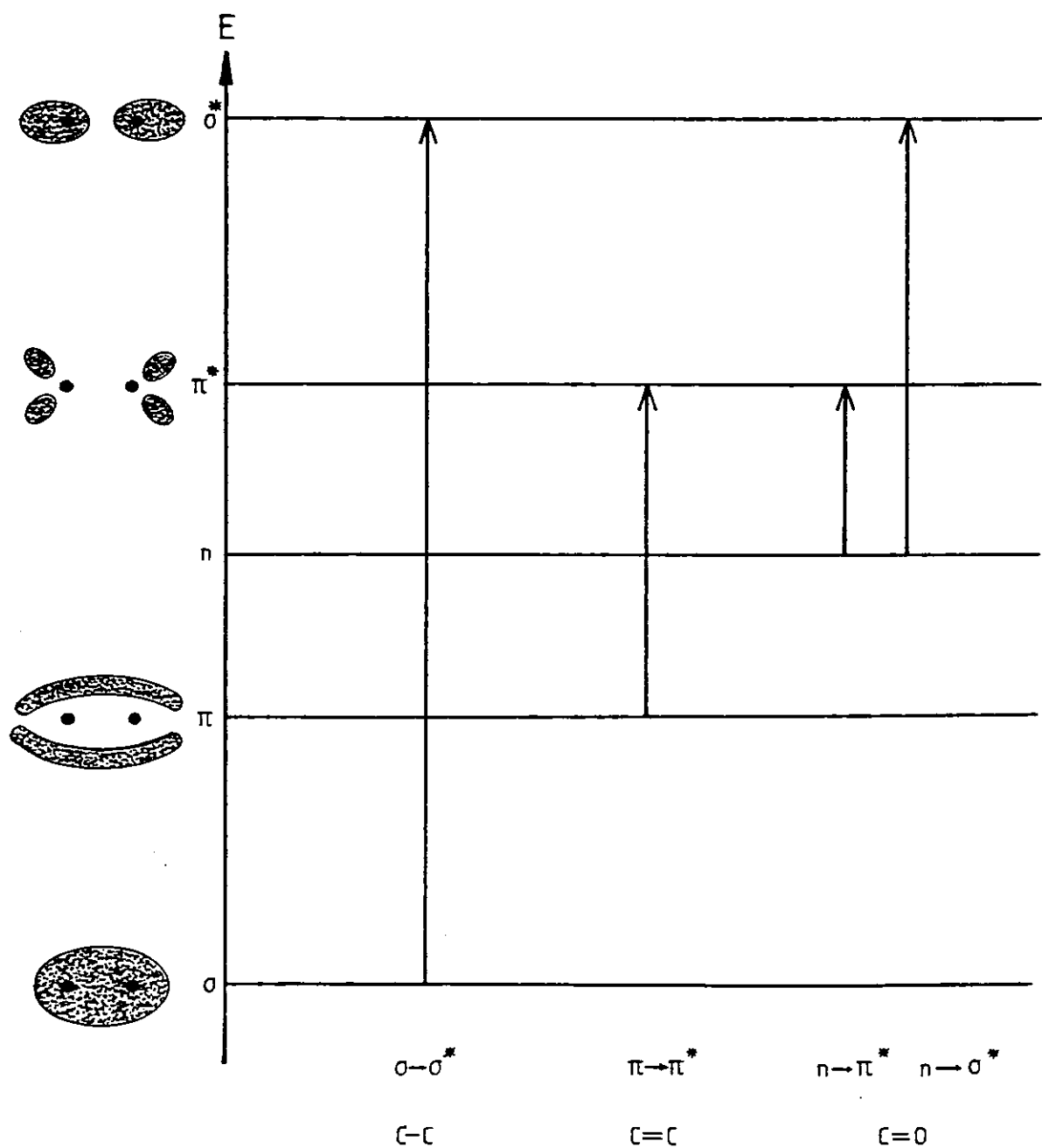


Figure 2-3 - Molecular energy levels with possible routes for Electronic Excitation.

$n \longrightarrow \pi^*$ Excitation from an orbital containing electrons not involved in bonding, to the π antibonding orbital.

Two further electronic excitation mechanisms are possible: charge transfer, involving photoinduced transfer of electrons from a donor atom, and d orbital splitting by ligand field effects in complexes. These mechanisms will not be discussed here.

In accordance with the Born-Oppenheimer approximation, rotational and vibrational lines will be superimposed on the electronic transition and the observed profile is usually that of a broadened band. For this reason, use of the UV-vis. region is limited for molecular fingerprinting methods. Instead, studies in this region can be used for the detection and determination of a variety of systems such as multiple bonding, conjugation, aromatic and heteroaromatic bonding and stereochemical phenomena.

The relative energies of the molecular orbitals involved, play an important role in the position and intensities of the observed bands and the four excitation cases which have been defined are usually found in different parts of the UV-vis. spectrum. $\sigma \longrightarrow \sigma^*$ transitions are of the highest energy and therefore appear in the high energy part of the spectrum, 120-200nm. This region is called the vacuum UV because air must normally be excluded from the measuring optics to avoid interference from the absorption of radiation by oxygen. Chromophores which possess double or triple bonds may also produce $\pi \longrightarrow \pi^*$ transitions in addition to $\sigma \longrightarrow \sigma^*$ transitions and these are of the lowest energy. For this reason, $\pi \longrightarrow \pi^*$ transitions are normally found in the visible part of the spectrum. If conjugation (alternate double and single bonds) is present in the chromophore, new π bonding clouds can be produced from the old ones and the transition

is bathochromically shifted.

The other two transitions involve excitation from a non-bonding orbital $n \longrightarrow \pi^*$, $n \longrightarrow \sigma^*$. The $n \longrightarrow \pi^*$ transition is "forbidden" because the group theory selection rules are not satisfied for this system. The transition is usually of low intensity. In contrast, $n \longrightarrow \sigma^*$ transitions are allowed and give rise to strong bands. The most common chromophores producing such absorptions are those with groups containing lone pairs of electrons. Carbonyl groups >C=O produce the classic $n \longrightarrow \pi^*$ transition at 280nm. The associated $n \longrightarrow \sigma^*$ transition is of course at higher energy and appears at 185nm.

The spectra of molecules, obtained in the liquid phase, usually consist of broad bands produced from dynamic interactions with solvent molecules. Although solvent molecules blur out the vibrational and rotational transitions, which are commonly encountered with gas phase spectroscopy, small frequency shifts occur because the polarity of the solvent slightly distorts the electron clouds of the molecule. In the solid phase cf. photoacoustic spectroscopy, this would not occur since no solvent is present and, moreover, at room temperature a large proportion of the molecules will be in the ground state, producing simplified spectra. However, many of the intermolecular interactions in solids are static and affect the energy level distributions, a reason why observed line profiles in solid phase spectra are usually sharper than in spectra obtained in the liquid phase.

2.3.2 Excitation Processes in the Near-Infra Red Region (near-IR).

The near-IR region of the electromagnetic spectrum can generally

be regarded as extending from the limit of the visible region at 800nm. (0.8 $\mu\text{m}.$), to 2.5 $\mu\text{m}.$, the beginning of the main IR region. This region may be isolated from both the UV-vis. and mid-IR regions because the processes responsible for the production of spectral transitions are different, consisting of low energy overtone and combination mode frequencies of the fundamental oscillations which occur in the mid-IR. Near-IR absorption bands are only observed if anharmonicity is present in the bonding system of the compound. If the degree of deviation from the simple harmonic oscillator model is known, it is possible to predict the positions of the overtone bands according to the equation derived by Kratzer (122):

$$\nu_n = n\nu_0(1 - nx + n^2y - n^3z + \dots) \quad \dots\dots\dots(2.9)$$

where x,y,z... are first second, third order (=0 for simple harmonic oscillation.) anharmonicity constants.

- ν_0 - fundamental frequency of the vibrational band.
- ν_n - is the frequency of the overtone of the n'th harmonic.

Anharmonicity is usually only observed for hydrogenic systems, as the mass of the hydrogen atom is low compared with the other atoms in bonding groups and the vibrational displacement is thus large. Overtone and combination bands (which are a summation of fundamental frequencies) of -CH, -OH, -SH and -NH groups are therefore useful for conducting quantitative, qualitative and structural studies on a variety of molecules containing these functions.

Near-IR spectroscopy has been less extensively studied than neighbouring regions and for this reason is less well understood. The assignment of spectral transitions has usually been based on empirical

approaches in the absence of extensive data on anharmonicity constants. Despite this, the near-IR region has several advantages for quantitative analysis which have been described in the classic review by Kaye (123) and more recently by Whetsel (124) and Willis (125). Several papers have been published which report quantitative studies, including determination of hydroxyl groups in glycols (126), polymers (127), aromatic aldehydes (128) and primary aromatic amines (129).

For the PAS studies presented in this thesis, the structural assignments were made by reference to a Colthup type group frequency chart (130) and by studying analogues of the compound studied. It remains apparent that more extensive study of the excitation processes in the near-IR is required so that a better understanding may be obtained of spectral behaviour and to fully exploit the utility of the region.

CHAPTER 3

QUANTITATIVE STUDIES WITH PAS

3.1 Instrumentation for Experimental Studies.

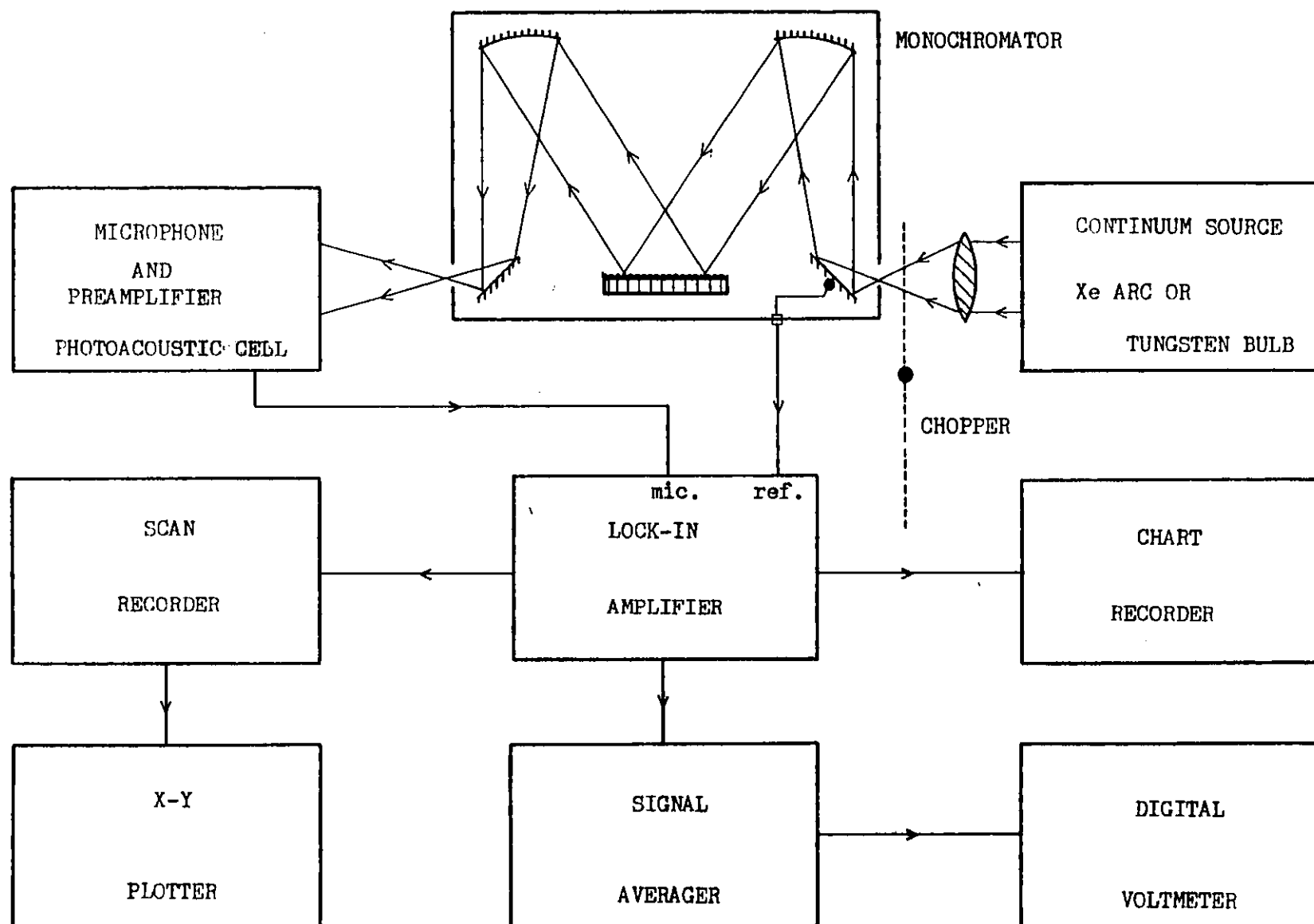
3.1.1 Introduction.

The essential components of a working PAS system are of the same modular type as in other complimentary molecular techniques, namely a continuum source of electromagnetic radiation, a wavelength dispersive system, a detector and data readout facility. These elements are shown in figure 3.1. PAS is unique however, in that the sample is housed in the same chamber as the detector and careful design of this composite photoacoustic cell is required. Additionally, as explained in chapter 2, the signal vector has to be monitored with respect to the phase of a reference signal obtained from modulating the incident continuum radiation falling on the cell window. Therefore two more components are required for the PAS system: a device for mechanically or optically modulating the incident radiation and a phase sensitive detector and amplifier with which the required physical and chemical data may be extracted from the sample.

PAS can, in principle, be applied in any region of the electromagnetic spectrum. Most studies have been restricted, however, to the UV-vis. and near-, mid- and far-IR regions and only these will be discussed in this section.

The ideal requirements of a radiation source for PAS are the ability to cover a wide range of frequencies from the vacuum UV through to the far infra-red, and to provide a high average radiant

FIGURE 3-1: Schematic view of PAS Instrumental system.



flux throughout this band of frequencies. In practice of course, no such source is available. Radiation sources which are commonly used for the UV-visible and IR regions are based on arc discharges and filament incandescent emitters. In the UV-visible region the most common source is the Xe arc obtained by passage of a large electrical current through Xe gas housed in a silica envelope. This source provides a high radiative flux throughout the range 230-2000 nm. Xe arcs with power consumptions $>1\text{kW}$. are not recommended for use with normal PAS monochromator systems because the increased dimensions of the arc result in much of the power being wasted. For the near-IR region the Xe arc lamp is usually unsuitable as there are a series of pressure broadened lines which appear in the emission spectrum in this region. The usual source for work in this region is the tungsten-halogen bulb which is available in useful sizes up to 400W. It consists of a coiled tungsten filament in a quartz envelope containing small amounts of a halogen, usually iodine, to reduce vaporisation of the tungsten. This allows the filament to be operated at a higher temperature than would normally be the case. The effective colour temperature of this source is ca. 2850K. and the continuum emission intensity has a maximum at a wavelength of approximately $1.6\text{ }\mu\text{m}$. Radiation sources for the mid-IR region have been traditionally of two types: (1) Globar-consisting of a silicon carbide rod which is resistively heated. (2) Nernst glower-consisting mainly of zirconium and yttrium oxides. This requires an additional heat source to initiate the glow discharge.

The use of high energy radiation sources for PAS has become very popular recently (131, 132). Dye lasers have many advantages over the conventional radiation systems, namely, high radiative powers, high

spectral resolution and the capability for optical modulation. Unfortunately the cost of such systems is extremely high and there is a necessity for frequent dye changes.

The theory which was discussed in section 2.1.3 predicted that the photoacoustic response function would be proportional to the intensity of the incident radiation I_0 . Spectra obtained in practice with PAS require a correction because the power spectrum of the particular emission source in use becomes superimposed on the PAS spectrum. This correction can normally be attained by dividing the spectrum by a spectrum obtained from a photoacoustically opaque material such as carbon black. Spectra obtained in this way are said to be "normalised."

There is a fundamental requirement in PAS to modulate the radiation source. This has been discussed in chapter 2. Modulation (chopping) may be achieved in two different ways:

- (1) Mechanical chopping using a rotating sector.
- (2) Optical chopping by controlling the switching of the emission source.

Mechanical chopping produces excellent reference signals, but vibrational coupling between the chopper and the PAS cell must be avoided. For this reason the chopper is placed as far as possible from the cell, usually in front of the entrance slit of the monochromator. Optical chopping creates no mechanical or acoustic perturbations and is capable of achieving higher frequencies than mechanical systems. Optical chopping does, however, produce a noisier reference signal for the phase sensitive detector because the switching of the high powers involved creates electrical spikes which are necessarily at the same frequency as the detection electronics and are therefore not

discriminated against.

The design of the photoacoustic cell has received much attention throughout the development of practical PAS of solids (133,134). In basic form it consists of a mechanically and acoustically isolated chamber containing a tray for carrying the sample, and a window transmissive to the radiation band selected. The cell also houses the microphone pressure transducer which should be sited away from those areas of the cell which are normally illuminated, to prevent extraneous signals from being generated by the microphone. The PAS cell should ideally be designed to maximise the signal-to-noise (S/N) response of the pressure transducer, and therefore the size of the cell is extremely important (135). The conversion of the thermal wave to the pressure wave detected by the transducer is dependent on the ambient temperature of the cell and the thermal diffusivity of the coupling gas. In a study by Eaton (136), the best coupling gas was found to be helium, producing pressure amplitudes up to twice those obtainable with air as a coupling medium. The photoacoustic cell may also be made acoustically resonant (137) such that the gain of the cell is maximised at one particular frequency. Such a cell would appear to offer a considerable improvement in S/N ratio because the noise levels usually appear at a variety of frequencies and the signal has now become frequency selective. One disadvantage is, of course, that operation of the cell is restricted to only one frequency, making it useless for depth or depth related studies.

The microphone has been the most common pressure transducer for use in PAS cells. The main requirement is for a high quality, highly sensitive microphone with good low frequency response. The microphones manufactured by Bruel and Kjaer (Hounslow, Middx.) are amongst the

best available and are commonly used in PAS systems.

Signal recovery from PAS systems for work in the solid phase, is usually accomplished with lock-in amplification techniques, driven by the first stage pre-amplifier of the pressure transducer. A lock-in amplifier consists of an A.C. amplifier with a phase sensitive detector. If the A.C. signal and the reference signal generated from the modulating device have the same frequency and phase, the output of the amplifier will be the total amplitude of the incoming signal. If the phase of the incoming signal falls to $\pi/2^\circ$ with respect to the reference signal, the output will fall to zero. The output of the amplifier can be maximised by manually or automatically adjusting the phase of the detector. In this way a lock-in amplifier can be used to produce a D.C. signal from an A.C. input function at a particular frequency, with excellent rejection of other unwanted frequency components.

3.1.2 Photoacoustic Instrumentation for use in Practical Studies.

The instrumentation used for studies in the U.V.-vis. region has been described elsewhere (138). The continuum source was a 300W. Xenon arc (type VIX-300 Varian Associates Ltd.) with a 25mm. diameter sapphire window and was run from a matched power supply at 15V 20A. The radiation from this source was focused through a variable speed rotating chopper (model 9479 Brookdeal Electronics Ltd., Bracknell) onto the entrance slit of a f/4 monochromator (MetroSpec DGO Ltd., Chobham, Surrey) equipped with a plane diffraction grating blazed at 300nm., mounted in a Czerny-Turner arrangement. The mirrors comprising this arrangement were concave front surfaced aluminium

reflectors. Radiation exiting from the monochromator was focused onto the PAS cell by a front surfaced mirror ($f=200\text{mm.}$). Two PAS cells were used for the studies: the first was home built and has been described previously (138), the other was a commercial design (OAS 401 EDT Research, London, NW10). Both cells contained a $1/2''$ capacitor microphone (type 4166 Bruel and Kjaer, Hounslow Middx.; 50mV./Pa.) which was polarised with a 200V. dry cell (120V for commercial cell). The electrical response from the microphone was processed at the input stage of a lock-in amplifier (model 9502 Brookdeal Electronics Ltd.) which was used in vector voltmeter mode. The reference signal for the amplifier was provided initially directly from the mechanical chopper but was subsequently modified such that a silicon phototransistor mounted inside the monochromator, was used to trigger the reference channel.

Signal recovery from the instrumental system was usually effected by using a digital scan recorder (model 4101, Princeton Appl. Res. Corp., Princeton N.J.), one channel of which was used to store the emission spectrum of the continuum source, obtained by running the photoacoustic spectrum of powdered carbon black (particle size $36\text{--}63\text{ }\mu\text{m.}$) and which was used to decouple the power translation from all recorded spectra. Signal registration was accomplished with an X-Y recorder (model 75000 Bryans Southern Instruments, Mitcham, U.K.). For quantitative measurements the output from the lock-in amplifier was processed by a signal averager (PARC model 4202) and the signal displayed on a digital voltmeter (type 701, Fenlow, U.K.).

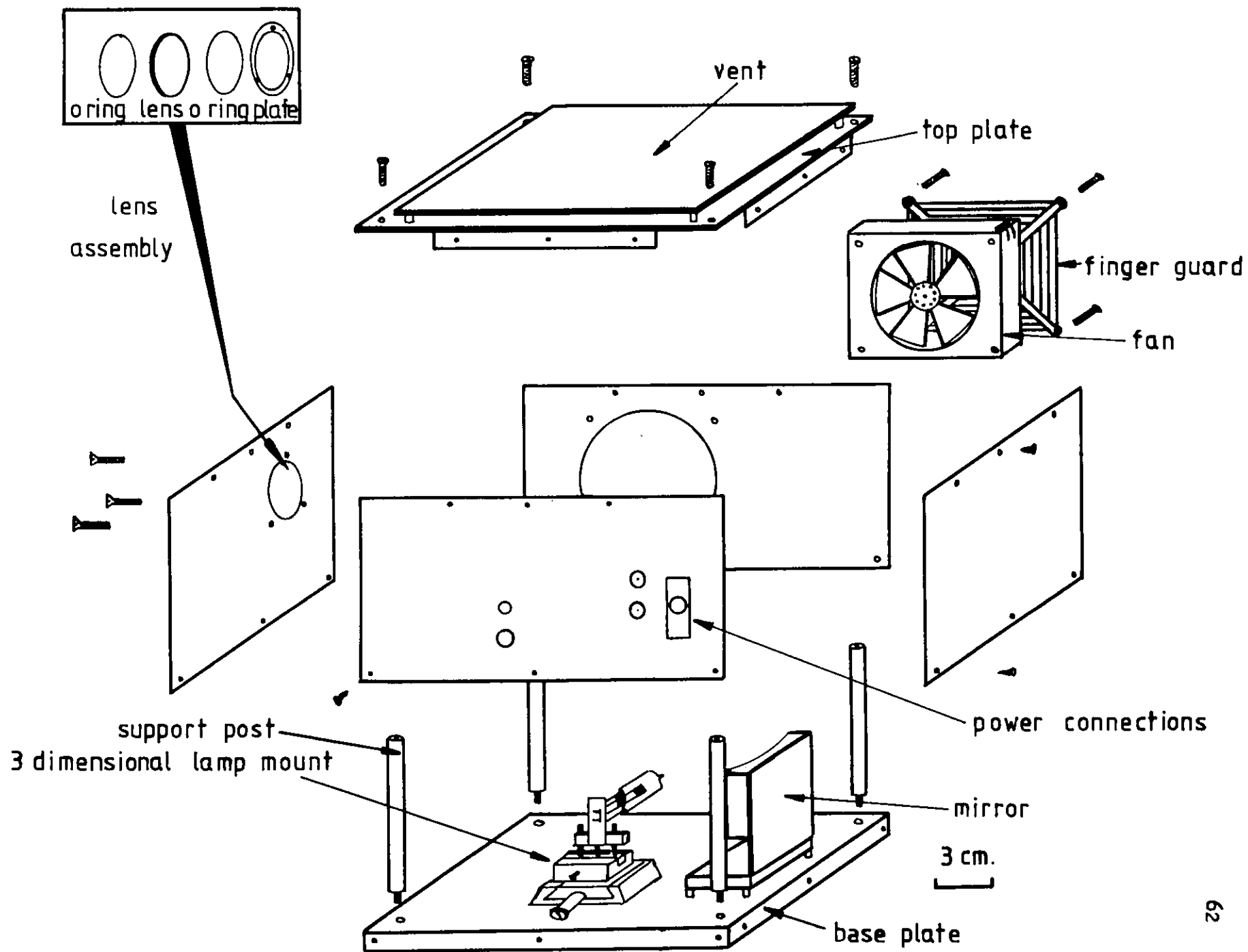
The instrumentation for use in the near-IR region has also been described previously (139). In initial form, the system consisted of a

250W. tungsten-halogen bulb (Philips, City House, Croydon, Surrey), the image of which was focused onto the entrance slit of an f/4 Czerny-Turner monochromator (MetroSpec DGO Ltd.) containing a plane diffraction grating (300 lines/mm., blazed 2.0 $\mu\text{m.}$, 50mm.x50mm.). The intensity of the bulb was adjusted by means of a "Variac" potentiometer. Interference from overlapping orders of diffraction, which is a severe problem in the near- and mid-IR, was removed by positioning a filter (cut on 1.3 $\mu\text{m.}$) at the exit slit of the monochromator. Radiation was focused through a 20mm. diameter silica window onto a home built PAS cell, constructed from aluminium and containing a capacitor microphone (type 4166 Bruel & Kjaer). Samples were inserted into the cell on a special aluminium tray (diameter 16mm., tray depth 3mm.) and the cell was sealed using a Parafilm (Gallenkamp U.K.) compression gasket. Other components of the system were as described for the U.V.-visible system except that signal processing was performed using a type 124A lock-in amplifier (PAR Corp.).

3.1.3 Modifications to Continuum Source (near-IR).

The continuum emission source for the near-IR system was found to provide poor power flux over its operated range, with associated degradation of S/N properties in the whole system. The source was therefore modified by upgrading to a 400W. quartz-iodine lamp (Philips type A0 239/7787, City House, Croydon, Surrey), which was located in a purpose built lamp housing and provided with a tri-dimensional racking assembly (diagram 3.2) to facilitate exact positional focusing of the filament at the entrance slit of the monochromator. A front surfaced

FIGURE 32: Exploded view of new near-IR continuum source and housing.



aluminium reflector was positioned behind the lamp and radiation was focused onto the entrance slit of the monochromator through a silica lens (diameter 25mm. $f=25\text{mm.}$). The lamp was powered from a supply specially designed to provide a stabilised voltage (36V @ 11A). The circuit diagram for this supply is shown in figure 3.3, which shows the principle of operation. Main channel power for the lamp is produced via a 36V 400VA mains transformer, the output of which is rectified and smoothed. The supply also incorporates a novel feedback system where voltage variation at the lamp is detected by an optoisolator (TIL 117) controlling the non-inverting input of an operational amplifier module (Texas RC 4136N). The feedback to the transformer is effected by using a triac (TIC 236M), the gate of which is triggered through a transistor (2N 4059) connected to the output of the operational amplifier module. Adjustment of the voltage supply is possible by means of a 10 turn potentiometer (5k. wirewound).

Operation of the lamp proved to be extremely successful and reliable in practice, producing S/N ratios of approximately twice those produced from the standard lamp. The working life of the new lamp also appeared to be improved when compared with the standard specification.

The second phase of instrumental modification in the near-IR was concerned with the design of an emission source system which could be modulated at very high frequency (5kHz.-5MHz.). As previously discussed, mechanical chopping systems are not suited for attaining high frequencies as they are subject to vibrational and balancing limitations. Similarly optical modulation has not been successful because large powers are usually involved and inductive spikes caused

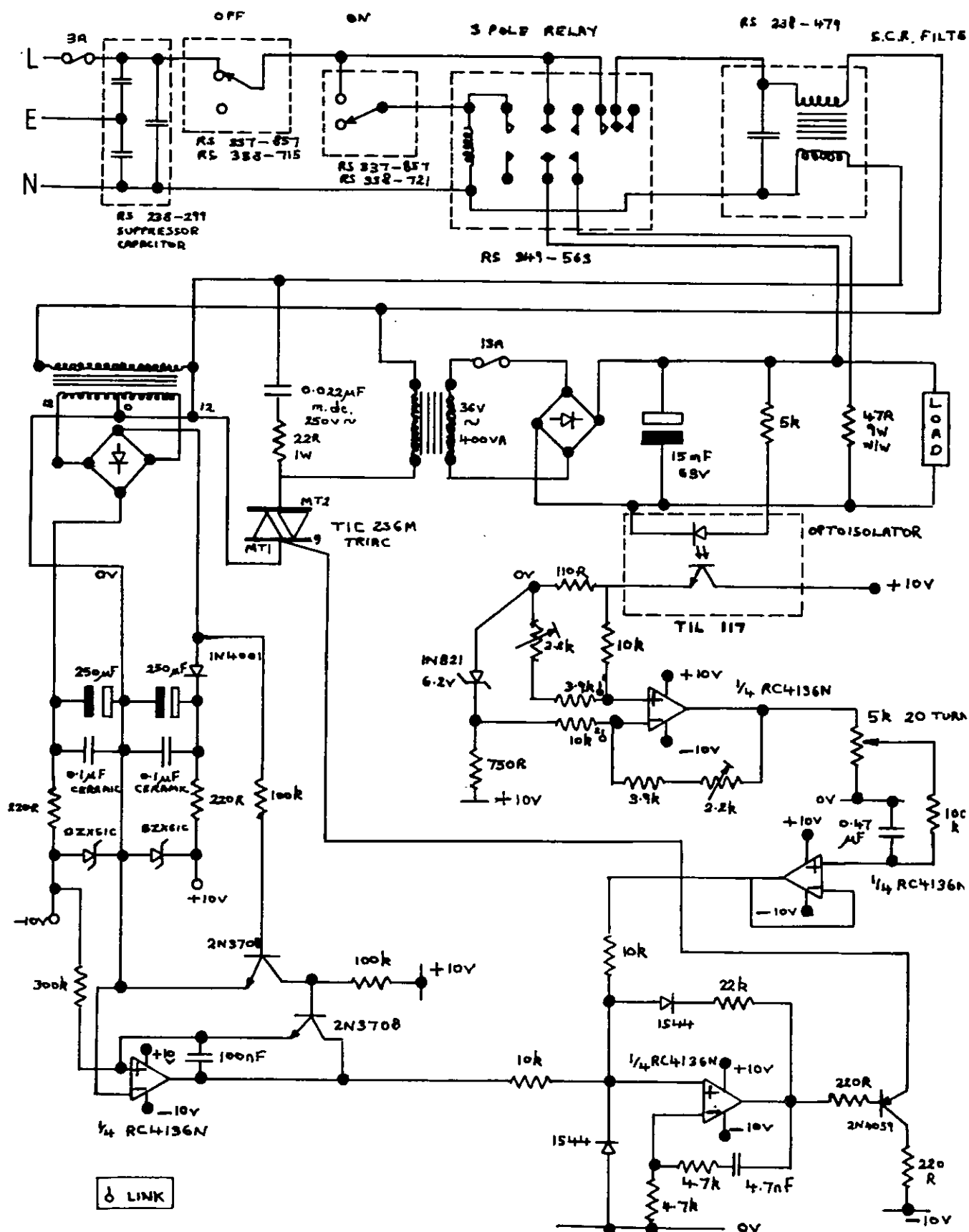


FIGURE 3.3: Stabilised Power Supply for near-IR Source.

by switching these powers cause interference in the detection system. To circumvent these particular problems it was decided to construct a photodiode emission system operating in a non-dispersive photoacoustic spectrometer. The advantages of using such a system are:

- (1) Low power consumption (84mW at 100mA).
- (2) Capability for extremely fast switching (=MHz.) with no interference with detection electronics.
- (3) Simplified instrumentation: no monochromator, scan recorder, chopper required- only a photoacoustic cell.
- (4) Low cost.

The photodiode assembly was designed to fit over the window (diameter 20mm.) of the near-IR photoacoustic cell and was constructed in an array of seven close packed diodes, figure 3.4. Each diode was a TIL 38 gallium-arsenide emitter with a peak output of 12mW. (100mA) at $0.96\ \mu\text{m}$., and a bandpass of $0.05\ \mu\text{m}$. The diodes were triggered by using a special electronic drive circuit, figure 3.5, the frequency being determined from a square wave modulation input derived from a signal wave generator (model 3300A Hewlett Packard). The system was not extensively tested because the photoacoustic cell was, unfortunately, fitted with a microphone transducer which did not have a flat frequency response beyond 8kHz. Clearly a piezoelectric transducer would be more suited for this system and the photodiode array could be used as the basis of a small dedicated instrument. Thickness measurements, particularly on laminates, would be easy to perform as a result of the wide dynamic range of frequency tuning. Preliminary experiments indicated that the power available to the sample using the photodiode array (84mW) placed over the cell was approximately three times more superior than using the conventional

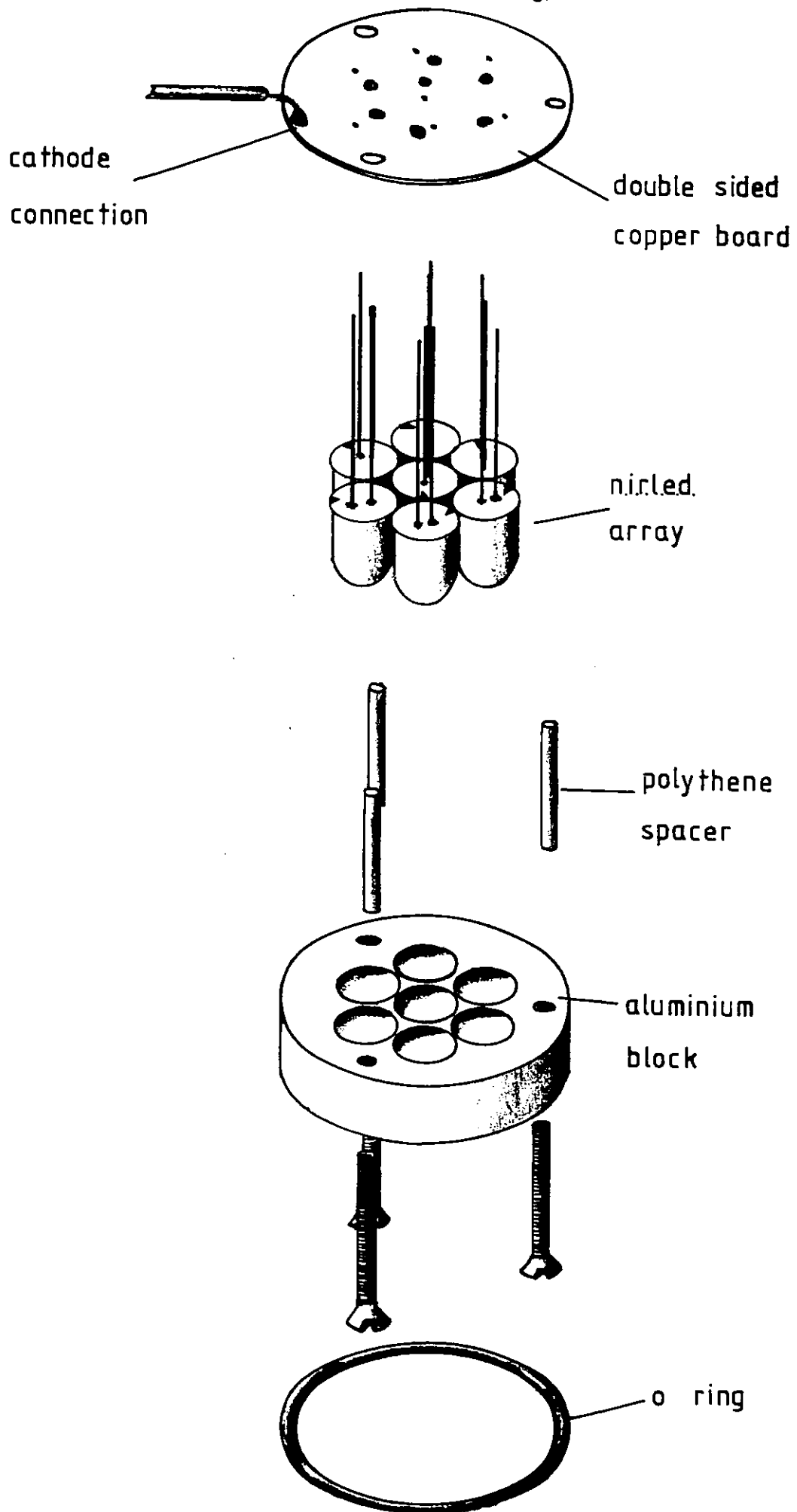


FIGURE 3-4 : Photodiode Array.

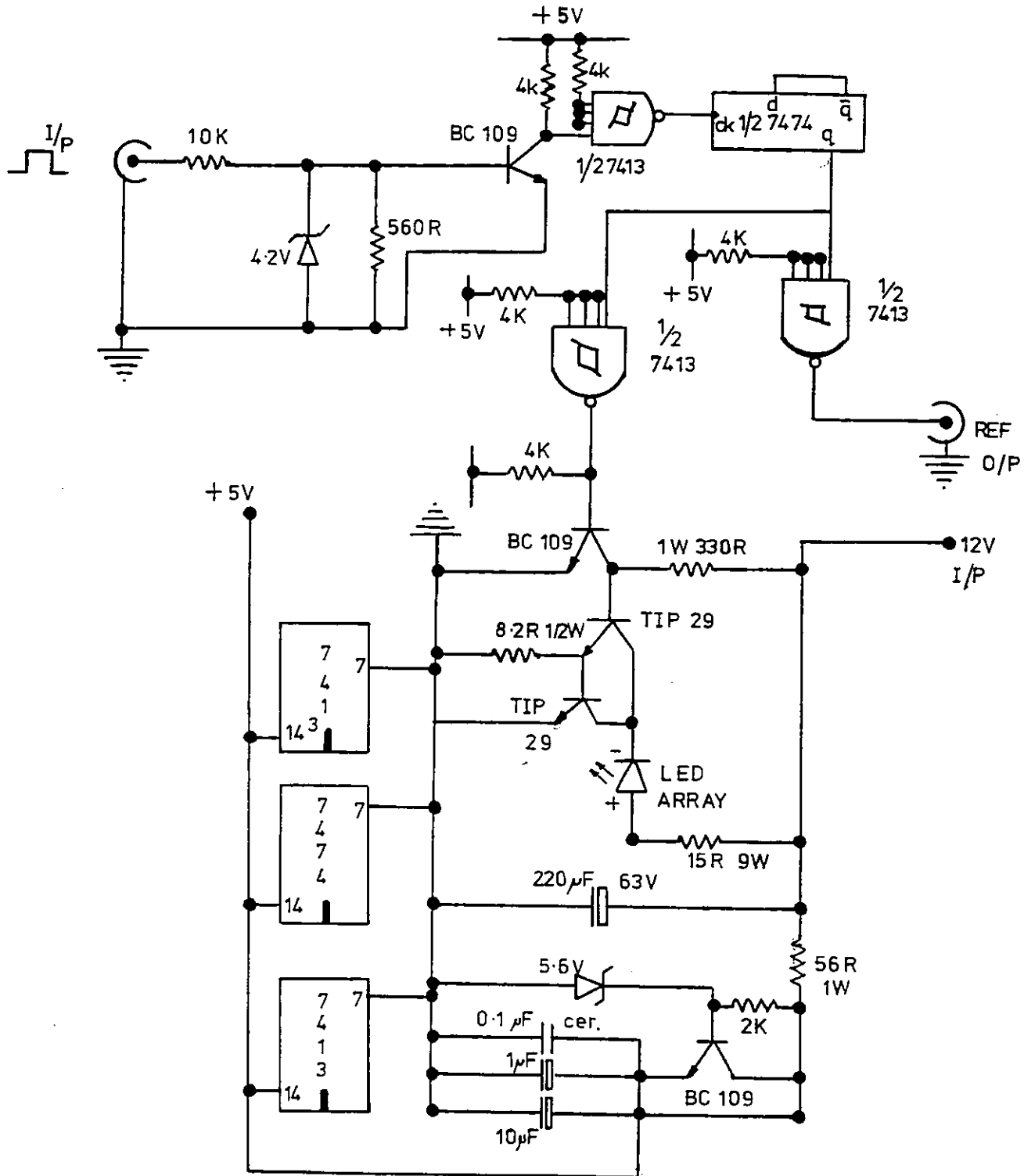


FIGURE 3-5: Trigger circuit for Photodiode system.

source (power estimated to be 29mW. with band-pass 0.03 $\mu\text{m}.$).

3.1.4 Instrumentation for Wavelength Modulation Spectroscopy.

Continuum source photoacoustic instrumentation, such as that described in this section is not capable of very high spectroscopic resolution because the band-pass used (10nm.U.V.; 0.03 $\mu\text{m}.$ near-IR) is necessarily large to meet the requirements of high power transmission through the monochromator. For some studies to be presented in section 3.3, a wavelength modulation facility was used which allows an apparent enhancement in spectral resolution to be obtained. This subject has been discussed recently by O'Haver (140).

Wavelength modulated spectra were obtained by driving the diffraction grating across the desired wavelength range whilst simultaneously oscillating the mirror focusing the dispersed radiation at the exit slit. The mirror (25x19mm.) was mounted on an open loop galvanometer providing total excursions of $\pm 14.5^\circ$ about the equilibrium point, and was powered by a triangular impulse from a signal generator (Hewlett-Packard model 3300A) -amplifier assembly. The reference signal for the lock-in detection was a square wave derived also from the signal generator. For obvious reasons no chopper was required for this instrumentation.

3.2 Quantitative Determination of Propranolol.

3.2.1 Introduction.

Traditionally, assay methods within the pharmaceutical industry

have been based on classical techniques or simple instrumental techniques such as gas-liquid chromatography and ultra-violet spectrophotometry. The rapidly changing requirements of the modern pharmaceutical industry however, have enforced the need for the development of new and faster techniques, which can cope with the diversity and the vast numbers of samples presented to the laboratory on a routine basis. The main reasons for the decline of these traditional methods may be summarised:

- (1) Classical methods require a high proportion of manual manipulative skill and are therefore time consuming and do not allow a high sample turnover rate.
- (2) Gas-liquid chromatography is not suitable for samples which have high melting points or are thermally unstable.
- (3) None of these techniques are easily adapted for batch or on-line analysis.
- (4) Requirement for sample dissolution.

These limitations have led to the appearance of new techniques, the most important of which are high performance thin layer chromatography (HPTLC) and high performance liquid chromatography (HPLC). The interchange of solvents used in these techniques can allow greater selectivity to be obtained and both are capable of very high resolution and separative power. On this basis, ionic compounds, polymers and labile compounds may be conveniently assayed and both techniques will play a dominant role in the future of the pharmaceutical industry. One disadvantage of the early techniques which has not been eliminated is the need for sample dissolution, an operation which will markedly increase the analysis time and which provides the opportunity for contamination.

If the pertinent features of photoacoustic spectroscopy are examined in relation to these current problems, a potentially valuable contribution to progress within this industry may be identified. These features are the capability for determining analyte concentrations non-destructively and without the need for extensive sample preparation procedures. In addition, the continued absence of reliable techniques for quantitative determination of separated components on TLC plates may allow PAS to be the technique of choice because quantitation may be accomplished in situ (106,109).

This PAS study was aimed at developing a quantitative method for the routine assay of a typical popular pharmaceutical product, propranolol, and to illustrate the advantages that PAS has to offer in comparison with the currently accepted method of analysis. Propranolol, marketed by ICI Chemicals Ltd., Runcorn, Cheshire under the trade name "Inderal," is a β -adrenergic receptor blocker which was introduced in 1966 (141) and is now universally accepted as a safe potent product for the control of cardiac arrhythmias, angina pectoris, hypertension and for hypertrophic obstructive cardiomyopathies in man. The marketed formulation, which has occupied a large share of the European and American β blocker markets, is available in the form of a series of compressed tablets in the range 10mg.-160mg. of the active ingredient in an inert diluent, table 3.1. The usual dosage is 20-40mg., three to four times per day. The molecular structure is shown in figure 3.6 together with the main diluent species, lactose.

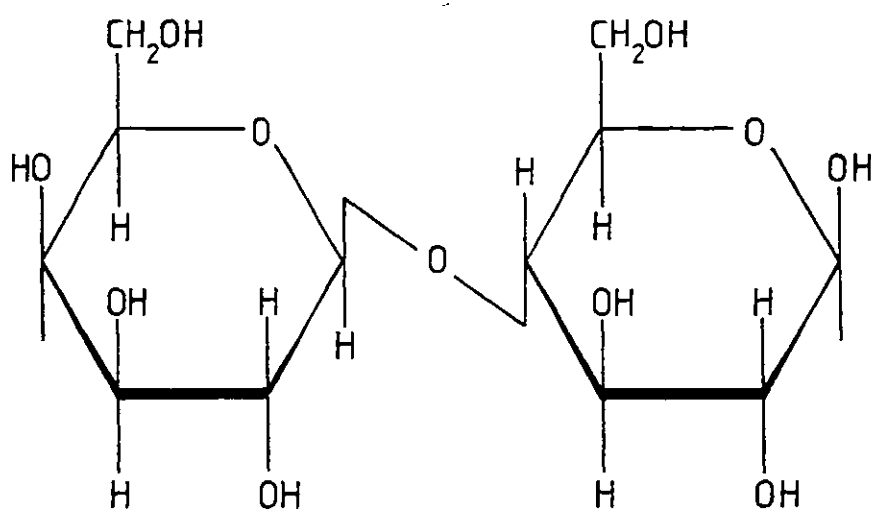
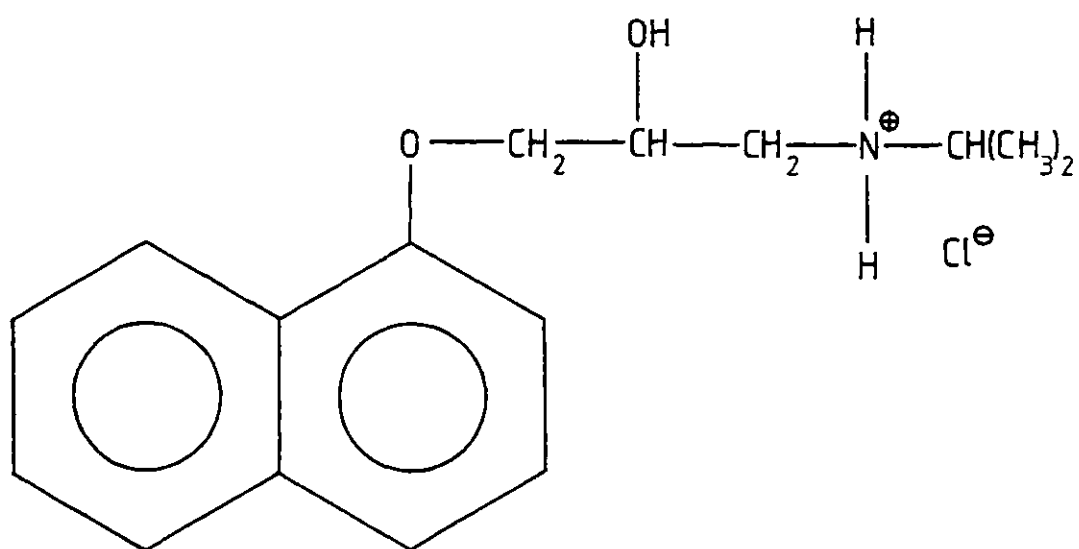


FIGURE 3-6 : Top-Structural representation of Propranolol,
1-(Isopropylamino)-3-(1-naphthyl-oxy)-2-propanol.

Bottom-Structural representation of Lactose.
4-(β -D-galactosido)-D-glucose.

Table 3.1 : Formulation data for propranolol.

mass active ingredient/mg.	diluent	%w/w.
10	lactose	10.5
40	lactose	20.0
80	lactose	28.6
160	calcium carbonate	36.0

Propranolol is an extremely interesting chromophore with a delocalised naphthyl electron system, which might be expected to give rise to an electron transfer in the UV region. This is linked to an alkyl chain possessing -OH, -CH, -NH and -CN groups absorbing energy in the near and mid-IR regions. Lactose, which is used as the main bulk forming agent in the tablets is constructed from two sugar rings, linked by an oxygen bridge, and -CH and -OH are the main structural groups which display absorption properties. In view of the optical properties of propranolol, it is not surprising that the current method of assay (142) involves spectrophotometric transmission measurement at 290nm. in methanol. The presence of other insoluble tablet excipients (gliders, lubricants, dispersers) necessitates a physical separation of the analyte resulting in a time consuming and tedious process and the requirement for dissolution of the sample.

3.2.2 Experimental.

Samples of propranolol and residual tablet species were supplied by ICI Pharmaceuticals Division, Macclesfield, Cheshire. The tablet range is normally sold with a pink identifying dye coating, but for these studies both uncoated and coated tablet ranges were supplied. All these materials were tested for purity in accordance with the

conditions stipulated in the British Pharmacopoeia 1973 and were found to comply. The claimed levels of the active ingredient were checked using the official method, by weighing five tablets into a graduated flask and dissolving in methanol (A.R.). The solution was filtered through a Whatman #42 paper after making to volume, and the solution diluted according to the tablet size being assayed. The absorbance of this solution was monitored at 290nm. against methanol blank, using a Pye-Unicam SP1700 spectrophotometer, and compared with a solution of pure propranolol similarly treated. From the ratio of the absorbance readings, the mass of propranolol in each tablet was computed and all the tablets supplied were found to be within the accepted limits, table 3.2.

Table 3.2 : Assay results on propranolol tablets.

tablet size/mg.	claim/% w/w	level found/% w/w
10	10.5	10.8
40	20.0	20.5
80	28.6	27.9
160	36.0	37.0

Sample preparation for the PAS studies was minimal and consisted of breaking down the tablet compression binding in an agate mortar and pestle, to a homogeneous powder, which was sealed into the cell on the aluminium sample tray. The particle size in the powder was the same as that comprising the compressed tablets and was approximately in the range 50-100 μm . A separate study revealed that particle size did not vary significantly from tablet to tablet within the same batch.

The instrumentation described in section 3.1 was used for both the near-IR and UV-vis. region studies. For quantitative studies the multipoint signal averager was used in its linear normalised mode.

3.2.3 Results and Discussion.

Normalised near-IR of pure propranolol and the main tablet excipient, lactose, were recorded and are shown in figure 3.7. Propranolol displays two major peaks in this region, one at 1.76 μm . and the other at 2.21 μm . Unfortunately structural assignments in this region cannot be rigorously applied because the link between the chemical environment of the particular chromophore and the frequency of the observed transition has been less extensively studied than the equivalent transitions in the mid-IR region. The observed bands for propranolol were assigned jointly from Colthup type frequency charts (130) and intensive studies of α -based naphthalene analogues. The analogues chosen were naphthalene, 1-napthoic acid, 1-napthyl acetic acid and 1-napthol, the structures of which are shown in figure 3.8. The spectra of these compounds were recorded from 1.0-2.3 μm . and the observed transitions compared. The two primary bands for propranolol were tentatively assigned as aromatic C-H transitions using these cross correlation techniques. Smaller bands were also observed in the spectra and were assigned similarly. These assignments are summarised in table 3.3.

Table 3.3 : Structural assignments for propranolol.

Observed transition/ μm .	probable structural group
1.39	C-H aromatic
1.54	N-H
1.76	C-H aromatic
1.88	O-H
2.12	O-H
2.21	C-H aromatic

Lactose, the main excipient exhibits several absorption bands, those

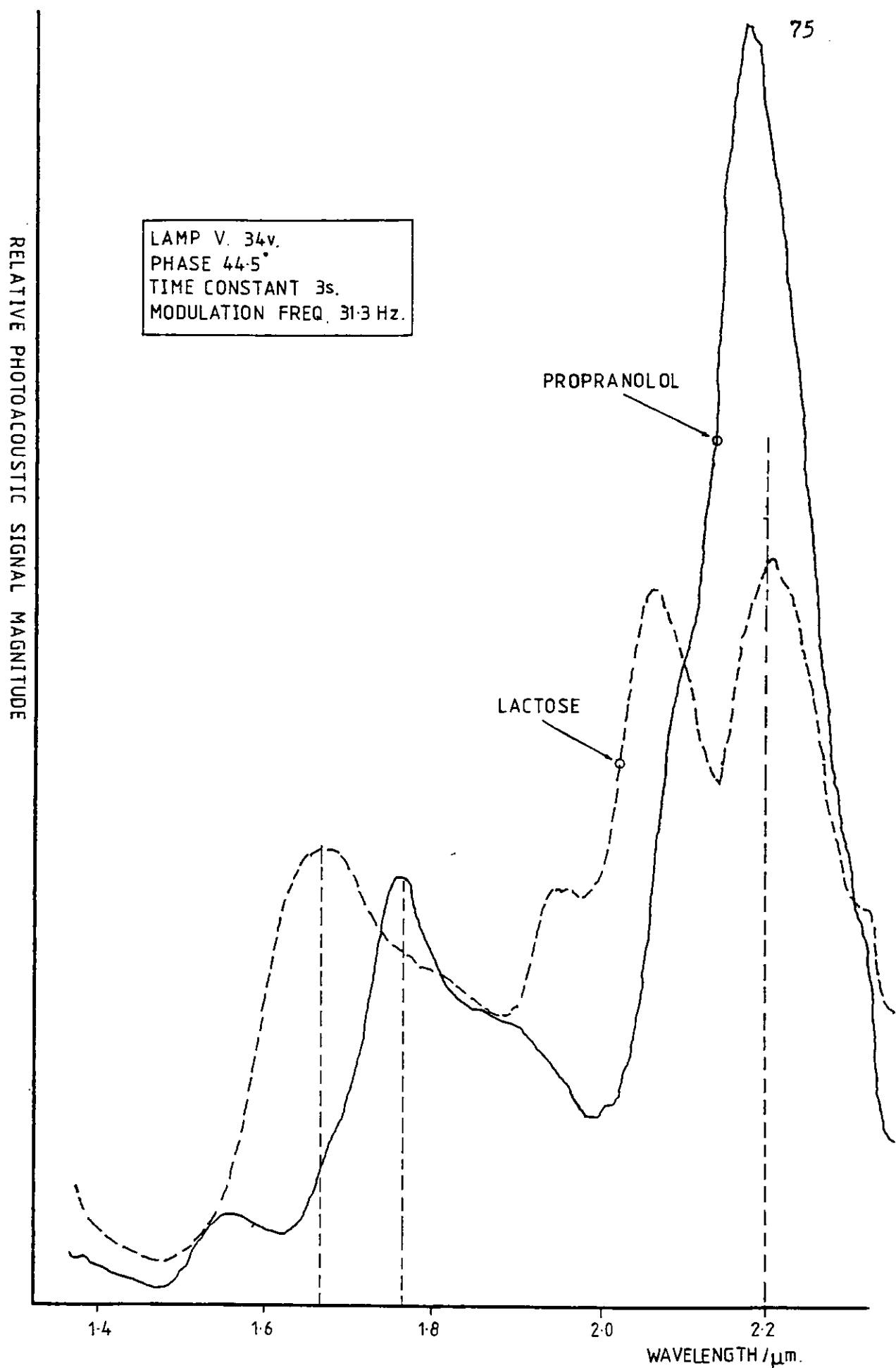
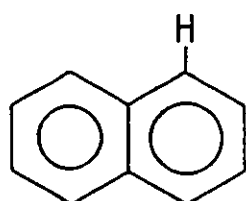
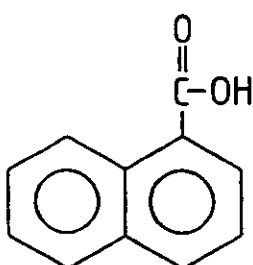


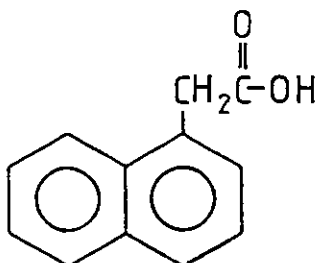
FIGURE 3-7: Normalised near-IR spectra of propranolol and lactose.



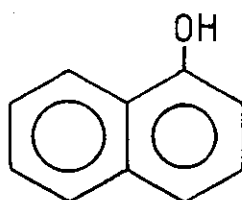
Naphthalene



1-Napthoic acid



1-Napthyl acetic acid



1-Napthol

FIGURE 3-8: α based analogues used for spectroscopic characterisation of propranolol.

at 1.65 and 2.25 μm . are the most important and can probably be attributed to -OH overtone transitions.

When the recorded spectra were considered from an analytical viewpoint, the 2.21 μm . aromatic vibration appeared to have the best potential for assay purposes, although some contribution from the background is present at this frequency. A thorough examination of the spectra revealed two possible modes for determination of propranolol in a sample. The first involved monitoring relative signal magnitude at 2.21 μm . as a function of the propranolol concentration in the mixture and subtracting the relative signal magnitude from a blank material composed of all the tablet excipients except propranolol, at the same wavelength. This background correction method was used to prepare a calibration curve for the tablet range.

The second method involved the computation of the quotient of the signal magnitude of the sample at 2.21 μm , the major peak for propranolol to that at 1.65 μm . the major peak for lactose. Contributions from both lactose and propranolol therefore dominated the value of this quotient and because the mole ratio of these two components changes as the concentration of propranolol increases in the mixture, the quotient value was indicative of the concentration of propranolol present. This particular method would be expected to be immune to errors and irreproducibility in sample loading, but might be subject to interference from other components in the tablet. In contrast, the signal magnitude method is specific for propranolol but requires standardisation in sample loading and suffers from unfavorable S/N limitations because of low source emission flux at this wavelength. This could be improved by the adoption of a more suitable source, such as a laser, with high radiative power in this

region.

Both the methods which have been described were used for evaluation of analytical calibration systems for standard propranolol uncoated tablet formulations and the results are shown in table 3.4.

Table 3.4 : Photoacoustic amplitude measurements for powdered uncoated tablets. Top-signal magnitude method. Bottom-ratio method.

tablet size/mg.	conc. /%ww	magnitude 2.21 μ m.		blank corr.
lactose	0.0	1.015		0.000
10	10.5	1.145		0.130
40	20.0	1.230		0.215
80	28.6	1.331		0.316
160	36.0	1.084		0.443
CaCO ₃	0.0	0.641		0.000
tablet size/mg.	conc. /%ww	2.21 μ m. sig. magnitude	1.65 μ m.	ratio
lactose	0.0	0.873	1.308	0.667
10	10.5	0.993	1.299	0.764
40	20.0	1.055	1.230	0.858
80	28.6	1.155	1.210	0.955
160	36.0	-	-	-
CaCO ₃	0.0	-	-	-

Both methods produced linear calibration curves. A study was made of the analytical precision using these methods by computing the relative standard deviation (rsd) on ten measurements, and was 0.05 for the ratio method and 0.06 for the peak height method. Data is included in table 3.4 from the 160mg. tablet which contained calcium carbonate as the main diluent in place of lactose. The spectrum of this tablet was recorded and is shown in figure 3.9. A band at 2.25 μ m. was again observed but there was minimal contribution at 1.65 μ m. and precluded the ratio method of assay. The close correlation of data obtained using the peak height method indicates the success with which the background correction procedures may be applied.

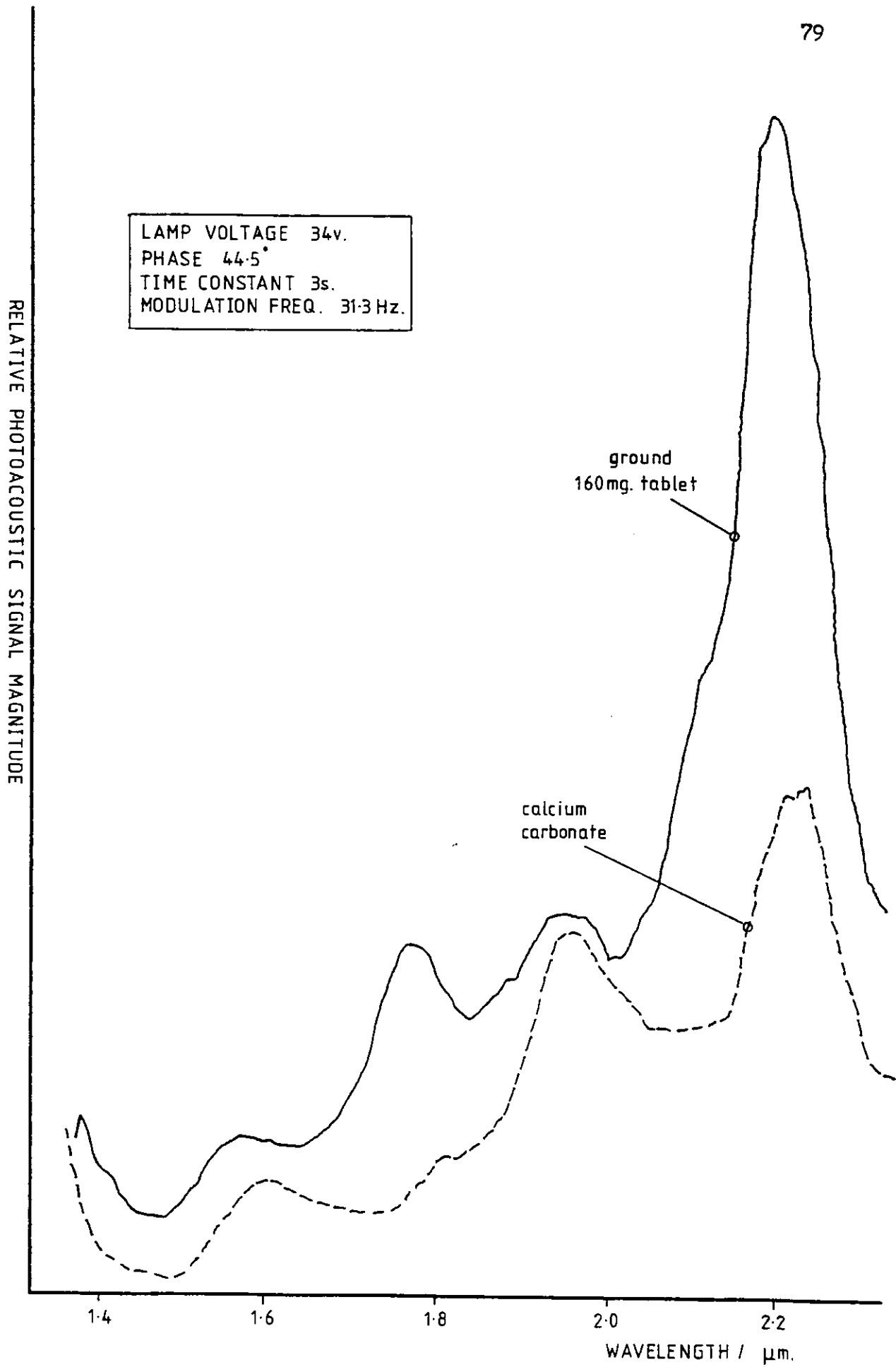


FIGURE 3-9: Normalised near-IR spectra of powdered 160mg. tablet and excipient, calcium carbonate.

Studies of the propranolol tablet range were also made in the ultraviolet region of the spectrum. The PAS spectrum, figure 3.10, was remarkably similar to that obtained during testing of the tablets by solution spectrophotometry and is characterised by a broad band at 290nm. with minimal interference from the other species in the tablets. Spectra for an artificially prepared set of standards ranging from 0-100% w/w propranolol were recorded and are presented in figure 3.11. The calibration curve drawn from measurements made at 290nm. as a function of propranolol concentration in the sample, is also shown in figure 3.12, and is fairly linear at low concentrations of propranolol. At higher concentrations, progressive negative deviation is observable, a phenomenon which has been noted frequently by other workers in making quantitative measurements using PAS. For this case, the curve remains linear up to 50% w/w propranolol which is higher than the level normally encountered in dosage forms and would therefore probably not affect the validity of measurements made on a routine basis. Progressive negative deviation in the working curve could be attributed to photoacoustic saturation, the condition where all the radiation impinging on the sample is absorbed within the thermal depth, μ_s . This is unlikely to be the case for the propranolol system because the optical absorption coefficient, β , is fairly small ($\epsilon=210$), and therefore the magnitude of l_β is fairly large. The reason for the observed deviation must instead be caused by some physical interference process. One such process could be scattering of the radiation by the residual components of the sample matrix, a phenomenon discussed recently by Burgraaf (119). If scattering were to occur, then the photon distribution in the sample would be altered and would produce a higher probability of an analyte particle absorbing

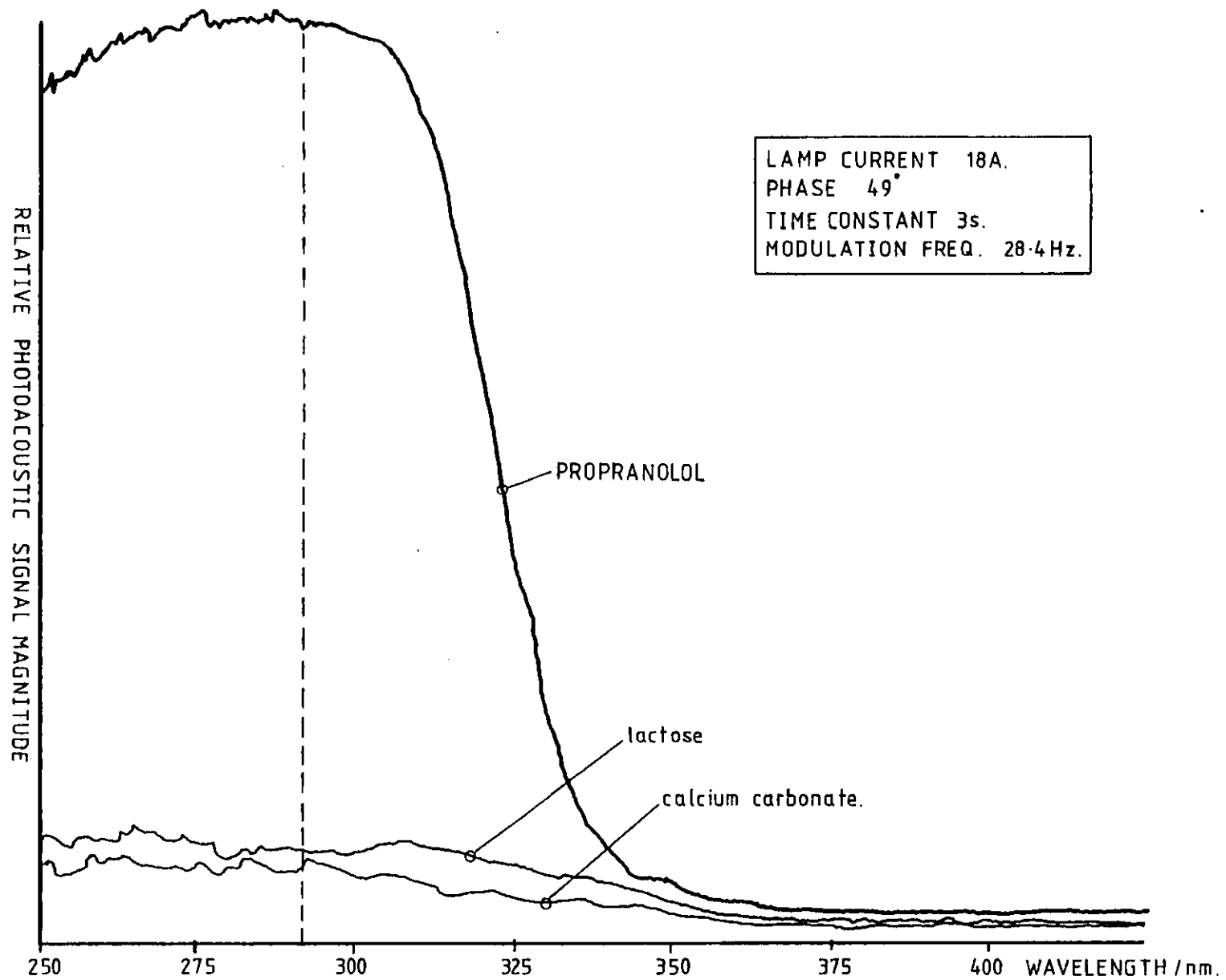


FIGURE 3.10 : Normalised ultra-violet spectra of powdered propranolol, lactose and calcium carbonate.

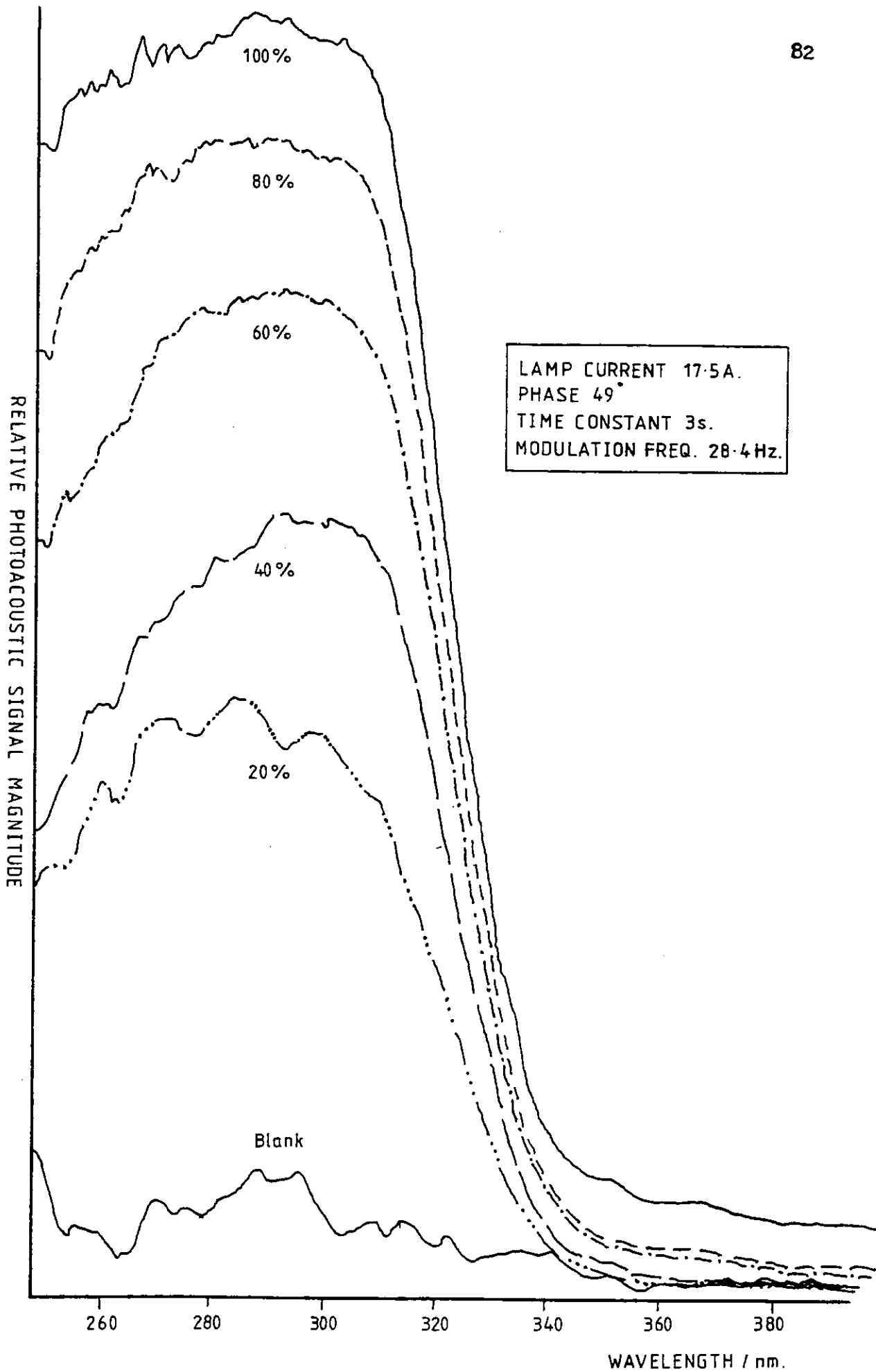
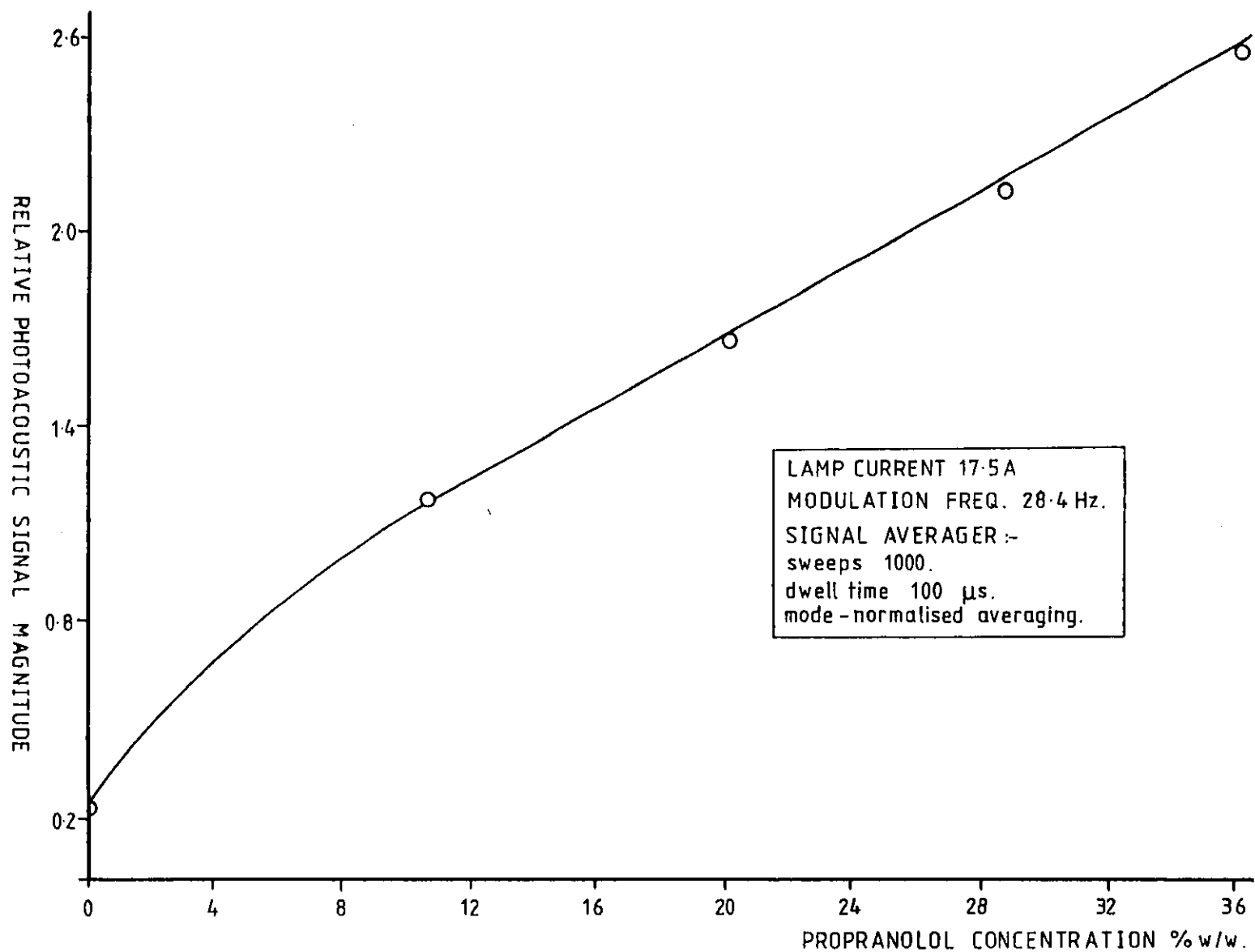


FIGURE 3-11: Normalised ultra-violet photoacoustic spectra of powdered mixtures of propranolol ranging from 0-100% w/w.

FIGURE 3-12 : Calibration for propranolol in powdered tablets. All measurements were made at 290 nm. (ultra-violet region).



the photons. On a macroscopic scale this would result in enhancing photon absorption by the analyte when present at low concentrations because the concentration of the residual components is correspondingly high.

An alternative mechanism can be derived by considering the thermal properties of the sample as the mass fraction of the analyte is increased. At low mass fractions, matrix particles may provide an alternative, more efficient pathway through the sample for the propagating thermal wave. At high analyte mass fractions, the efficiency would be smaller, resulting in curvature of the working curve.

3.2.4 Studies with Intact Tablets.

The studies which have been described were confined to measurements made on powdered uncoated tablets. Quantitative data involving intact tablets, uncoated and coated, is extremely desirable, because sample preparation would be minimal and automation of the entire production programme of the product could be envisaged. Accordingly, a pilot study for intact propranolol tablets was conducted to assess if this concept was feasible. Spectra were recorded for both uncoated and film coated tablets by sealing into the photoacoustic cell on the aluminium sample tray and scanning between 1.0 and 2.3 μm . in the near-IR and 250 and 400nm. in the UV-vis. These spectra are presented in figures 3.13 and 3.14. For each case, the background was recorded by scanning across the same wavelength limits for magnesium oxide powder (AR), sealed into the cell. Magnesium oxide is widely used for such purposes in reflectance spectroscopy.

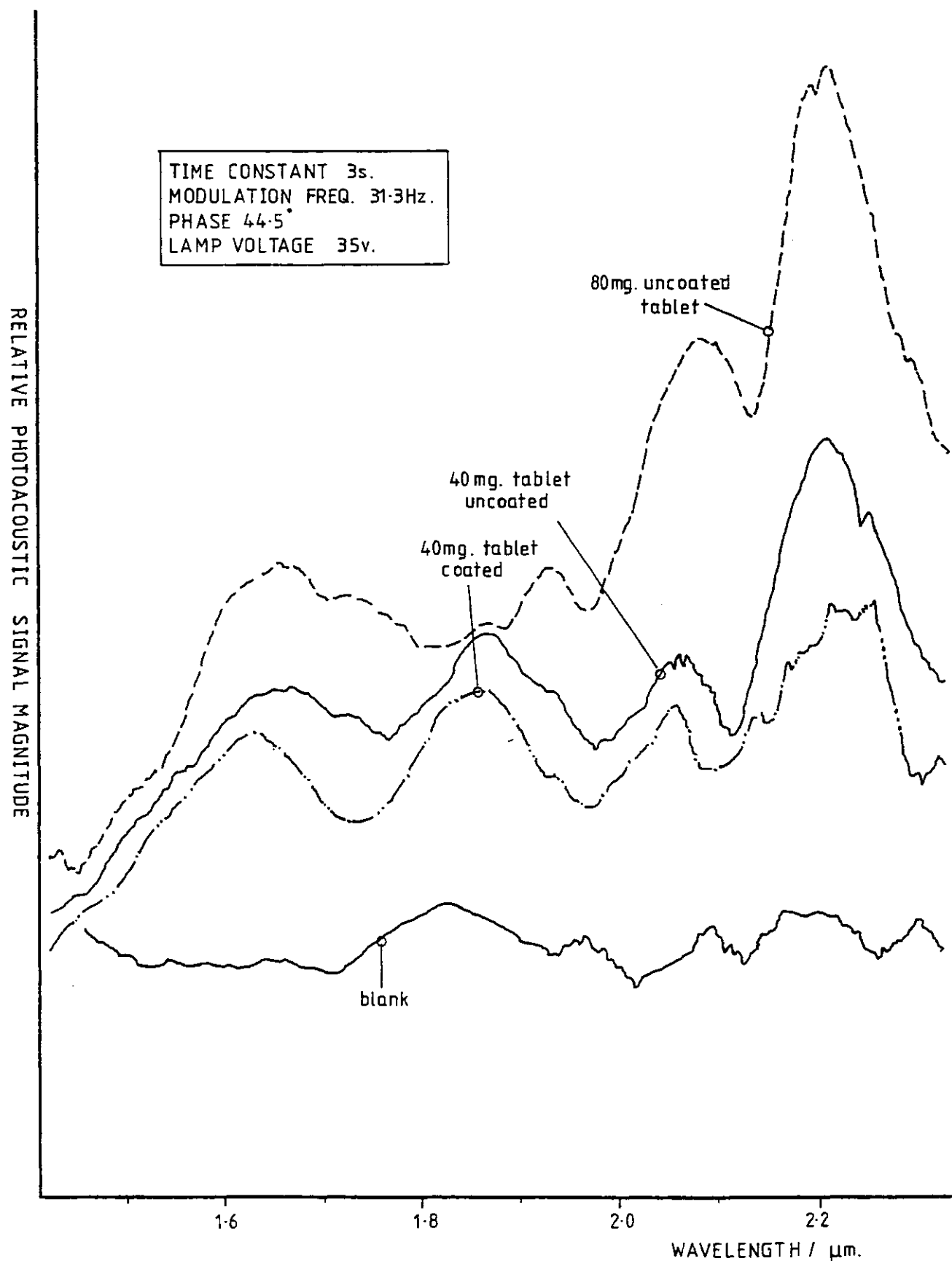


FIGURE 3-13: Near-IR spectra of intact propranolol tablets. All spectra normalised against power spectrum of source. Note similarity of coated tablet spectrum to the spectra of the uncoated tablets.

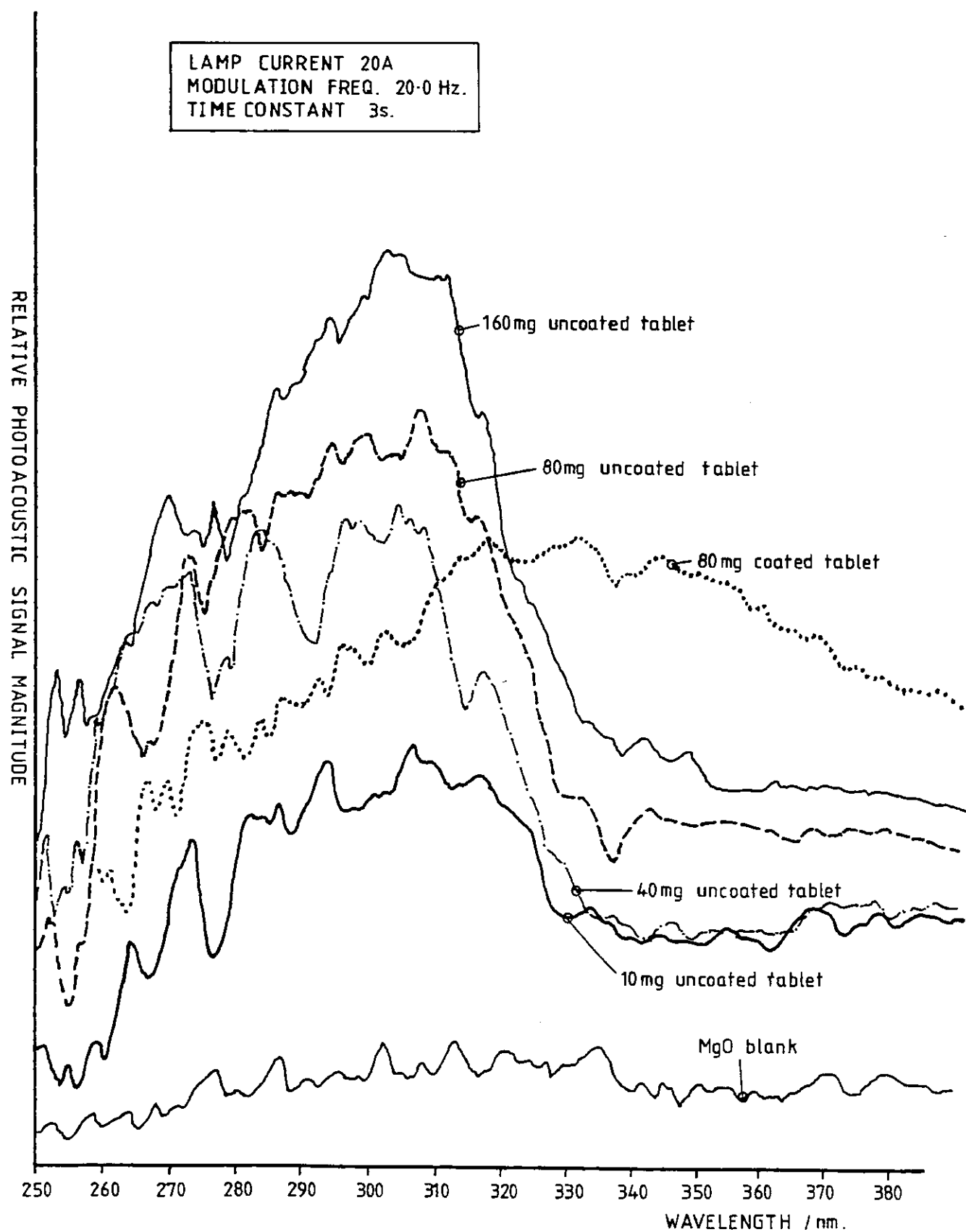


FIGURE 3-14 : Normalised ultra-violet photoacoustic spectra of intact 10-160mg tablets.

In the near-IR region, spectra were obtained for the 80mg. uncoated tablet and the 40mg. uncoated and film coated tablets. The identifying features of the propranolol spectrum recorded for the powdered tablets are again clearly visible and it is interesting to note that the presence of the film coating does not have any significant effect on the structure of the spectrum. The film coating appears to be optically transparent in this region, at the selected modulation frequency 31Hz.

The spectra obtained in the UV-vis. region for the total tablet range show a general maximum at 300nm. and are again structurally similar to those obtained previously with the powdered tablets. These spectra also exhibit a crude correlation between the mass fraction of propranolol in the tablet and the peak height of the spectra at 300nm. Exact measurements were not made because the spectra had to be corrected for the variation in physical size through the tablet range, and the correction was not considered accurate enough for calibration purposes. The spectrum obtained for the film coated tablet (40mg.) is a broad band with a maximum at 330nm. It is probable that the pink dye coating on the tablet interferes with the propranolol absorption peak at 300nm. The coated tablet range does not therefore appear to be amenable to assay in the UV-vis. region on the basis of these studies.

For all measurements obtained on the intact tablets, S/N ratios were significantly poorer than for the powdered studies. For this reason no quantitative measurements were made. The PAS cell, was, in addition, considered inadequate for more exacting studies because the sample tray was specifically designed to accommodate powdered material. Despite these problems, an assay method based on intact tablet samples appears to be feasible and would represent an exciting

step in the future role of PAS for quantitative analysis.

3.3 Determination of Fat Content of Milk Powders.

3.3.1 Introduction.

The analysis of food products often involves laborious analytical sample preparation procedures owing to the complexity of the matrix. The determination of fat in dried milk powders has traditionally been accomplished by solvent extraction in specially designed tubes (143) with petroleum ether followed by gravimetric analysis of the extracted fat, the so-called Mojonnier method. This approach is subject to several problems, which are the requirement for specially designed apparatus and for a high degree of analytical skill on the part of the operator. In practice, the fat which is released from the milk powder has a tendency to partition between the aqueous and organic layers of the solvent extracting system with the consequent formation of an emulsion. The accuracy of this method is therefore extremely questionable, and there exists a need for more satisfactory methods for routine analysis. Recently Ahmed and Goldstein (144) developed a method for the quality control of fat in dried milk using diffuse reflectance spectroscopy. This was claimed by the authors to be faster than the wet chemical method with an estimated analysis time of fifteen minutes. The replacement of the classical approach by an instrumental method in this way enables rapid determinations to be accomplished and opens the possibility of automating the entire process. The classical approach will always be the method of choice for primary reference determinations, but instrumental techniques such

as diffuse reflectance appear to offer significant advantages in terms of speed and simplicity of sample preparation procedures.

Against this background, PAS was selected for a study of the determination of fat in a range of milk powders. PAS would be admirably suited for this application, with rapid sample preparation, non-destruction of the sample and relative immunity from scattered radiation when compared with diffuse reflectance spectroscopy (145). In the work to be described, an empirical approach was considered because no absolute quantitative theory has been developed to cope with all the variables in the system.

3.3.2 Experimental.

Milk powders are produced commercially by two processes (1) drying the liquid product on heated rollers-roller dried milk; (2) evaporating the liquid product by spraying in a heated chamber-spray dried milk. The fat content is usually within a narrow range determined by the breed of cow supplying the milk, but can be varied by skimming techniques.

For these studies a range of spray dried milk powders representing five different fat contents were supplied by Unigate Dairies Ltd. All the powders contained milk fat and were sieved so that the particle size was in the range 38-63 μm . The removal of surplus water is extremely important to prevent attack by microorganisms and the samples were stored over silica gel in a desiccator for twenty four hours prior to analysis. Oven drying of milk powders results in denaturing of the protein and partial oxidation of the fat and for this reason was not attempted.

The fat contents of the samples claimed by the manufacturer were checked by the Mojonnier method. The sample, in duplicate, (1g) was weighed directly into a separating funnel, previously dried to constant weight, and water (10ml.) added until the sample was completely dispersed. Ammonia solution (25% ;2ml.), was added to completely dissolve the protein. Ethanol (10ml.) was then added and the mixture shaken gently. Diethyl ether (25ml.) was added to the mixture and the funnel shaken to facilitate extraction of the fat. Light petroleum (25ml ;40-60°) was added and the process repeated. After the two layers had separated, the organic layer was separated into a vessel previously dried to constant weight. The extraction was repeated a further two times and the combined ether extracts were heated over a water bath under a stream of air for one hour to remove the ether and residual solvents. The beaker was then dried to constant weight at 60°C and the mass of fat collected, determined by reweighing the beaker. The fat content of the sample was computed after consideration of the initial weight of sample and subtracting the blank determination obtained by repeating the procedure and omitting the milk powder. The results of the assays are presented in table 3.5.

Table 3.5 : Fat contents of milk powders by Mojonnier method (143).

claim %ww	tolerance %	level found %	tolerance %
0.50	not supplied	2.0	± 0.5
0.86	not supplied	2.0	± 0.5
2.0	not supplied	2.0	± 0.5
23	not supplied	22	± 1
36	not supplied	36	± 2

It is apparent from the results that the error in the determination becomes significant at low concentrations of fat in the milk powder, and the limitations of this method were ably demonstrated. After

careful consideration, the manufacturers claimed levels were adopted as standard as these had been obtained with specifically designed glassware, although there were some doubts about the accuracy of the results. An additional sample was prepared by mixing equal quantities of the 23% w/w sample and the 2% w/w sample to provide a more complete set of standards.

The instrumentation described in section 3.1 was used to obtain PAS spectra in the near-IR region. For quantitative measurements a multipoint signal averager was used in its linear normalised mode.

3.3.3 Results and Discussion.

Quantitative spectra of the standards were recorded between 1.3 and 2.3 μm . and are presented in figure 3.15. All the milk powders produce four peaks in this region and these were assigned from a Colthup frequency chart and from a previous reflectance study (146). The assignments are presented in table 3.6.

Table 3.6 : Band assignments- milk powders.

band head/ μm .	transition	source
1.39	-OH	lactose
1.62	-OH	lactose
1.75	-CH	fat
1.93	-OH	lactose, H_2O

The bands of major interest are the -OH overtone of lactose, a main constituent of the milk powder, which occurs at 1.62 μm . and a band at 1.75 μm . which can be assigned to a first overtone vibration of the -CH methylene group of the fat. This band is usually strong for fats

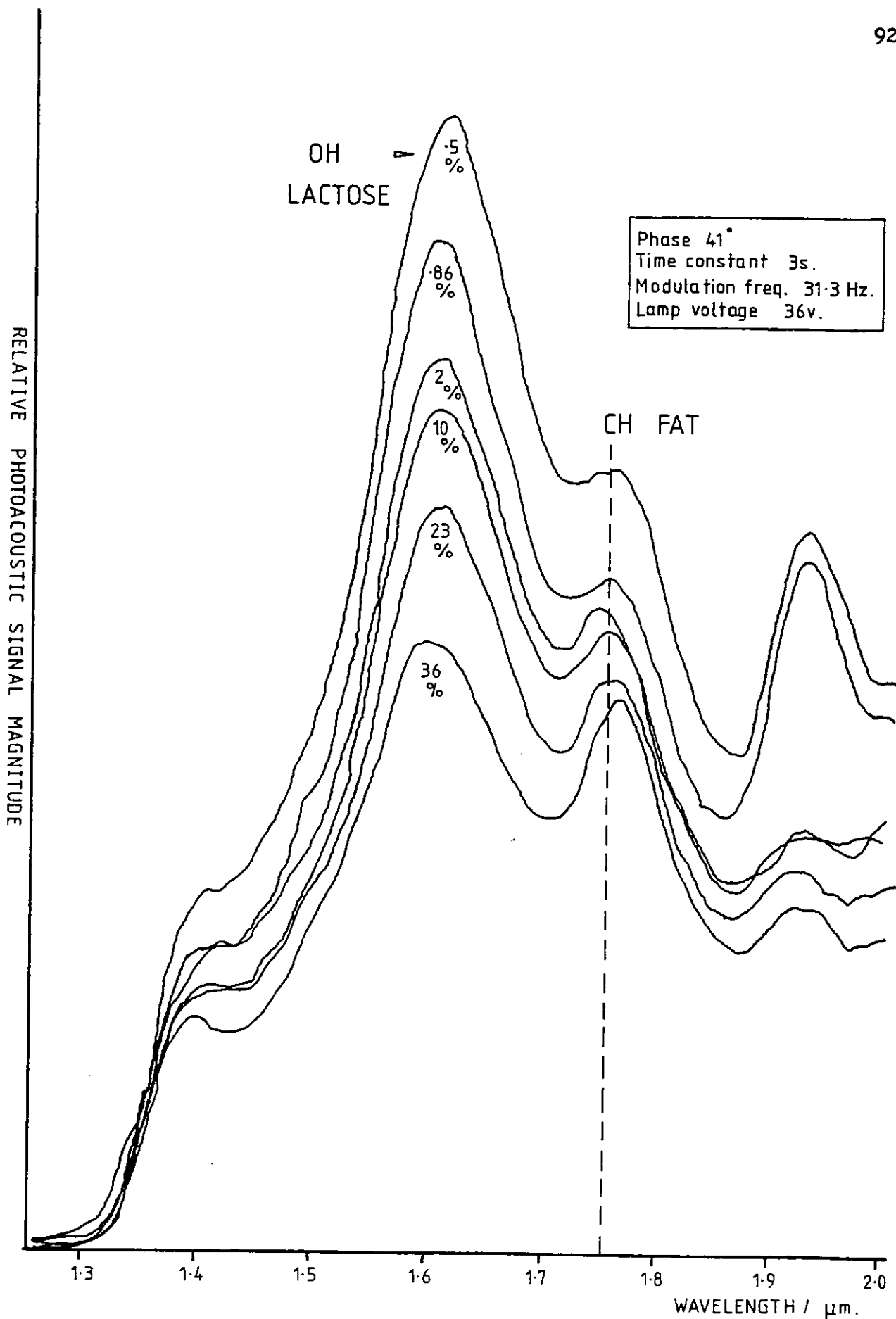


FIGURE 3-15: Normalised near-IR spectra of spray dried milk powders containing fat levels 0.5-36%.

because long chains are involved with a correspondingly high number of methylene groups. The most important characteristics of the observed spectra are immediately apparent. As the fat content increases in the sample, the -OH band at $1.62\ \mu\text{m}$. becomes less intense and the -CH band at $1.75\ \mu\text{m}$. becomes more intense. Another major feature of the spectra is that the intensity distribution of the total spectral profile appears to decrease as the fat content in the sample rises, which may be attributable to an alteration in the thermal properties of the sample.

Two methods for the quantitative determination of the fat are tenable, a method based on peak height measurement at $1.75\ \mu\text{m}$. and a ratio method involving computation of the quotient of the PAS signal magnitude at $1.75\ \mu\text{m}$. and at $1.62\ \mu\text{m}$. as a function of the concentration of fat in the sample. Both of these methods have been described in section 3.2.3. Quantitative measurements collected by applying these methods are summarised in table 3.6.

Table 3.6 : Quantitative data for milk powders (a) peak height method ; (b) ratio method.

fat content / %	peak height $1.75\ \mu\text{m}$.	magnitude $1.75\ \mu\text{m}$.	magnitude $1.62\ \mu\text{m}$.	ratio $1.75/1.62$
0.5	0.00	10.30	15.50	0.66
0.86	0.20	9.80	14.85	0.66
2.0	0.25	8.00	11.30	0.71
11	0.65	8.90	12.05	0.74
23	0.94	7.87	9.70	0.81
36	1.65	7.45	8.20	0.91
(a)		(b)		

Calibration curves for both methods are shown in figure 3.16. Examination of these curves reveals a close correlation between the photoacoustic response function and the concentration of fat in the dried powder, but no further conclusions may be drawn without

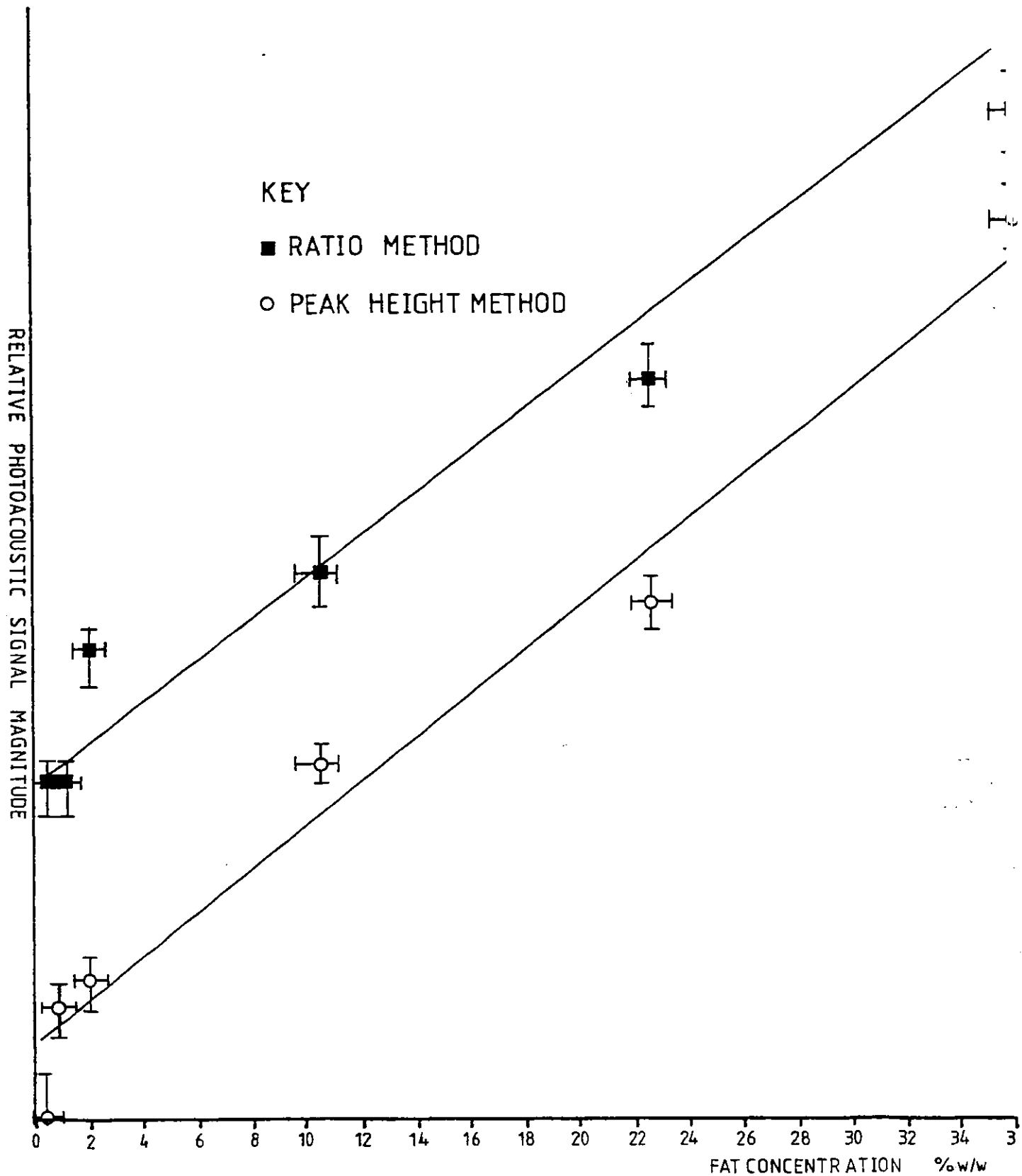


FIGURE 3-16 : Calibration curves for fat in milk powders, by ratio and peak height methods. Signal averager conditions - dwell time 100 μ s. : number sweeps 1000 : sensitivity 0.2 v/div. : mode-normalised averaging.

provision of a more reliable set of standards. The correlation coefficient for a linear fit for both sets of data was, however, calculated to be approximately 0.97.

If the spectra presented in figure 3.15 are examined in further detail, it becomes apparent that there is an inadequate resolution of the -CH overtone at $1.75\ \mu\text{m}$. and the lactose -OH band at $1.62\ \mu\text{m}$. This could contribute to loss of accuracy and precision with this technique. The poor resolution was primarily a function of the monochromator, the spectral bandpass of which was calculated to be $0.03\ \mu\text{m}$., when employing a large slit width of 2.5 mm. This large slit width could not be altered, because the PAS system is primarily noise limited by the detector and a high throughput of radiative flux is mandatory for acceptable S/N ratios. Instead, an "artificial" method of improving the apparent resolution of the spectra was used employing wavelength modulation spectroscopy. This has been discussed recently by O'Haver (140) and by Kirkbright *et al.* (147). The instrumentation for this study has been previously described. (section 3.1).

The first order derivative spectrum of the 2% w/w milk powder may be observed from figure 3.17, superimposed on the zero order (primary) spectrum obtained using the conventional scanning approach. The resolution of the bands is readily apparent. A calibration curve was plotted from data obtained from the resolved spectra, using the peak height method and was of a similar shape to those previously obtained. Unfortunately, the wavelength modulation method does not allow discrete measurements to be made at a set wavelength and therefore signal averaged results were not obtainable, however the use of such a system appears to be highly successful in improving the spectral resolution if studies are to be made on recorded spectra.

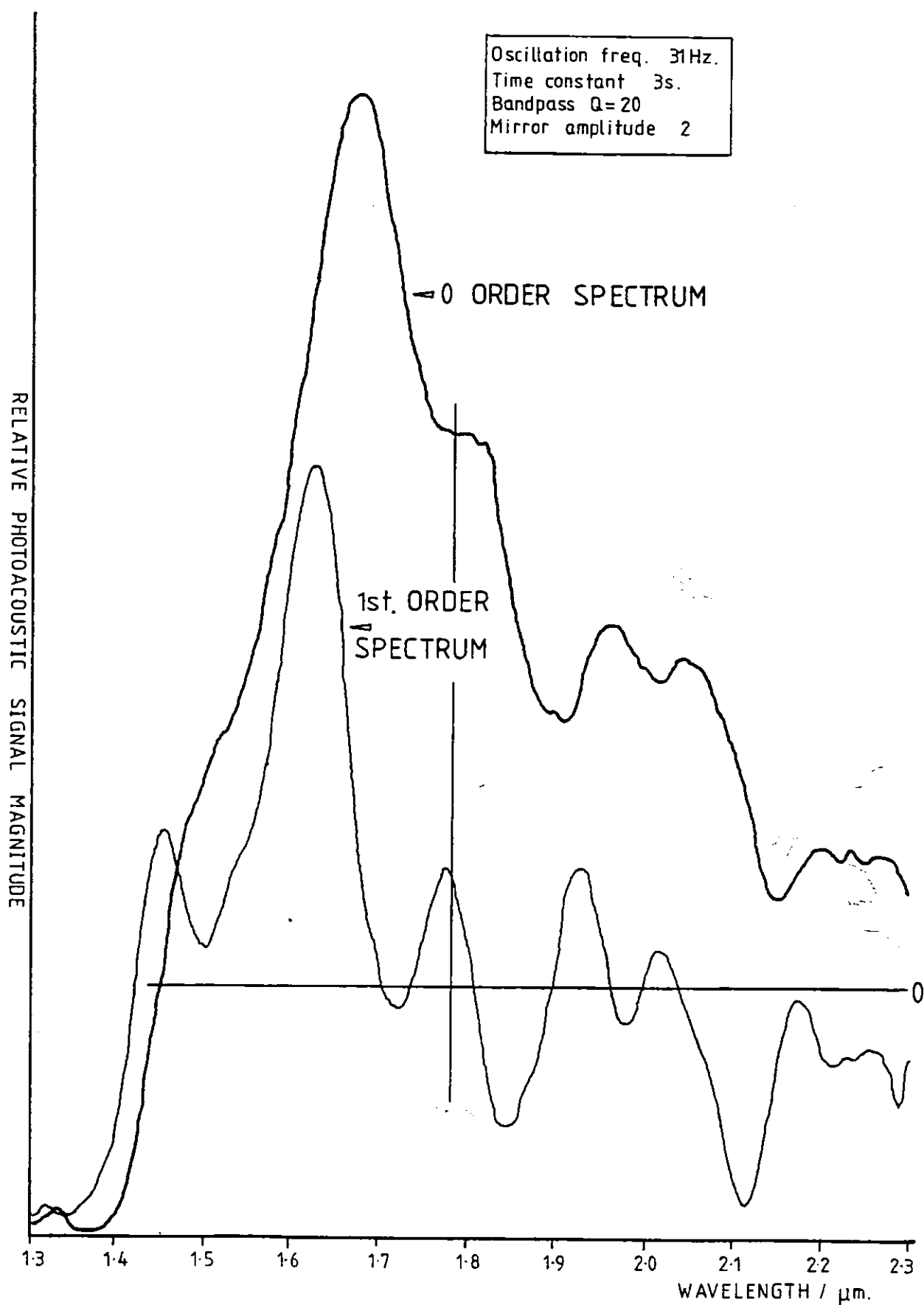


FIGURE 3-17: Zero and first order normalised differential photoacoustic spectra of the 2% spray dried milk powder. Zero line designates $dS/d\lambda=0$.

3.4 Conclusions.

The results presented in this chapter demonstrate that useful calibration curves can be prepared for the possible routine assay of the β -adrenergic receptor blocker, propranolol, and for the level of fat in spray dried milk powders. In the absence of a complete theoretical picture for quantitative PAS, for these studies, an empirical approach was assessed. Particle size is a major physical variable affecting the magnitude of photoacoustic amplitude functions and for this reason the particle size was closely controlled for both systems.

The assay of propranolol in the near-IR may be accomplished by the use of two methods, measurement at a specific wavelength and by obtaining the ratio of measurements performed at two wavelengths. Both approaches appear to be valid for the purposes of calibration. The first method is fairly sensitive to variation in sample loading but could easily be automated by use of a single dedicated non-dispersive instrument. For the continuum source used in these studies, there was little useful power available at the selected wavelength, 2.31 μm ., and data of higher quality could be obtained by converting to a radiation source with a maximum radiation intensity more closely matched to this area of the spectrum, such as a gas or diode laser. In contrast, the second method, based on measurement of amplitude ratios, would be expected to be immune from small changes in sample loading but might be subject to interference from non-analyte material.

In the UV-vis. region, a band at 290nm. in the photoacoustic spectrum may be used to determine the amount of propranolol. Curvature of the calibration graph at propranolol levels above 50% would not

seriously affect analytical results because the levels to be determined are usually $\leq 36\%$. Some mechanisms have been proposed to account for this curvature, which are based on scattering effects and the alteration of thermal propagation through the sample as the concentration of matrix species is varied.

If all relevant problems are addressed, PAS could be the method of choice for the determination of propranolol and similar pharmaceutical products on a routine basis, and useful results have been obtained which indicate that quantitative data may be obtainable on the solid intact formulations with no sample preparation demands.

The assay of fat in dried milk has traditionally been performed by wet chemical solvent extraction and gravimetric analysis. This method is highly unsatisfactory, with a tendency for the formation of emulsions and partitioning of the fat between the aqueous and organic layers of the extraction system. Results using PAS indicate that fat could be determined rapidly by measurement at a single wavelength or at two wavelengths, with non destruction of the sample. PAS could be superior to diffuse reflectance spectroscopy for this application because extensive compensation for scattering effects is not required.

It has been shown that the use of differential spectral techniques appears to improve the available resolution for measurements on the spectra of these milk powders. This could be beneficial for diagnostic studies on milk powders and similar products but is probably of limited use if signal averaged measurements are required at discrete wavelengths. However, in this case quantitative measurements can be made from the recorded spectra.

CHAPTER 4

INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

4.1 THE INDUCTIVELY COUPLED PLASMA4.1.1 Introduction.

Atomic spectroscopy is concerned with the interaction of radiation with atomic species, producing quantised energy changes in the electronic structure surrounding the nucleus. Because associated internal energy components, such as vibration and rotation are absent, atomic spectra consist of series of sharp lines corresponding to discrete energy changes in the electron distributions. Although in theory, each line would be truly monochromatic, this is never observed in practice because several line broadening processes occur, including broadening by the spectrometer used for viewing and dispersing the radiation.

In the U.V.-vis. region of the electromagnetic spectrum, atomic spectral studies can be made by measuring (a) the amount of radiation, from an external excitation source, which is absorbed by the atomic population-atomic absorption spectroscopy, AAS, (b) the amount of radiation emitted from the atomic population after excitation with a suitable spectral source-atomic fluorescence spectroscopy, AFS, and (c) the amount of radiation emitted from the atomic population after raising the population to high temperature-atomic emission spectroscopy, AES.

The fundamental component of all these techniques is the atom cell or reservoir, the site where the atomic population is generated.

Because free atomic populations are rarely met in laboratory ambient conditions, special techniques are used to produce them and the atom cell or reservoir can be regarded as an "active" environment.

As in all areas of analytical chemistry, atomic spectroscopy has had to cope with the increasing demands posed by industrial and environmental protection concerns. This has been reflected in atomic spectroscopy by sustained interest in the development of new atomic reservoirs. If atomic emission spectroscopy is considered, the atomic reservoir would have the following important characteristics (148),

- (1) Good stability.
- (2) Good sensitivity.
- (3) Ability to excite a wide range of elements.
- (4) Freedom from interferences.
- (5) Reproducible sample introduction.
- (6) Ease of operation.

In addition, a wide calibration range and low initial / operating costs would be desirable. For many years the main excitation sources for optical emission spectroscopy have been sparks, arcs, discharge lamps, lasers and of course flames, but none of these have all the ideal characteristics. This situation has been dramatically influenced by the recent emergence of high frequency plasma sources which now threaten to dominate analytical atomic emission spectroscopy. The reason for the widespread acceptance of plasmas has been due to three important properties : high temperatures, an inert excitational environment and excellent stability. Why these particular properties should have such an important influence will be found in later discussions.

A plasma may be loosely defined as a gas, which is ionised to an extent where its fundamental properties are modified, although a more rigid definition will follow in the next section. The plasma is usually sustained in a flowing stream of a suitable inert gas, and can be considered to be an electrical flame. However any resemblance with the combustion flames which we are all familiar with is confined only to visual similarity. Combustion flames are formed by the endothermic and exothermic chemical reactions of the oxidant and fuel species which limits the highest temperature (ca. 4500K) that can be attained. Such limitations are not a feature of the plasma source and large amounts of power may be transferred to it to produce temperatures in excess of 10000K without the chemical interferences which are so typical of combustion flames.

The principal plasma sources that are now being used for emission spectrochemical analysis are the D.C. plasma jet, the gas stabilised arc, the microwave plasma (MIP), the capacitively coupled microwave plasma (CMP) and the inductively coupled plasma (ICP). The development of these sources has been described in a series of papers by Greenfield et al. (148 - 150).

The origins of the ICP may be traced to the first successful attempt to sustain a plasma at atmospheric pressure, which is credited to Babat (151) in 1947. Babat was able to inductively couple radiofrequency power from a large vacuum tube to a static column of air in a discharge tube. The discharge which was started at reduced pressures and maintained up to atmospheric pressure ended with the plasma touching the tube walls which therefore melted. This problem was overcome by Reed (152) in 1961, who designed a plasma torch with a vortex controlled stream of argon which both stabilised the plasma and

isolated it from the tube walls.

The potential of the plasma source in analytical spectroscopy was recognised by two independent groups of workers, Greenfield et al. in the United Kingdom and Fassel et al. in the United States. Greenfield et al. (153) used a silica torch consisting of three concentric tubes, two of which had tangential inlets for the gas to create the vortex stabilisation effect. This plasma was operated at 36MHz. and sample was passed through the centre tube at a velocity sufficient to penetrate the centre of the discharge. The axial pathway formed in this manner converted the discharge from an ellipsoidal plasma to an annular plasma. These two cases may be identified in figure 4.1. Fassel et al. (154) decided to use laminar gas flows in their torch to reduce turbulence and improve stability and their torch was operated at 3.4MHz. At this stage they did not recognise the importance of forming a discharge with an axial channel for the sample aerosol, and it is likely that in their ellipsoidal plasma, the sample passed round the outside of the discharge and did not experience the high temperatures necessary for excitation. In a later publication, Dickinson and Fassel (155), duplicated Greenfield's concept, reverting to a centre channel plasma and were able to obtain detection limits superior to any previously published for the ICP. The formation of the annular plasma was also disregarded by Veillon and Margoshes (156) who removed the central tube altogether, and it was therefore not surprising, in retrospect, that they found serious solute vaporisation interferences. This effect was almost certainly a result of poor power transfer to the sample.

So began the development of the ICP, at a time when competitive atomic reservoirs were successfully solving routine analytical

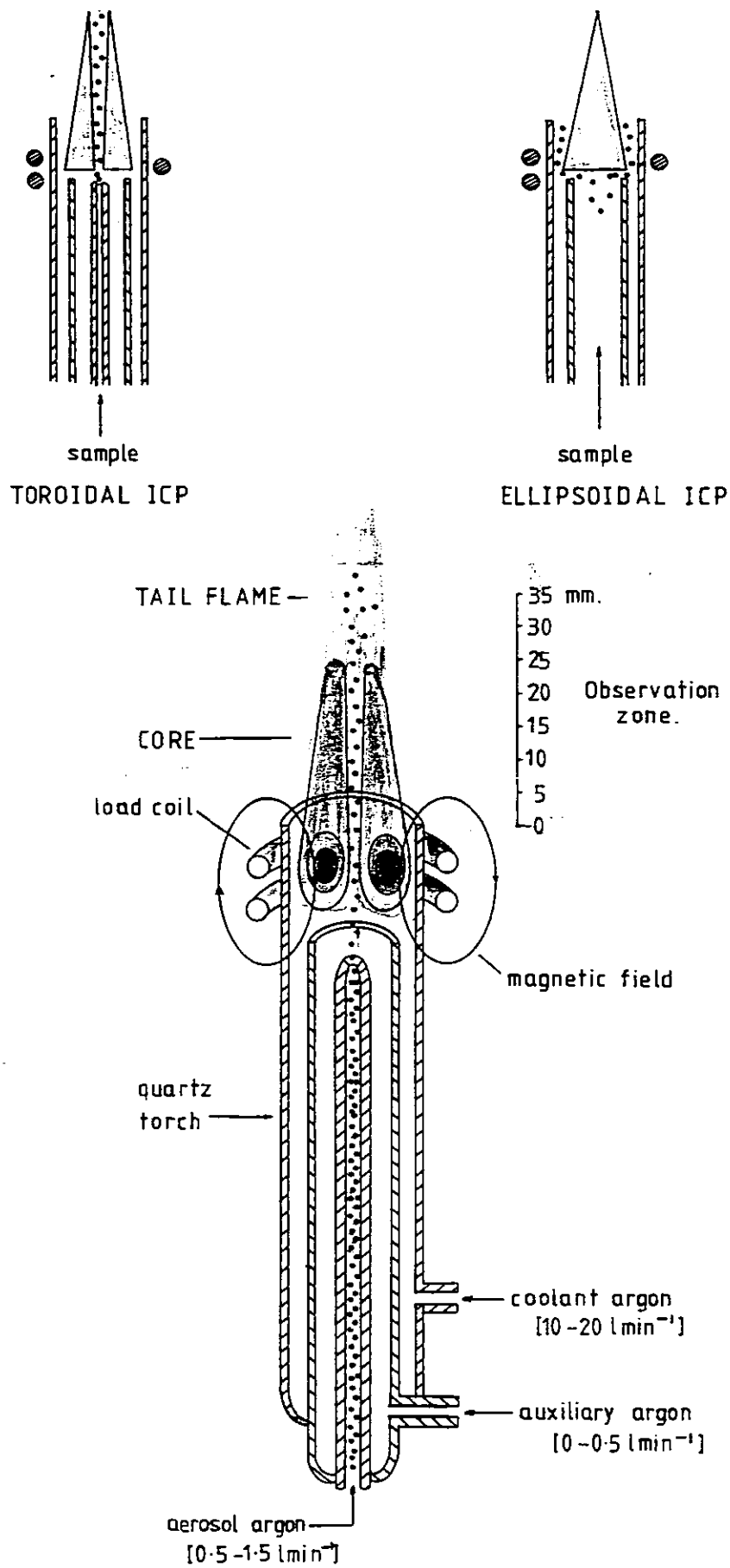


FIGURE 4-1: Schematic representation of the ICP torch and discharge.

problems. The continuing success of the ICP has demonstrated the remarkable potential of this particular excitation source.

4.1.2 Discharge Characteristics of the ICP.

Discharge Formation.

The ICP discharge is typically created in a special torch constructed from quartz or boron nitride comprising of three concentric tubes. A circular induction coil (load coil) is placed around the top of the torch and is supplied with radiofrequency power from a suitable generator. An inert gas is introduced tangentially between the outer and middle tubes and if this is seeded with electrons from a high voltage discharge, filamentary ion paths are created through the gas. Power may then be applied to the induction coil, inducing an oscillating magnetic field which is axially orientated inside the torch, and this forces the ions and electrons to be accelerated along closed annular paths on each half cycle of the field. In this manner eddy currents are induced in the gas stream which spontaneously heats up with formation of a stable plasma, figure 4.1.

The function of the middle tube is to improve the vortex stabilisation and to separate the plasma from the walls of the outer tube (coolant tube). Gas may also be introduced tangentially between the middle tube and the central injector tube and is normally used for thermally isolating the plasma from the end of the torch.

Physical Properties.

The plasma which is created within and above the load coil may be resolved into two distinct regions. An extremely intense, bluish-white non-transparent core extends from the base of the plasma to about two centimetres above the load coil and is characterised by intense continuum emission originating from ion/electron recombination and Bremsstrahlung processes. Above the core is a slightly transparent flame like tail extending from about 1.5 to 3.5 cm. In this region, the continuum emission, which gives rise to a high background, is reduced by several orders of magnitude, and is of most use for spectral observations of analyte species. The temperatures that are reached depend on the spatial location in the plasma and vary from ca. 4000-9000K.

The formation of an annular plasma, by establishing a central injection channel is of paramount importance to the analytical utility of the ICP. The channel is formed by using a central injector tube with a narrow tip (1.5mm.), so that the sample will emerge at a velocity sufficient to penetrate the plasma. A high velocity is necessary to overcome two barrier effects which would normally cause deflection of the sample around the plasma : (a) a thermal barrier is caused by the expansion of the hot gases in a direction normal to the boundaries of the plasma. (b) attenuation of the oscillating magnetic field occurs at the boundaries of the plasma and produces a region of kinetic pressure in the core. This results in axial flow of plasma gases towards the boundaries creating a barrier on the external surface, often termed the magneto-hydrodynamic barrier or skin effect and also causes temperature maxima in the plasma to be displaced from the central axis.

The Debye Radius.

We have already seen that a plasma is a volume of gas containing a significant proportion of ionised species. Despite this abundance of charged particles, the plasma is collectively neutral, and it can be shown (157) that to maintain a 1% difference between the number densities of ions and electrons in a sphere of radius 1mm., requires a potential difference of nearly one million volts, if an electron density of 10^{16} cm^{-3} is assumed. A potential of this magnitude cannot be accommodated in the gaseous phase because all particles are free to move such that the charge imbalance is neutralised. At much smaller distances it is clear that thermal disturbance of the particles will have some influence on this, and the concept of the Debye shielding radius, ρ_D , can be used to characterise that distance where the electric field of the particle extends before it is effectively screened by particles of opposite charge.

This criterion allows us to use a more stringent definition of a plasma, which is that the plasma state will exist when the macro dimensions are larger than the Debye screening radius. The Debye radius is given by the expression :-

$$\rho_D = \sqrt{\frac{\epsilon_0 k T_e}{2 e^2 N_e}} \dots\dots\dots (4.1)$$

where ϵ_0 is the permittivity of vacuum.

k is the Boltzmann constant.

T_e is the absolute temperature.

e is the charge on the electron.

N_e is the electron density.

The particular dimension of the Debye radius for the case of the ICP is approximately $0.1 \mu\text{m}$. which is exceeded by several orders of

magnitude in analytical ICP's.

Plasma frequency.

The plasma frequency is correlated to the Debye radius in as much as it represents the resonant frequency for collective oscillations of the particles from their equilibrium positions. The plasma frequency is given by the expression :-

$$\nu_p = \sqrt{\frac{e^2 N_e}{4 \pi^2 \epsilon_0 m_e}} \quad \dots\dots\dots (4.2)$$

where ν_p is the plasma frequency, Hz.

m_e is the rest mass of the electron.

If equation 4.2 is evaluated for the case of the ICP, the resonant frequency is approximately 3×10^{11} Hz. which corresponds to radiation of wavelength 1mm. (far infra red). If ν_p is known, equation 4.2 can be used for the determination of the electron density in the ICP by measuring the cut-off frequency of propagated radiation through the plasma, which will occur when the propagating radiation frequency and the plasma frequency coincide.

Local Thermodynamic Equilibrium.

In emission spectroscopy, the energy intensity of the radiation emitted per unit time at a particular frequency is given by :

$$I = A_{ij} h \nu N_i \quad \dots\dots\dots (4.3)$$

where N_i is the number of atoms in the i 'th level.

h is Planck's constant.

ν is the frequency of the observed transition.

A_{ij} is the Einstein transition probability for the transition from level i to j .

For practical work the relative intensity is usually measured and a calibration graph constructed, because the quantity N_i is not known. If the emission source were in complete thermodynamic equilibrium, this would not be necessary, because the fraction of the total number of atoms in the i 'th state N_i/N could be obtained from the Boltzmann equation:

$$\frac{N_i}{N} = \frac{g_i}{U(T)} \exp \left[-\frac{E_i}{kT} \right] \dots \dots \dots (4.4)$$

where g_i is the statistical weight of the i 'th level.

($g_i = 2J_i + 1$; J_i angular momentum quantum number)

E_i is the energy of the i 'th level.

T is the temperature.

$U(T)$ is the partition function summated over all possible

states and is given by $U(T) = \sum_i g_i \exp(-E_i/kT)$.

This may be evaluated because the electric field in a plasma will reduce the ionization limit to give a finite number of levels.

k is the Boltzmann constant.

The Boltzmann equation may be extended to two successive ionisation stages to yield the Saha equation:

$$\frac{n_e N_z}{N_{z-1}} = \frac{2U_z(T)}{U_{z-1}(T)} \left[\frac{2\pi m_e kT}{h^2} \right]^{3/2} \exp(-(E_{ion} - \Delta E_{ion})/kT) \quad (m^{-3}) \dots \dots \dots (4.5)$$

where n_e is the electron density.

N is the particle density.

z is the particular ionisation stage.

E_{ion} is the ionisation energy of species in state $z-1$.

m_e is the mass of the electron.

Thermodynamic equilibrium is the condition where all energy transfer from one state to another is exactly balanced by the inverse process. If this holds true, then the velocity distribution of all species would be Maxwellian, and the Boltzmann and Saha equations would be applicable.

Thermodynamic equilibrium cannot be observed in practice because the process of observing it must lead to unbalanced loss of radiation from the system. However, there may be a state where the energy distribution of the particles obeys these laws but radiative processes do not. This state is called local thermodynamic equilibrium (LTE). Therefore for a plasma to be in LTE, the rate of depopulation of an energy level by electron collisions must be at least ten times the rate of depopulation by radiative emission (158), and again the equations will be applicable. If this is the case there will be one value of the temperature, T , of the plasma and this can be used as a definition of temperature. If the plasma is not in LTE, as happens when the ground state is relatively populated, all particles will follow the Boltzmann and Saha laws in different ways, and a number of temperature terms appear : T_e , the electron temperature; T_a , the temperature of the atoms; T_{exc} , the temperature of the atoms in different states of excitation.

For the establishment of LTE in a plasma, collisional de-excitation pathways must dominate. This is likely to be true for high electron densities in the plasma. Griem (159) estimated the electron density necessary, to be :

$$n_e \geq 9.2 \times 10^{23} \left[\frac{E_2}{E_H} \right]^3 \left[\frac{kT}{E_H} \right]^{1/2} \quad (\text{m}^{-3}) \quad \dots\dots\dots(4.6)$$

where E_2 is the energy of the upper level of the resonance line.

E_H is the ionisation energy of hydrogen.

This relation is approximately true if the resonance line is optically thin (absorption coefficient of species multiplied by path length through the gas < 1). For the laboratory ICP this is true for most species. If the resonance line is self absorbed, then the necessary electron density may be reduced by about one order of magnitude.

Existence of LTE in the ICP has been a subject of some controversy. In his early work, Reed concluded that LTE did exist and this was substantiated by other work. Mermet (160) in 1975 was the first to report significant departures from the LTE state and has been substantiated by other workers. The ICP is now popularly believed (161, 162) not to be completely in LTE.

4.1.3 Analytical Utility.

The credibility of the ICP as an atom cell for analytical atomic emission spectrometry is based on three desirable properties: high temperature, a passive chemical environment and excellent stability. The analyte is commonly determined in the tail flame of the plasma after establishing a narrow axial channel. The high temperature of the core ensures that the sample matrix is efficiently vaporised before the analyte reaches the viewing zone and one of the attractive features of the ICP is the remarkable freedom from matrix interference. Some of the perspectives that govern the analytical utility of the ICP will now be discussed in detail.

Detection Limits.

The notion of detection limit (DL) may be interpreted to mean the

lowest concentration or mass of analyte that can be reliably determined. From a more scientific approach, the detection limit has been defined as the amount of analyte which produces a signal of more than twice the standard deviation (σ) of the background noise, although some workers prefer to use 3σ .

Detection limits are usually imprecise because it is fairly difficult to measure the background noise with any accuracy and the detection limit is usually computed by extrapolation from much higher concentrations. Additionally, the detection limit can be considerably improved by using special signal recovery techniques and these should ideally be specified when reporting any detection limit data.

In an ICP, the analyte encounters a very hot environment and it follows from the Boltzmann equation (4.4), that a large proportion of atoms will be in the excited state. The residence times of the analyte in the plasma are long in comparison with flame spectrometry and the net result is that analyte emission in the ICP is extremely intense. If this is combined with the stability and the low background from the plasma tailflame it is easy to understand why the detection limits, for a wide range of elements, are extremely low, and in numerous cases superior to any other atomic spectrochemical technique. A list of solution detection limits routinely attainable in an ICP compared with typical values for flame atomic absorption, atomic emission and atomic fluorescence spectrometry are shown in table 4.1.

Linear Calibration Range.

Although the advantages of the ICP were quickly recognised from its inception in 1964, it was not until 1974 that Kirkbright and Ward

Table 4.1 ICP detection limits compared with other techniques (163)

Element	ICP : $\mu\text{g /ml.}$	Flame : $\mu\text{g /ml.}$		
		AAS	AFS	AE
Ag	0.004	0.005	0.0001	0.008
Al	0.002	0.03	0.005	0.005
As	0.04	0.1	0.1	50
Au	0.04	0.02	0.05	4
B	0.005	6	-	30
Ba	0.0001	0.05	-	0.002
Be	0.0005	0.002	0.01	0.1
Bi	0.05	0.05	0.05	2
Ca	0.00007	0.001	0.000001	0.0001
Cd	0.002	0.001	0.00001	0.8
Ce	0.007	-	0.5	10
Co	0.003	0.005	0.005	0.03
Cr	0.001	0.003	0.004	0.004
Cu	0.001	0.002	0.001	0.01
Dy	0.004	0.2	0.3	0.05
Fe	0.005	0.005	0.008	0.03
Ga	0.014	0.07	0.01	0.01
Gd	0.007	4	0.08	2
Ge	0.15	1	20	0.5
Hf	0.01	8	100	20
Hg	0.2	0.5	0.02	40
Ho	0.01	0.1	0.1	0.02
In	0.03	0.05	0.002	0.003
La	0.003	2	-	2
Lu	0.008	3	3	0.2
Mg	0.0007	0.0001	0.001	0.005
Mn	0.007	0.002	0.002	0.005
Mo	0.005	0.03	0.06	0.1
Na	0.0002	0.002	-	0.0001
Nb	0.01	1	1	0.06
Ni	0.006	0.005	0.003	0.02
P	0.04	-	-	-
Pb	0.008	0.01	0.01	0.1
Pt	0.08	0.1	-	2
Rh	0.003	0.03	0.1	0.02
Sb	0.2	0.1	0.05	0.6
Se	0.03	0.1	0.04	100
Si	0.01	0.1	-	5
Sn	0.3	0.02	0.05	0.3
Sr	0.00002	0.01	0.01	0.0002
Ta	0.07	5	-	20
Te	0.08	0.1	0.05	200
Ti	0.003	0.09	0.1	0.2
Tl	0.2	0.03	0.008	0.02
U	0.03	-	-	10
V	0.006	0.02	0.07	0.01
W	0.002	3	-	0.5
Y	0.0002	0.1	-	0.04
Zn	0.002	0.002	0.00002	50
Zr	0.005	5	-	10

(164) predicted that the dynamic calibration range of the ICP would be superior to flame systems. One of the disadvantages of flames used for atomic spectrometry is self absorption in the long path length of the optical cell, a factor which limits the calibration range to about two orders of magnitude. In the ICP, analyte emission is viewed perpendicularly to the narrow axial channel and for most elements, the plasma may be considered to be optically thin. Linear ranges in an ICP can therefore be established over five or six orders of magnitude. Major, minor, trace and ultra-trace constituents in the same sample can often be determined in a single dilution and this represents one of the significant advantages of the ICP, compared with other techniques.

An examination of the axially viewed (end on) plasma has been carried out by Demers (165), who used an air deflector screen to protect the optics from hot gases and to reduce interference. He found that because of the longer pathlengths, detection limits could be improved by up to one order of magnitude relative to the side viewed plasma, with no viewing zone optimisation requirements. Significantly though, Demers claimed that the linear ranges were equal to or better than the side viewed case. It is doubtful however that this is a general property, and has not been substantiated by other workers.

Interferences.

Interferences pertaining to emission spectroscopy may be divided into three types ; spectral, chemical and physical. Spectral interferences, which have been the scourge of flame emission spectroscopy, involve the registration of unwanted radiation in the

optical measurement window. In the ICP, spectral interference can occur from the overlapping of lines from other elements in the sample, from argon species which form the plasma and from molecular band emission from atmospheric gases entrained at the top of the plasma discharge. The interference observed will be a function of the resolving power of the spectrometer. Spectral interferences in a 40MHz. plasma have been investigated recently by Mermet and Trassy (165). Most types of spectral interference can be reduced by careful design of the spectrometer and using very narrow bandpasses to isolate the wavelength of interest, but the need for such a system does unfortunately increase the cost of an ICP system considerably. The selection of the working wavelength is also predictably of considerable importance since many spectral interferences may be avoided by moving to another line in the spectrum. Until recently, the choice of wavelength for the analyst without plasma expertise, has been difficult because the only comprehensive set of line tables has been the MIT wavelength tables of the NBS copper arc. The recent introduction of wavelength tables (167) relating to measurements made in the ICP has been long overdue.

The spectral background of the ICP is relatively pure because argon species predominate. Entrainment of nitrogen, water, carbon dioxide and oxygen can occur at the top of the torch and these species will produce band spectra in the plasma. Air entrainment (168) can be prevented by extending the torch by several centimetres above the load coil and viewing the discharge through the tube walls.

After early investigations had been completed, there was initial euphoria at the apparent lack of chemical interferences in the plasma. This was to be expected because the sample passes through the high

temperature core which efficiently volatilises and dissociates the matrix and other chemical species before detection of the elements of interest in the tail flame. For example, investigations of the classic interference effect in flames, between calcium and phosphorus, owing to the formation of thermally stable calcium phosphate, revealed that in the case of the ICP, the interaction was virtually insignificant. This euphoria was somewhat abated when it was realised that chemical interferences generally do exist although these were nothing like as significant as in flame methods.

Physical interferences which occur in the plasma may be generated from a change in the operating conditions of the plasma or from alteration in the characteristics of the sample introduction system. In general these interferences are common to those encountered in other techniques.

Optimisation of Working Conditions.

In general the best performance from an ICP will be gained when it is used at optimal conditions. If these are selected, good detection power, reduced interferences and extended calibration ranges may reasonably be expected. Optimised conditions are required for each species to be determined because several variables associated with the plasma have a critical influence on the emission characteristics. These variables are:-

- (1) The power coupled to the discharge.
- (2) The height of observation.
- (3) The flow rates of the coolant, plasma and injector gases.
- (4) The monochromator slit width and resolving power.

(5) The voltage gain of the detector.

The plasma may be optimised by selecting conditions such that the signal to background (S/B) and signal to noise (S/N) ratios achieved for the particular case are maximised.

Unfortunately, it is not advisable to optimise one individual variable before moving to another (termed a univariate search), as all the variables are interrelated. It is clear therefore that if one variable is optimised at a particular position, then this might not be true after the next variable has been optimised.

One way to successfully optimise the plasma for analytical performance has been demonstrated by Ebdon et al. (169), who used a simplex optimisation procedure based on that reported by Nelder and Mead (170). In this method Ebdon et al. chose a five dimensional simplex, defined by six points in variable space, and each of the variables was altered according to the variable step simplex algorithm. On the basis of these optimisation results Ebdon et al. were able to derive some interesting conclusions which hitherto had not been ascertained.

From a purist viewpoint, rigid optimisation of all parameters is required if the maximum advantage of the plasma is to be exploited for each individual element. However, in many cases a set of compromise conditions is needed so that a variety of elements may be determined with reasonable speed and reliability. This is of particular relevance if simultaneous multielemental analysis is necessary, and compromise conditions can, conveniently, often be selected by a simple univariate procedure.

Multielement Analysis.

One principal advantage of emission spectroscopy when compared with absorption methods, is the capability for rapid multielement analysis. ICPAES is of course an emission method, and therefore the signals from all analyte species in the discharge will be generated simultaneously. In theory, it is possible to determine a wide range of elements in one sample merely by dispersing the emitted radiation from the plasma and employing a multichannel detection system (171,172). The capability for rapid multielement analysis has been one of the propensities most used in marketing of commercial ICPAES instrumentation, and is commonly achieved by using a polychromator or by using a monochromator with a rapid sequential scanning facility.

A polychromator is a spectrometer where the dispersing device is fixed and several detectors are arrayed around it at positions where the desired emission lines are diffracted. The advantage of this approach is that true simultaneous multielement analysis is achieved, although the number of elements so determined, is limited to the number of detector channels in the spectrometer and how closely they can be arranged. Alternatively, multielement analysis is possible by utilising a fast sequential scan across selected lines using a conventional monochromator. The sequential routine is not truly simultaneous, but it is often possible to determine a large number of elements in an extremely short time, particularly if the monochromator is microprocessor controlled. Moreover the sequential method can cope with an unlimited number of elements, which is not achievable with a polychromator.

Noise and Background Limitations.

One of the most important factors which will limit the performance of any instrumental technique is its inherent S/N performance. The ICP is considered to be source noise limited, that is to say that the fundamental noise restriction is a function of the source rather than the detection system. An evaluation of the noise characteristics in the ICP has been carried out by Belchamber and Horlick (173), who found that the noise spectrum for 0-500 Hz. was caused by rotation of the plasma discharge aggravated by air entrainment at the top of the torch. They were able to reduce this by extending the torch above the load coil. Significantly these workers also concluded that the dominating noise feature from 0-5 Hz. was that caused by irreproducibility in the introduction of sample. It is probable that most deterioration in analytical performance is caused by the sample introduction system and not by the stability of the plasma discharge. This therefore represents one very good reason why much effort needs to be expended in improving the present generation of sample introduction techniques for use with the ICP.

4.2 Sample Introduction into the ICP.

4.2.1 Introduction.

It is now recognised that the stability and operation of the ICP discharge and optical system are not the major cause of degradation of

analytical performance using this technique. Instead the introduction of sample is probably of crucial importance on a fundamental basis and only recently has attention been focused on the development of superior introduction systems. It was explained in chapter 1 that the ICP discharge represents a case where the atom cell possesses characteristics far removed from the ambient environment and as such the sample introduction system must successfully be the interface between the two cases. This places great demands on the design of suitable introduction systems and these can only be developed if there is an understanding of the phenomena of sample transport into the discharge. There is therefore an urgent need for definitive studies of this process and also the development of new and novel methods. A pictorial representation of state of the art sample introduction techniques is shown in figure 4.2.

4.2.2 Introduction of Liquids.

The introduction of samples into the ICP has almost exclusively centred on the introduction of liquids by continuous feed nebulisation. The reason for this has partly been the lack of any successful method for the direct introduction of solids, and because extensive nebuliser technology was available from the longer established technique of AAS. Unfortunately the demands on a nebuliser for use in ICPAES are different to those in AAS and there are conflicting requirements for low nebulising gas velocities to increase the residence time of the analyte in the plasma and high nebulising gas velocities (500 m/sec.) for the production of a fine aerosol. The result of this has been an effective compromise where the uptake rate

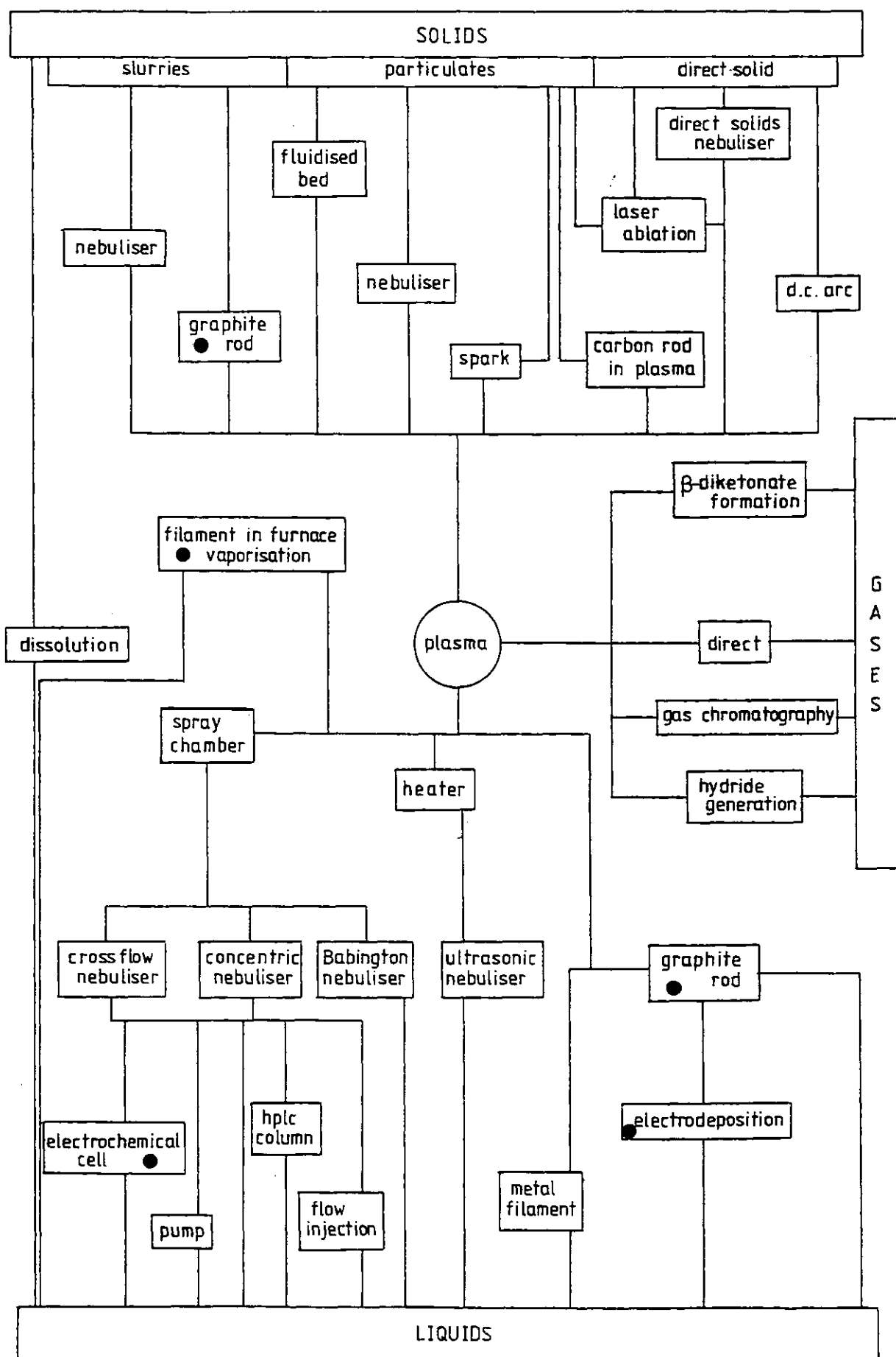
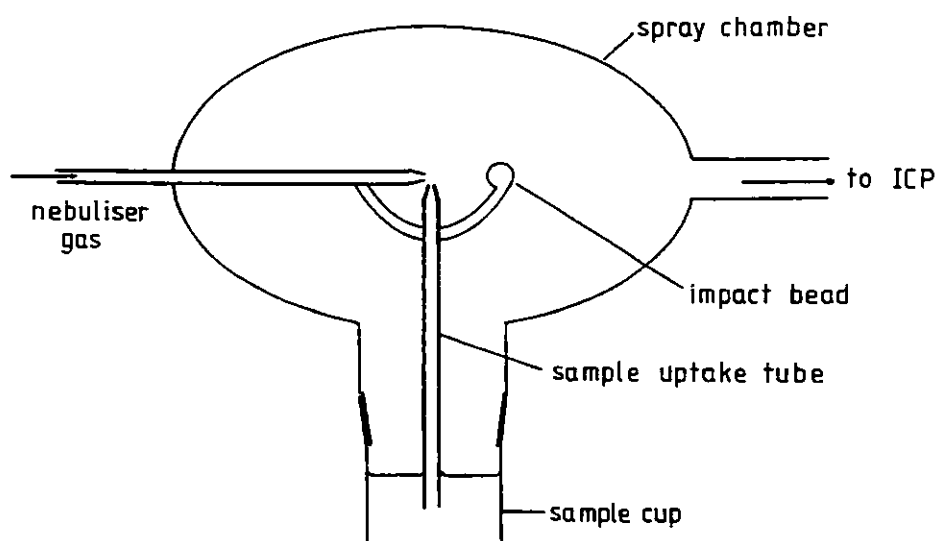


FIGURE 4.2: Methods for the introduction of samples into the ICP. ● denotes study reported in this thesis.

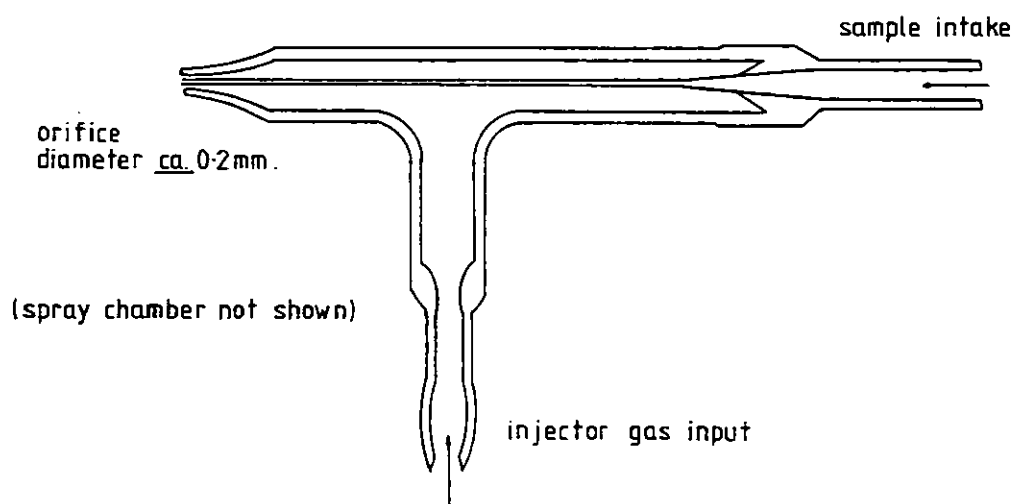
is ca. $3\text{cm}^3/\text{min.}$ at $1\text{l.}/\text{min.}$ gas flow (cf. AAS $8\text{cm}^3/\text{min.}$ at $6\text{l.}/\text{min.}$ flow), and is the principal reason why nebulisers for the ICP have extremely low mass transport efficiencies (ca. 2%). A review of pneumatic nebulisation for the ICP has recently appeared (174).

The two established pneumatic nebuliser types for the ICP are the concentric type, such as the Meinhard (31) design, and the crossflow type (30) and are used in conjunction with a spray chamber for separation of the larger droplets. Both nebulisers are shown in figure 4.3. The concentric nebuliser is prone to sample blockage of the gas orifice when solutions of high dissolved solids content are nebulised and the crossflow type is difficult to align accurately and has poor stability resulting from dimensional changes in the tube mountings. Many workers have sought to improve upon these basic designs and this has led to the appearance of several nebulisers claiming to be superior to those already in existence. One of the primary limitations of existing nebulisers is the need for capillary tubes which aggravate blockage when solutions of high dissolved or suspended solids are used. An early attempt to eliminate the need for capillary tubes (175) involved a nebuliser incorporating a fritted disc. The disc was obtained from a Buchner funnel and sample was bled over the face of this disc held at an angle of 45° . Aerosol was produced by the passage of argon through the pores of the frit and the optimum efficiency was claimed to be as high as 60% when using a gas flow rate of $0.2\text{l.}/\text{min.}$ However drift and memory effects were also observed which limited the use of this device.

The most promising development in nebuliser technology is attributable to Babington (36). In his design the liquid is made to flow over the surface of a sphere and the surface of the liquid film



CROSS FLOW NEBULISER
after Browner *et al.* (1976)



CONCENTRIC NEBULISER
(Meinhard type.)

FIGURE 4-3 : The two most common types of nebulisation systems fitted to inductively coupled plasmas.

is ruptured by passing gas at very high pressure through a slot drilled in the sphere. This represents a completely different type of nebuliser because the thin film is directly converted to fine aerosol without passing through the primary and secondary nebulisation stages which are typical of conventional nebulisers. In conventional nebulisers also, much of the energy of the gas stream is used for propelling the liquid down the capillary tube and little is available for aerosol formation. This is not a feature of the Babington design because the liquid is in the form of a thin film and only surface cohesive forces operate. The primary advantage of the Babington nebuliser is the capability for producing an aerosol from almost any liquid, even if highly viscous. The potential of the Babington nebuliser was quickly recognised and it was adapted for the ICP by Garbarino and Taylor (177) and a commercial version, the MAK nebuliser is now being marketed. The basic Babington concept has been adapted by Wolcott and Sobel (178) and by Suddendorf and Boyer (38) to produce high solids nebulisers. Both of these consist of a V shaped groove along which the sample solution passes. A similar approach has been used recently by Ebdon and Cave (179) who used a peristaltic pump for the delivery of sample solution.

Nebulisers for the ICP are usually coupled to the injector tube through a spray chamber, which acts as a aerosol droplet sorter. Large droplets fall out of the gas stream and pass to waste while small droplets (5 $\mu\text{m.}$) pass through. The spray chamber can also be heated to improve the transport process. Two types are popular ; the Scott type (180) based on continuous passage through two concentric tubes (double pass chamber) and the cyclone chamber where aerosol is injected tangentially to set up a vortex. A treatment of spray chambers is

given in a publication by Schutyser and Jannsens (181).

Fundamental studies of the nebulisation process as applied to the ICP have been discussed in a series of papers by Browner et al. They developed a monitoring system for the size characterisation of droplet sprays (29) and applied this to the sizing of sprays from various nebulisers (182). Investigations were also conducted to ascertain the characteristics of droplet distribution in the spray chamber (28) and lately to monitor the evaporation characteristics when organic solvents are used (183).

Sample introduction of aerosol produced by the use of ultrasonic frequencies has been extensively tested. In theory this is well suited for the ICP because the aerosol is finer and the droplet size is directly controllable by the frequency selected and not by the injector gas flow rate. The production of fine aerosol results in greater mass transport efficiency (10-20%) and detection limits in the plasma are often lower than those attainable with pneumatic nebulisation (184). Ultrasonic nebulisation was first investigated by Hoare and Mostyn (185), and is now used in either of two modes : continuous feed, where the solution is pumped continuously onto the transducer plate, and batch type, where a discrete volume of liquid is placed onto the plate or an inert interface. Because the overall efficiency is higher when employing ultrasonic nebulisation, significant amounts of the solvent will enter the plasma with attendant instability and consumption of power. To circumvent this, aerosol desolvation systems are usually required and a number of desolvation interferences are then possible. A common effect is the deposition of analyte onto the transducer plate at high temperatures

and produces severe memory effects. Loss of analyte may also occur in the desolvation apparatus (186). Other disadvantages of the ultrasonic approach are the long clean-out times necessary to avoid memory effects and some matrices can also attack the transducer plate. Most of these problems have yet to be solved and consequently ultrasonic nebulisers are not as popular as those of the pneumatic type.

4.2.3 Introduction of Gases.

Gases may be introduced into the ICP in small quantities, and the introduction process is relatively straightforward. The introduction of gaseous samples has centred exclusively on hydride generation, the general principles of which have previously been discussed. The most comprehensive study of hydride generation is given in a series of papers by Thompson et al. (187-189), who have investigated the principles and interferences in the simultaneous determination of trace concentrations of arsenic, antimony, bismuth, germanium, selenium, tellurium and tin. The method was also applied to the determination of trace constituents in soils and sediments (65) and herbage (190). Wolnik et al. used hydride generation for the determination of arsenic, bismuth, germanium, antimony, selenium and tin in foods (191).

Hydride generation as commonly performed with sodium borohydride reduction is only applicable to certain elements in groups 4,5 and 6 of the periodic table. The method is not therefore directly applicable to the determination of metals. However, the convenience of gaseous introduction for metals has been retained in the method of Black and Browner (11) who formed the volatile β -diketonate complexes of iron,

zinc, cobalt, manganese and chromium. This was achieved in a 10 ml. reaction vessel fabricated from borosilicate glass and fitted with a six port valve to allow separate purging of the inlet system or sample vessel with argon. The β -diketonates were produced by adding the ligand reagent to the sample in the reaction vessel and heating for ten minutes at 130°C. The detection limits achieved were generally superior to those obtained by pneumatic nebulisation and the method was employed for the determination of iron, zinc and chromium in bovine liver and blood serum.

4.2.4 Introduction of Solids.

Little attention has been directed to the analysis of solid samples in the form of powders, particulates, vapours or slurries by direct introduction into the ICP despite the potential advantages to be gained by reduction of sample handling. Presumably the reason for this has been the difficulty of uniformly dispersing the particles in the injector gas stream and the diversity in physical form which characterises the solid state. Little use has been made of the powder feed technology used for engineering applications of plasmas.

One of the first general attempts for introduction of solids was that of Human et al. (192) who adapted a high voltage spark operated at 50 Hz. for elutriating electrically conducting solids, but the total analysis time was extremely long. This arrangement was subsequently modified by Scott (193), such that powder could be elutriated into the plasma by the action of an energetic spark between two electrodes placed above the sample, but the attainable precision was no better than 15-30%. The analysis of powders by feeder methods

is still not possible with acceptable precision and appears to have been abandoned in favour of other approaches.

The basic problem of inconsistency of sample transport to the plasma in a carrier gas stream, which has typified all previous attempts for solids introduction has been circumvented by Salin and Horlick (194). In their method small amounts of sample, in the form of powders, solids or desolvated liquids are inserted directly into the middle of the plasma discharge on a cup graphite electrode. The torch was modified so that the central aerosol tube could be replaced with a quartz tube containing the rod and the method was used for the determination of zinc in a set of five powdered samples with a detection limit of 0.1ng. zinc. A similar approach is now being used by Kirkbright et al. (195), although studies have so far been restricted to the analysis of solutions.

Laser ablation of solid material was first attempted by Abercrombie et al. (195) for the analysis of airborne particulates and has lately been investigated by Thompson, Goulter and Sieper (74). In this arrangement, the solid sample was inserted into an ablation chamber and subjected to a pulse of energy ≈ 1 J. from a ruby laser. Ablated particles were swept into the plasma in the argon stream. The application of this device to the determination of metals in low alloy steel produced precision values ranging from 2% for iron and nickel to 24.6% for chromium, copper and silicon. The detection limits were significantly poorer than with macro techniques. The authors concluded that poor precision was caused by particle segregation and inhomogeneity of the sample.

4.2.5 Discrete Sample Introduction of Liquids.

Discrete introduction of microlitre samples into the ICP appears to offer advantages when compared with continuously operated nebulisation systems. The analyte is injected into the plasma as a discrete pulse and therefore the transient population of emitting species in the measurement window of the plasma can be greater than with continuous dynamic operation. For this reason superior detection power can often be realised. In addition to this, only small quantities of solution are required and makes this approach attractive for the analysis of samples where the available volume is restricted (eg. clinical, biological, forensic samples).

Direct nebulisation of microlitre samples into the ICP has been attempted. Thus Greenfield et al. (197) injected 1-25 μl . samples from a micropipette or syringe into the inlet of a crossflow nebuliser for the analysis of oil, blood and organic compounds. An order of magnitude increase in sensitivity was observed when a heated spray chamber was employed. A similar arrangement was used by Knisely et al. (198) for the analysis of 100 μl . quantities of whole blood, obtaining a respectable precision of 3%. Injection of small volumes using a peristaltic pump to reduce physical interference from solutions of high viscosity has been recommended by Broekart and Leis (199). Uchida et al. (200) investigated discrete nebulisation with an overview to simultaneous multielement analysis. Yttrium was used as an internal standard to improve the precision.

The most promising approach for the discrete introduction of liquids is the transient injection from electrothermally heated metal and carbon filaments similar to those used for GFAAS. Dahlquist (201)

developed and subsequently patented a graphite yarn vaporiser for the injection of microlitre samples into the ICP, but this did not attract significant interest.

Nixon et al. (202) used a metal filament for the analysis of 50 μ l. samples, with a precision of 4% *rsd.* and were able to obtain superior detection limits to those using pneumatic nebulisation, although there were severe interelement effects and spectral interferences.

An electrothermally heated graphite rod device (GRV) was investigated by Kirkbright et al. In a preliminary assessment, (54,203) detection limits for sixteen elements were obtained and matrix, interelement and sample transport effects examined. Interference in the determination of arsenic and selenium was shown to be caused by pre-vaporisation loss of analyte and sample transport inefficiency. This was circumvented by the use of Se(VI) as a matrix stabiliser. Formation of refractory carbides on the rod with certain elements was found to degrade the flexibility of this device. This problem was solved by Kirkbright and Snook (204) by adding 0.1% *v/v* halocarbon to the injector transport gas. The halogen preferentially formed a volatile compound with the analyte and precluded the formation of the carbide. Graphite rod electrothermal vaporisation has successfully been used for the investigation of biological matrices (205), whole blood (206) and doped cadmium mercury telluride (207).

In spite of the apparent advantages of electrothermal vaporisation when compared with traditional nebulisation methods, there has been little interest in this particular form of sample introduction. This is perhaps surprising if the success of GFAAS is considered. However there are recent signs (208) that the potential of

electrothermal devices is recognised.

4.3 Instrumentation for the ICP.

4.3.1 General Requirements.

The components of a working ICP system comprise a high frequency power generator and impedance matching network, the plasma torch itself, a spectrometer system and detector and a suitable system for the introduction of samples.

Generator.

The high frequency generator is needed to supply large amounts of power, free from ripple, to maintain the plasma discharge, and therefore a vacuum power tube is normally used. The frequency of the generator is produced by an oscillator which has appeared in two forms, a free running oscillator and a crystal controlled oscillator. In the free running type the frequency is fixed by the values of components in the tank circuit (including the load coil), and will vary according to the impedance of the plasma. The power transfer, however stays fairly constant and consequently no tuning is necessary for maintaining the plasma over extended periods of time. The crystal controlled generator, in contrast, works at a fixed frequency, which as the name suggests is produced from a piezoelectric crystal, often coupled to a frequency doubler, but the generator is usually designed to operate at a fixed output impedance. For this reason, the coupling

of power to the plasma has to be accomplished by an impedance matching system (using variable vacuum capacitors), which must necessarily compensate for changes in the plasma impedance during initiation and operation.

Most work has been accomplished using generators with output powers of 2-5 kW. From an early stage in the development of the ICP, there were two conflicting schools of opinion as to the best power level to use for analytical work; one faction (209) advocated the use of low powers, which can be provided by more compact generators and are convenient to use, the other, notably led by Greenfield et al. have worked with high powers (up to 15 kW.), and propose several cogent advantages for this strategy, namely greater sensitivity, frequent improvement in precision, elimination of band spectra and chemical interferences. It should be noted however that Greenfield et al. were working with a plasma cooled by nitrogen rather than argon, which requires high powers to dissociate the nitrogen triple bond. It is doubtful therefore if the use of high powers as recommended by these workers can necessarily be extended to plasmas sustained on argon, and Ebdon et al. (210) have demonstrated recently that optimal excitation does take place at very low powers in their argon plasma.

There has been a similar conflict of opinion in the choice of operating frequency. The formation of an annular plasma might be expected to be easier at high frequencies (ca. 50 MHz.) because the skin depth of the plasma which varies with frequency, will be smaller. This has not been verified experimentally and presently, the choice of frequency is based more on the technology and cost of generator construction than the performance criteria of the plasma discharge, and the most common frequency has been 27.1 MHz. However, an

exhaustive study of the influence of the generator frequency is presently being carried out by Mermet et al. (211) and it is hoped that this may help to clarify the precise effect of frequency on the discharge characteristics of the analytical ICP.

Design of Torch.

The central piece of equipment in any plasma system is the torch, which is required to produce and maintain the discharge. The design and alignment of the torch have a critical influence on the ease of plasma ignition and the characteristics of the plasma discharge. The most common configuration is an arrangement of three concentric tubes mounted inside a circular load coil as depicted in figure 4.1 and the gas inlets are usually tangential to facilitate vortex gas flow dynamics. Most torches have been constructed from silica, a material with low thermal expansion and excellent transparency to ultra-violet radiation, but a torch fabricated from boron nitride has been reported (212) and appears to be superior in terms of machinability, and resistance to adverse thermal and electrical conditions.

The only rigorous study of torch design has been that of Barnes and Schleicher (213) and Allemand and Barnes (214), who used a computer programme to optimise the design of the torch, and tested 36 different torch configurations for ease of ignition, stability and confinement of sample. The latter workers were also able to define a configuration factor, the ratio of the diameters of the two outer tubes, and concluded that a plasma was easier to sustain in a torch with a large configuration factor.

A major problem with the acceptance of ICPAES is the high cost of

running the instrumental system. The total consumption of gas is usually ca.15-20 l/min., and large quantities of gas are required if the plasma is to be run for long periods. Whilst careful design of the torch will drastically reduce argon consumption, several studies have concentrated on other methods to reduce the demand for gas. Thus Kornblum et al. (215) evaluated a torch with ancillary water cooling and were able to sustain a satisfactory discharge with a flow rate as low as 2 l./min. Savage and Hieftje (216) have also designed a miniature ICP torch which permitted approximately three fold reduction in argon consumption, and could be run at lower powers than normal torches.

The ICP can theoretically be sustained with any gas provided that sufficient power is available, and argon is usually used for the purposes of cost, inertness and ease of plasma formation. Plasmas operating on nitrogen (217), and mixtures of argon and nitrogen (218) have been advocated because sample decomposition and vaporisation is predictably improved, as a result of the higher thermal conductivity of nitrogen. Plasmas operating on nitrogen will however require higher powers and exhibit lower temperatures than their argon counterparts and the choice of gas is normally dictated by the personal preferences of the analyst concerned.

Spectrometer and Detector.

A spectrometer is required to characterise the emitted radiation from species in the plasma and the types employed for ICPAES are similar to those used in other emission methods. The main requirements are for high resolving power, freedom from dispersing element defects,

good transmission of radiation and rejection of stray light interference. Grating instruments have almost exclusively superceded prisms as dispersing devices because the dispersion is linear; the use of holographic gratings recently has produced a new generation of high resolution spectrometers with unrivalled performance characteristics. Much effort has also been expended on the design of spectrometers for multielement analysis and has led to the appearance of sophisticated sequential scanning monochromators (219). Simultaneous multielement analysis can be accomplished with polychromators which are most often configured in a Rowlands circle (220).

The last component in the chain is the detector, which has universally been the photomultiplier tube. This excellent device has the long linear range, stability and sensitivity and response time necessary to process emission signals from the ICP source, and is available with different response curves for any region of the U.V.-vis. spectrum. In common with other areas of spectroscopy, self scanning photodiode arrays are increasingly encroaching into ICPAES (221), and have the particular advantage that simultaneous imaging of the whole plasma is possible. This would be of considerable benefit for spatial studies in the ICP which are not possible with the mono-channel photomultiplier tube.

4.3.2 Instrumentation used in this Work.

The instrumentation used for the ICP studies presented in this thesis was similar to that described by Gunn et al. (222), and the main components are shown in schematic form in figure 4.4. Radiofrequency power was produced from an H.F. crystal controlled

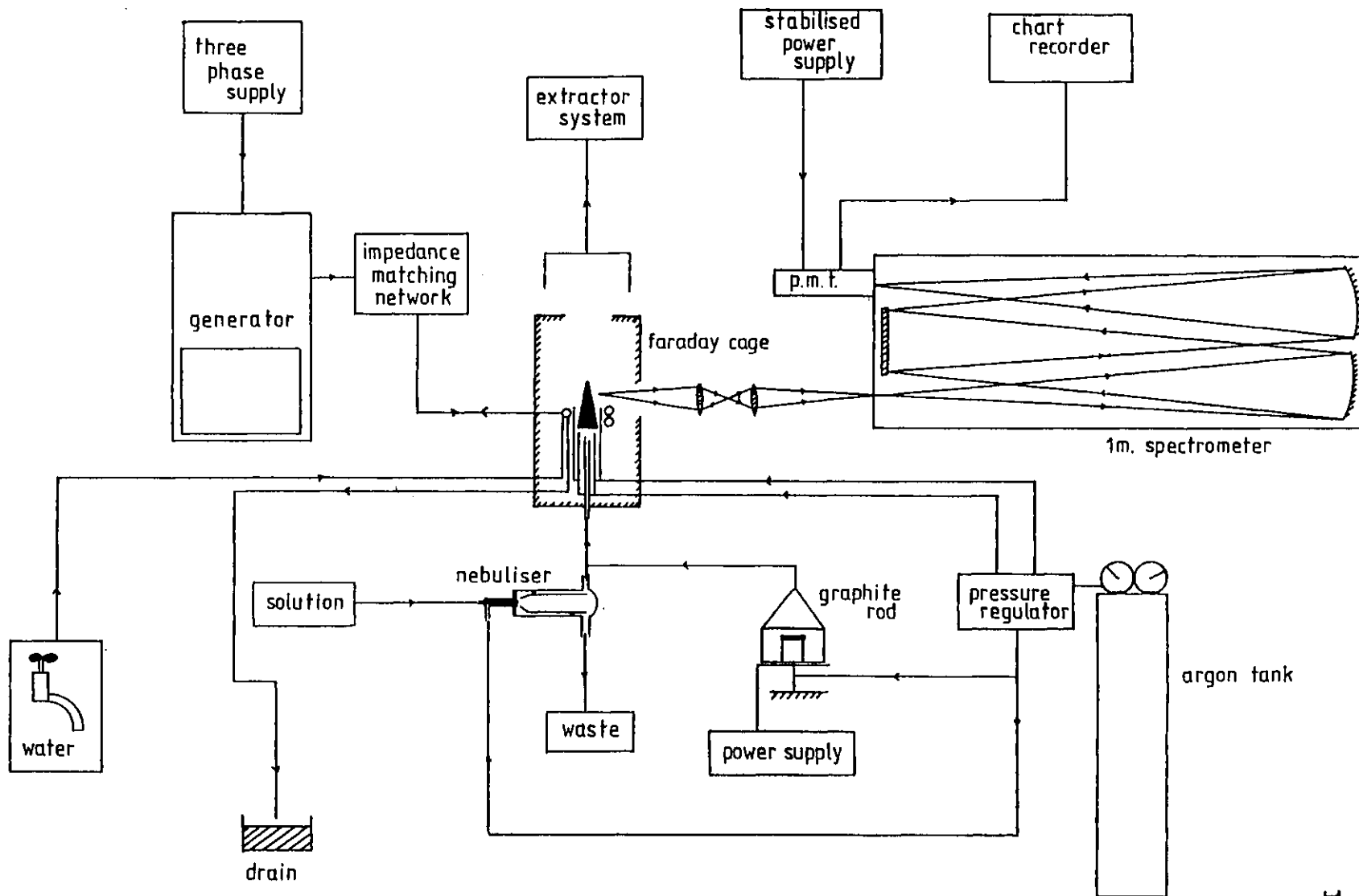


FIGURE 4.4 : Schematic representation of the instrumentation used for ICPAES studies.

generator (model 120-27 International Plasma Corporation, Hayward, California) employing a Colpitts oscillator and was continuously tunable to deliver 0-2.5 kW. power at 27.16 MHz. The output impedance of the generator was 50Ω . Power transfer to the plasma was adjusted through a manual impedance matching network, terminating at a 1.5 turn water cooled copper load coil (6mm. o.d., coil diameter 26mm.).

The plasma was confined in a demountable, fused silica, torch which consisted of three concentric tubes mounted in a machined brass base and provided with tangential gas inlets. The configuration was similar to that shown in figure 4.1. (configuration ratio 0.88; source- Heraeus Quartz Products, Unit 3, Oyster Lane, Weybridge Surrey). The injector tube tip was of a diameter such that the linear velocity of sample into the plasma was 9.4 ± 0.3 m./sec., and a residence time of sample in the plasma ca. 2.6 msec. was calculated. The brass base of the torch was designed so that a gap of 13mm. existed between the top of the outer tube and the top of the middle tube, and the load coil was positioned at a level adjacent to the top of the middle tube. The silica tubes were cemented into the base with silicone rubber which facilitated easy replacement of any desired tube, whilst maintaining sufficient rigidity for operation. The injector tube was, however, cemented into position using epoxy resin to produce extra rigidity.

The plasma torch which has been described was operated exclusively on argon supplied from 300' pressurised cylinders and was split to provide three gas flows (1) Coolant supply 16-18 l/min. (2) Auxiliary (plasma gas) supply 0-1 l/min. (3) Injector gas supply 0.1-2 l/min.

The plasma discharge was surrounded by an aluminium Faraday cage designed to contain the magnetic and electrical components of the R.F. wave and this was fitted with an aperture for viewing the plasma and a tri-dimensional racking assembly for spatial imaging of any desired region of the plasma onto the entrance slit of the monochromator.

Several methods for sample introduction were used for studies reported in this thesis and are fully described in the appropriate sections. The basic device, however, was a borosilicate glass concentric nebuliser (model T-230-A3, Meinhard Associates, Tustin, California.) with a nominal solution uptake rate of 3ml./min. operating at a gas flow rate of 1.0l/min. and 30 psig. pressure differential. The nebuliser was mounted in a Scott type (180) double pass spray chamber which served to isolate the larger aerosol droplets to waste.

Optical transfer of the plasma image to the entrance slit of the monochromator was effected using two fused silica biconvex lenses (5cm. diameter, $f = 7.5\text{cm.}$). These were mounted between the plasma and the monochromator in a $4f:2.7f:4f$ arrangement to produce a 1:1 upright image at the entrance slit. Spectral characterisation was achieved with a 1m. Czerny-Turner configured scanning monochromator (Hilger Monospek 1000) equipped with a plane diffraction grating (1200 lines/mm.) blazed at 300nm., and providing a reciprocal linear dispersion of $8.2 \text{ \AA} / \text{mm.}$ This spectrometer incorporated a 13 stage end-window photomultiplier tube (6256B EMI, Hayes, Middx.) to facilitate radiation detection. The effective operating range of the tube was 175-650 nm. The high voltage for the tube was produced from a

stabilised power supply (model 475R Brandenburg Ltd., 939 London Rd., Thornton Heath, Surrey) adjustable between 10 and 2100V. Signal registration could be accomplished by connecting the output of the PMT across a 20 k Ω ballast resistor to drive a fast response potentiometric (Y-t) chart recorder (Servoscribe model RE 541-20) and all measurements reported in this thesis were prepared by transcribing the recorded signals.

CHAPTER 5
ELECTROCHEMICAL PRECONCENTRATION
AND SAMPLE INTRODUCTION INTO THE ICP.

5.1 Introduction.

The importance of trace elements (concentration $\approx \mu\text{g/g.}$) in mediating biological, environmental, chemical and industrial processes is well known. Considerable attention has been directed recently to the determination of trace element species for studies of pollution, catalysis, toxicology, biological metabolism and industrial materials design. This has only been possible since the recent emergence of powerful analytical techniques which are capable of reliably detecting analyte species at these low levels. Consequently the understanding of trace element mediation is still in infancy.

Soon after the development of the ICP for analytical purposes, it was quickly recognised as an ideal source for performing trace element analysis, because the high temperatures involved auspicate excellent detection power and there is freedom from the matrix effects which usually complicate trace analytical determinations. For ultra-trace analysis (concentration $\approx \text{ng./g.}$), however, the ICP, employing pneumatic nebulisation, is not adequately sensitive when compared with graphite furnace atomic absorption spectroscopy (223), neutron activation analysis (224) or electrochemical techniques (225). This limitation is not primarily a function of the ICP source itself, but is mainly a consequence of the poor overall sample transfer efficiency (ca. 2%) when pneumatic nebulisation is used for sample introduction. Electrothermal vaporisation may be used to improve the sample

introduction efficiency (54) but a number of interferences arise from the vaporisation and transport of analyte to the plasma which have yet to be fully elucidated.

The alternative way to improve detection capability whilst retaining the simplicity and reliability of the nebuliser is to preconcentrate the elements of interest prior to nebulisation into the ICP. The standard methods of preconcentration are : evaporation of solvents, complex / chelate extraction, surface adsorption, ion-exchange and electrodeposition, most of which have been previously described in chapter 1. Electrodeposition techniques have been used for preconcentration quite extensively because the procedures are relatively fast when compared with chemical preconcentration methods and automation of the process to provide continuous preconcentration is readily achieved. Earlier workers have reported the use of electrodeposition techniques for preconcentration of trace elements prior to determination by atomic absorption spectroscopy but attention has centred almost exclusively on deposition of analyte on metals or graphite prior to electrothermal atomisation and atomic absorption spectroscopy. Such an approach was first reported by Fairless and Bard (226) who deposited copper on a carbon rod and predicted that concentrations as low as 1.6×10^{-10} M could be determined. Lund et al. also used deposition on graphite for the determination of trace elements in a salt matrix (227) and on tungsten⁽²⁵²⁾ for determining cadmium in sea-water. The only publication to describe a flow cell for electrochemical preconcentration is that of Frick and Tallman (228) who recently developed a flow cell for the determination of mercury in water. In this design, solution was passed through a HGA 2100 graphite furnace which was subsequently detached from the apparatus for the

determination of deposited analyte by atomic absorption spectrometry.

For the studies described here, an electrochemical preconcentration method employing a flow cell was assessed for the continuous collection of trace analyte before nebulisation into the ICP. Such a cell would permit on-line preconcentration, with the possibility of separating analyte from the matrix, which is important where the matrix would normally block the nebuliser or where interference effects in the plasma would result. Additionally, the system could be used for simultaneous multi-element ultra-trace analysis which is not possible with competing electrochemical techniques.

The electrochemical cell used in this study was of the wall-jet design and the principle of operation with the ICP is shown in figure 5.1. The solution for analysis is pumped into the cell which contains a glassy carbon electrode held at the reduction potential of the element of interest. Over a period of time, sufficiently high amounts of the element are accumulated such that detection is possible and the potential of the electrode is scanned in an anodic direction to rapidly strip the accumulated metal back into electrolyte solution. This solution is pumped to the nebuliser of the ICP for determination. Several variables affect the deposition efficiency and hence the preconcentration factors obtainable. These variables have been investigated with respect to the model element copper and the feasibility of multi-element determination is discussed.

5.1.1 The Wall-Jet Electrode.

An electrode design based on the wall-jet principle was first

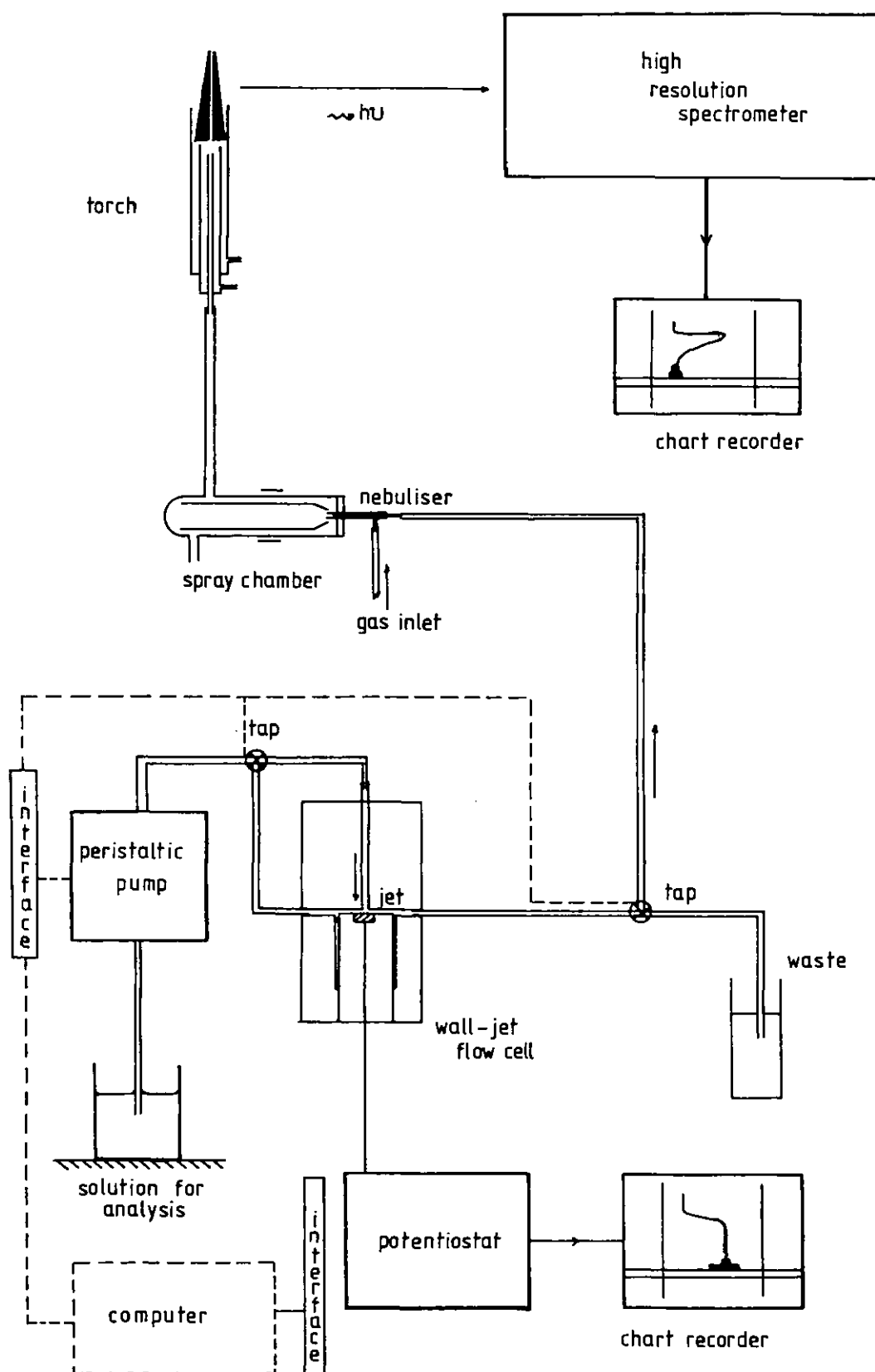


FIGURE 5.1 : Sample presentation for the ICP : arrangement for electrochemical preconcentration employing the wall-jet flow cell.

proposed by Yamada and Matsuda (229) in 1973. In this design a submerged jet of liquid is delivered through a nozzle planar to an electrode normal to the direction of flow and spreads radially across the electrode in a laminar fashion. By developing the earlier theory by Glauert (230), Yamada and Matsuda were able to derive an equation for the limiting diffusion current where:

$$I_d = (1.60k)nFC^0 D^{2/3} \nu^{-5/2} V^{3/4} a^{-1/2} R^{3/4} \dots\dots\dots(5.1)$$

where: I_d = Limiting diffusion current.

k = Proportionality factor.

n = Number of electrons transferred.

F = Faraday's constant.

C^0 = Bulk concentration of depolariser.

D = Diffusion coefficient of depolariser.

ν = Kinematic viscosity of the solution.

V = Volume flow rate of the solution.

a = Jet nozzle diameter.

R = Radius of the disc electrode.

More detailed treatment of the mass transfer characteristics of the wall-jet electrode has been given by Chin and Tsang (231) using a convective diffusion model considered for both laminar and turbulent flow. The wall-jet cell was selected for this work because it possesses several desirable characteristics (232):

(i) High sensitivity; rapid convectional diffusional mass transfer occurs at the point of impact resulting in good sensitivity and therefore good detection power.

(ii) Cell volume can be varied for any type of application, without modification of theory.

(iii) Sensitivity dependence on volume flow rate high ($i \propto V^{3/4}$).

(iv) Reference and counter electrodes are effectively downstream from the working electrode and can be located in an equidistant manner.

5.1.2. Properties of Glassy Carbon as an Electrode Material.

The popularity of mercury based electrodes originated from the ease with which the electroactive surface could be renewed. However the mechanical limitations of the mercury electrode started a search for other types of electrode material. Solid electrodes have received much attention and one of the newer types of electrode is that based on glassy carbon, a hard, non-porous, shiny material obtained by pyrolysis treatment of carbon. The advantages of glassy carbon are:-

- (1) Wide dynamic operating range -1.3V cathodic to +1.5V anodic, facilitating both electro-reduction and electro-oxidation equilibria.
- (2) Can be easily cleaned and the surface can be renewed by mechanical polishing.
- (3) Minimal interference from surface adsorption of matrix species (a considerable problem with the use of alternative solid electrodes eg. Pt.). The electrode is therefore extremely reliable and reproducible. It is possible that the high linear velocity of the jet stream cleans the electrode of adsorbed material to give these properties.

5.2 Experimental.

Wall-jet Cell.

The wall-jet cell used in these studies was designed and constructed in the workshops at Imperial College for general research work and was adapted for application to preconcentration. The cell was constructed of perspex in two parts, figure 5.2, and could be

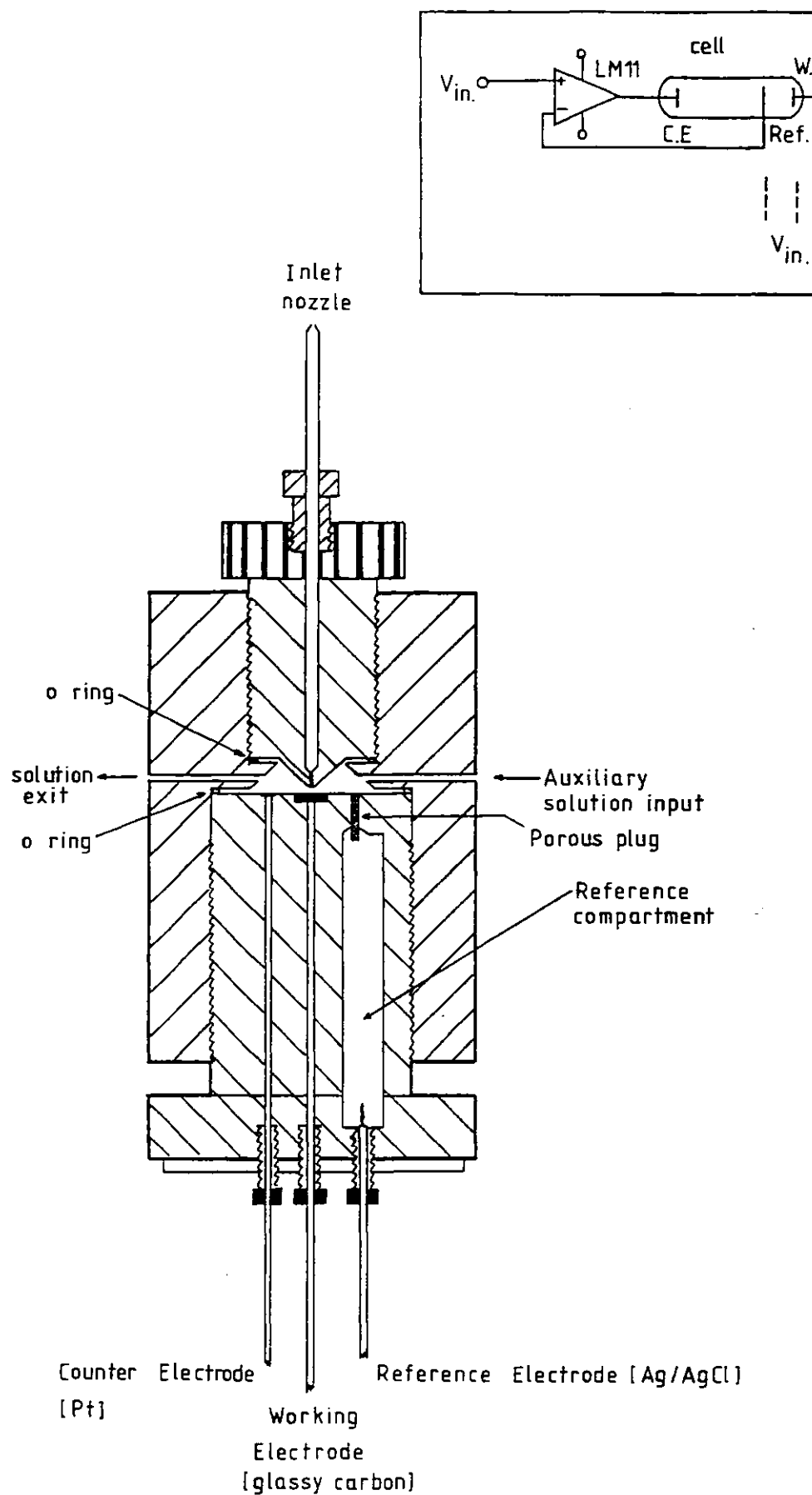


FIGURE 5-2: Wall Jet Cell - vertical cross section. Inset - potentiostat arrangement.

dismantled for periodic mechanical polishing of the electrode. The lower part comprised the wall of the cell and had at its centre a glassy carbon disc electrode of 5mm. diameter. To one side of this working electrode was a platinum disc counter electrode (diameter 2.5mm.) and to the other side a silver/silver chloride reference electrode connected to the solution chamber via a vycor glass plug. Both electrodes were effectively downstream of the working electrode and all the electrodes were equiplanar.

The upper part of the cell comprised the solution inlet nozzle and two solution exchange ports which were diametrically disposed; one used for solution exit to the nebuliser or to waste, the other for auxiliary inlet of solution during the stripping process.

The perspex body containing the nozzle was threaded so that the distance between the nozzle tip and the glassy carbon working electrode could be accurately controlled. The effective volume of the cell was the space between the electrode wall and the nozzle body and was approximately 750 μ l.

Electrode Maintenance.

The performance of the glassy carbon electrode is critically dependent on the surface characteristics of the electrode and this should be free from imperfections or scratches if optimum performance is to be retained. Before initial use, the electrode was mechanically polished using successively finer grades of carborundum paper followed by two grades of alumina (1.0 and 0.3 μ m.) to produce a mirror like finish. Repolishing and cleaning of the electrode at periodic intervals was accomplished by using A.R. Ethanol.

Ancillary Equipment.

A potentiostat was designed and constructed for the accurate control of the working electrode potential with respect to the reference electrode, based on a simple J-FET operational amplifier arrangement and three-electrode system shown in figure 5.2. The wall-jet cell was connected via its solution exit port to the solution intake of the nebuliser by a length of Tygon tubing (i.d. 1mm.) and solutions were pumped into the cell and thence to the nebuliser using a peristaltic pump (Technicon Corp. Tarrytown, New York). Alternatively, solution could be diverted to waste using a manual tap system to bypass the nebuliser.

The ICP instrumentation has been previously described in chapter 4. For all measurements described here, the plasma system was operated under compromise conditions defined from a univariate optimisation and these are listed in table 5.1.

Table 5.1: Plasma operating conditions.

Forward power 1.0kW. Reflected power <2W. Viewing height 25mm.ALC.* Coolant flow rate 13 l./min. Plasma gas flow rate 1.0 l./min. Injector flow rate 0.8 l./min. Nebuliser uptake rate 2.5ml./min. Spectrometer entrance and exit slits 35 μ m. PMT EHT 1.0kV.
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* ALC Above load coil.

Operation of cell.

For normal operation of the cell, solutions were pumped into the cell through the inlet nozzle at predetermined rates and the analyte deposited on the glassy carbon electrode by holding its potential,

with respect to the reference electrode, at the ^{chosen} reduction potential of the analyte. After sufficient time elapsed to accumulate the analyte it was rapidly stripped off the electrode (<500ms.) by application of a fast anodic scan, and pumped to the nebuliser of the ICP. The emission profile of the analyte was recorded as a function of the flow stream content, by selection of the appropriate analytical emission wavelength. Superior emission profiles were found to result from stripping of analyte into solution pumped through the auxiliary inlet rather than the nozzle because this was found to result in less dispersion of analyte in the solution stream. To reduce the electrical resistance between the electrodes a strong electrolyte (0.1M KCl) was incorporated in all solutions used. A recorder connected to the potentiostat was used to obtain stripping voltammograms simultaneously with the emission profiles recorded with the ICP.

Reagents.

Wherever possible, reagents of the highest purity were used, in view of the low concentrations of analyte likely to be encountered. Solutions of 0.1M KCl were prepared from "Aristar" KCl and de-ionised distilled water. Copper and other metallic impurities were removed using an Amberlite IRC 718 ion-exchange bed. Solutions of copper were prepared as 1000 ppm. stock solutions in 0.1M KCl. Lesser concentrations were prepared by serial dilution with de-ionised distilled water.

Signal Recovery.

Emission profiles from stripped species pumped to the ICP were recorded on a potentiometric chart recorder. Quantitative data was prepared by integrating the areas under the profiles using a "cut and weigh" method.

5.3 Results and Discussion.

5.3.1 Preliminary Study and Effect of Oxygen.

A preliminary study was performed to determine the half-wave potential for the reduction of copper on glassy carbon. For this study, the cell was used in polarographic mode and a cyclic voltammogram recorded for a 1ppm. solution, 0.1M in KCl, deposited for 1min. The voltammogram is shown in figure 5.3 and the plating and stripping potentials thus determined are listed in table 5.2.

Table 5.2: Deposition characteristics of copper.*

Element	Copper
Half-wave potential	+0.20V.
Stripping potential	1.+0.33V. 2.+0.54V.
Deposition potential used	-0.35V.
Stripping potential used	+0.80V.
* <u>vs.</u> Ag/AgCl reference electrode.	

The voltammogram is characterised by a single reduction wave when scanning from anodic to cathodic potentials, corresponding to the process $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}^0$. The returning anodic scan exhibits two stripping peaks in chloride media; the first appears at +0.33V. and is assigned as the one electron oxidation process, $\text{Cu}^0 \longrightarrow \text{Cu}^+ + \text{e}^-$, the second appears at +0.54V. and is much smaller than the first wave. This is assigned as the one electron oxidation process $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{e}^-$. Although both of these peaks are naturally recorded electrochemically

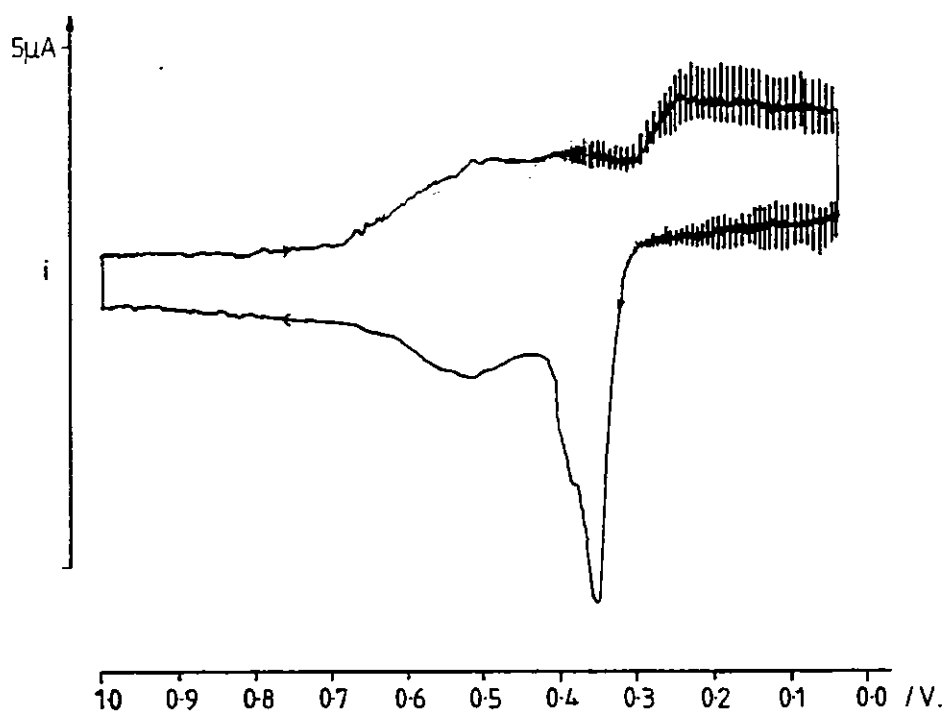


FIGURE 5-3 : Cyclic voltammogram 0.5ppm copper at wall-jet electrode. 3ml/min. scan 25mv/s.

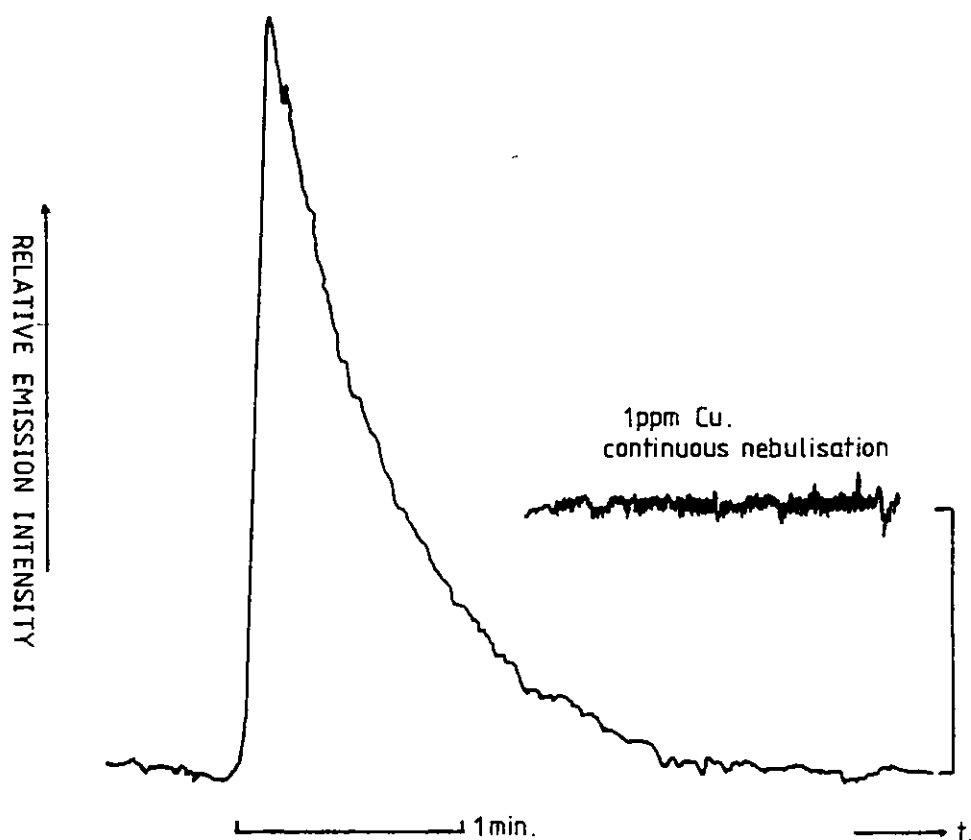


FIGURE 5-4 : Emission profile from plasma after stripping from wall-jet electrode, and pumping through nebuliser. 1ppm copper deposited 10mins. Flow rate 3ml/min. Total area under profile represents mass deposited.

and can be separated, only one peak would be recorded by the ICP if the electrode is used for electrochemical preconcentration, because the ICP is only element selective and not electron selective as in electrochemical analysis. The deposition and stripping potentials finally used for copper were chosen to ensure that the relevant equilibria were shifted in favour of the desired reduction and oxidation processes.

The cell was subsequently connected to the ICP and after collection of 1ppm. copper in 0.1M KCl for ten minutes, the emission signal at 324.75 nm. Cu(I) was recorded as a function of time. Figure 5.4 represents a typical emission profile obtained by these means, compared with the steady state emission signal normally obtained by conventional pneumatic nebulisation. The emission profile essentially simulates a flow injection curve and is typified by a rather broad dispersion. This was not expected because the flow rate employed (3.0ml./min.) should purge the total cell volume (710 μ l.) in less than 30s. The total base width of the dispersion curve however is equivalent to a purge time of 110s. It was concluded that the wide dispersion was caused by poor flow dynamics in the cell chamber such that stripped analyte was partially recycled in the cell chamber before purging to the nebuliser. Some minor dispersion in the spray chamber of the ICP sample introduction system might also be expected.

After extensive studies, it was evident that some interference with the potential applied to the working electrode and hence the deposition and stripping processes was occurring. In these initial studies, the cell was operated in close proximity to the plasma source, tests on which showed that the electric field component (E field) from radiofrequency power leakage from the plasma, induced a

+0.25V. offset at the electrode. Attempts to compensate for this, by deliberately selecting a -0.25V. offset with respect to the potentiostat voltage scale, were not successful because the E-field component did not stay constant. Instead the electrochemical cell was removed to a location (2.9m. away) where the E field had decayed to 1/100th. of its original value. No further interference was observed. To accommodate the increase in cell/plasma separation, the tube connecting the cell to the nebuliser intake was extended to 3m. An experiment was conducted to assess the effect of tube length on the emission profile characteristics, the results of which are shown in figure 5.5. Clearly, the appearance time (i.e. that time between initiating the stripping scan and appearance of the stripped analyte at the nebuliser) is proportional to the connecting tube length, as might reasonably be predicted. Of more significance however is the effect of tube length on the emission peak dispersion, measured in terms of half-width. The results obtained indicate that the peak half-width is independent of connecting tube length to a limit of 3.75m. and further purport that diffusion in the connecting tubing cannot be the limiting dispersion mechanism which therefore must originate from the cell. All further experiments were conducted with a cell/plasma separation of 2.9m.

Oxygen is a notorious interferent in electrochemical determinations. Saturation of solutions by atmospheric oxygen will normally occur to produce a level of approximately $2.5 \times 10^{-4} \text{ M O}_2$ at saturation and two reduction waves are produced corresponding to the processes: $\text{O}_2 \longrightarrow \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O}$; these waves appear at -0.1V. and extend cathodically, which for electrochemical determinations, often produces

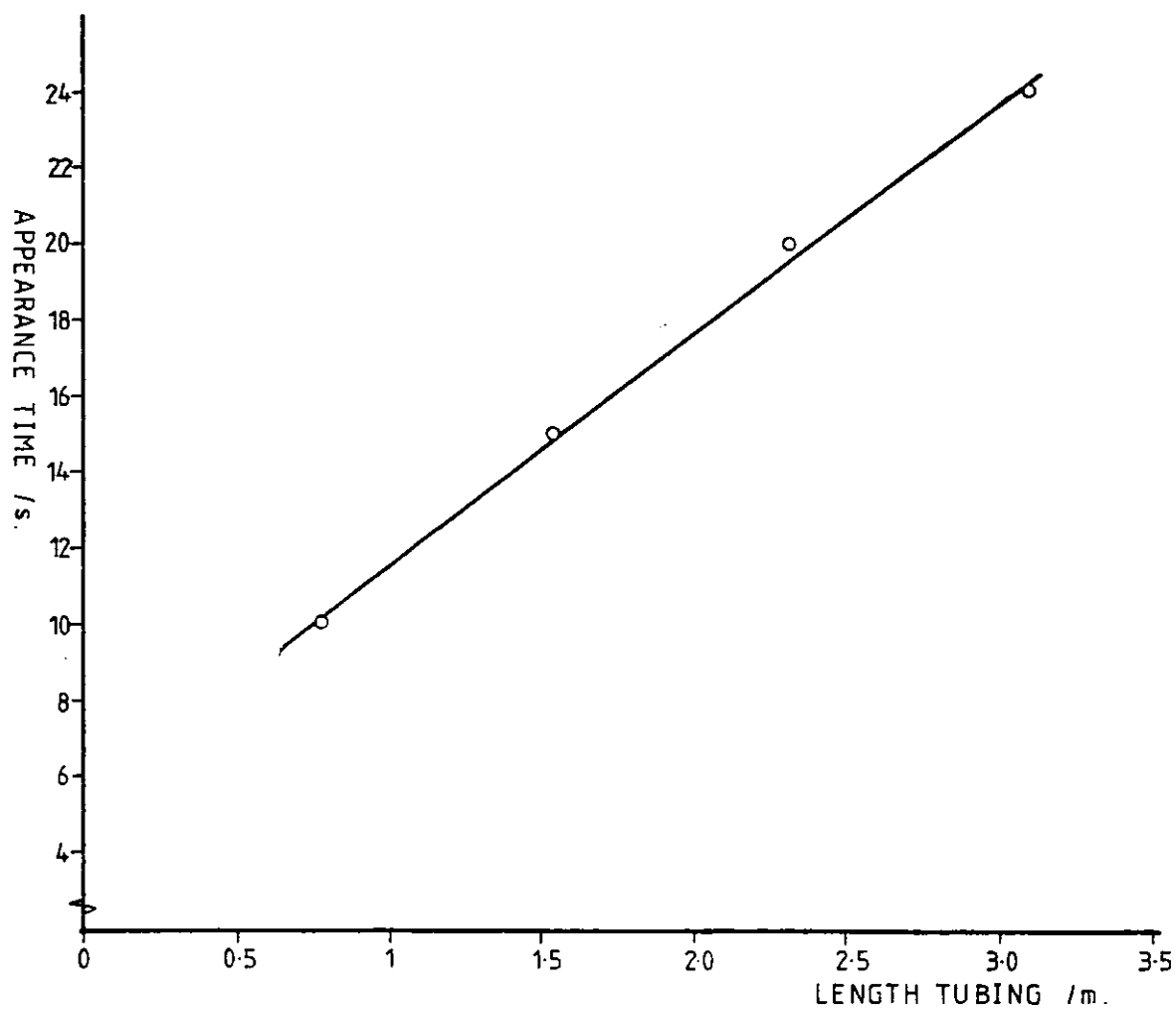
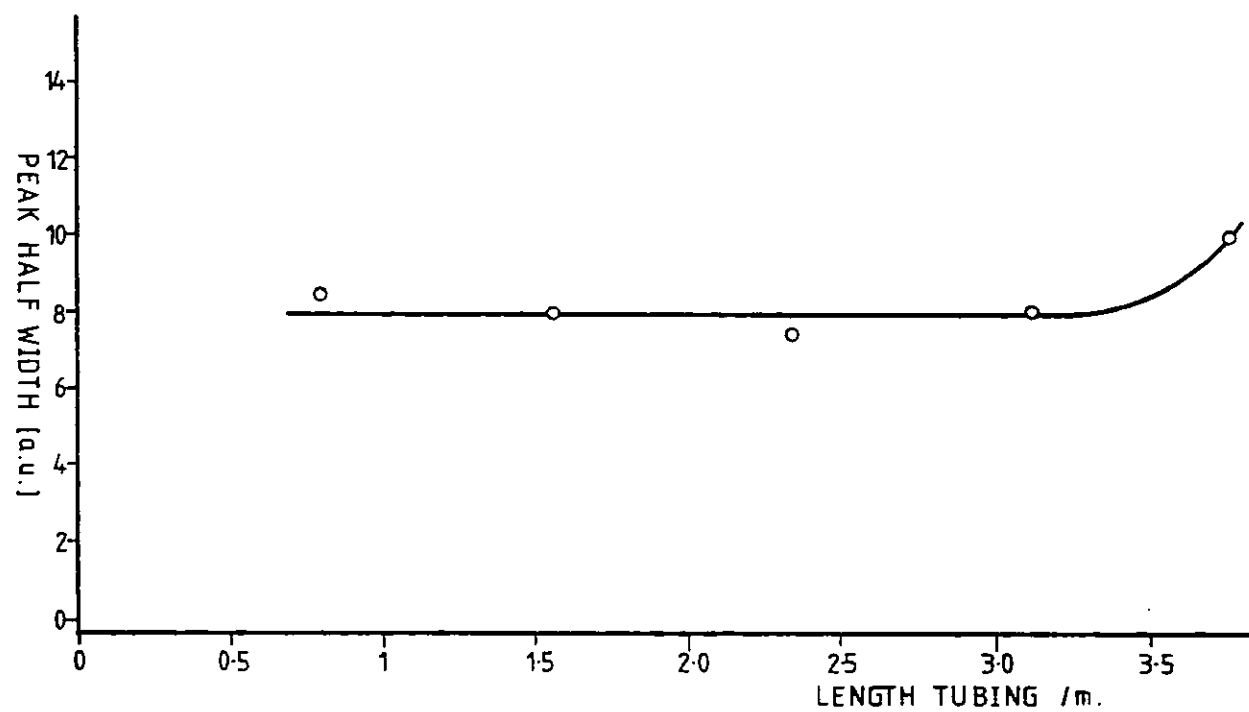


FIGURE 5-5 : Effect of connecting tubing length, between plasma and cell, on peak half-width and appearance time at plasma after stripping.

severe wave overlap with the analyte. There is also some evidence to suggest that the presence of oxygen alters the chemical and physical properties of the electrode. The interference effects just outlined are normally prevented by purging the solution prior to analysis with an inert gas, such as nitrogen, to remove all dissolved oxygen. For electrochemical preconcentration and sample introduction into the ICP, wave overlap would not matter because the emission signal of a specific analyte species is recorded. Minimal interference from dissolved oxygen would be predicted. An experiment designed to verify this was performed in which the area under the emission time profile for 1ppm. copper solutions was recorded with and without the presence of oxygen. No significant deviations were observed and no long term degradation of electrode performance was found. Oxygen apparently does not interfere with the deposition and stripping processes at the glassy carbon electrode, as monitored by the ICP. All studies were conducted without deoxygenation of solutions except when cyclic voltammograms were required.

5.3.2 Optimisation of Wall-Jet Performance.

The primary aim of these studies was to use the wall-jet cell as a preconcentrating device for material before sample introduction into the ICP. Several variables were therefore optimised to obtain the best preconcentration efficiency for such use. It is important to note that the parameters selected do not necessarily correspond with those that would be chosen for normal electrochemical analysis because the requirements are different.

Jet-Electrode Separation.

No provision is made in the Yamada equation for the separation of nozzle and electrode disc, although the treatment by Chin and Tsang (231) does attempt to quantify this. In the Yamada equation, the separation is assumed to be fixed at a position to give laminar flow over the electrode. Experiment clearly shows, however, that the jet-electrode separation has a critical effect on performance and was optimised here by measuring the emission signal from stripped copper following deposition from a 1ppm solution, deposited for 5mins., after varying the jet-electrode separation. A similar study in which the stripping current was measured was also made, but the flow rate through the cell was varied between 1.6 and 8.0 ml./min. The results of these studies are illustrated in figure 5.6. Both plots reveal that the optimum deposition efficiency occurs for a separation of 1.5mm. and additionally this optimum appears to be independent of flow rate for the range studied. At jet-electrode separations less than 0.5mm., severe fluctuations were observed in the emission and stripping current signals. The probable reason for this is constriction of the flow path when small separations are selected, causing disruption in the flow of fluid over the electrode.

Flow Rate Dependence.

Having established the optimum jet-electrode separation, the dependence of electrode response with volume flow rate through the cell was investigated. Inspection of the Yamada equation reveals that the electrode response is proportional to the volume flow rate in the

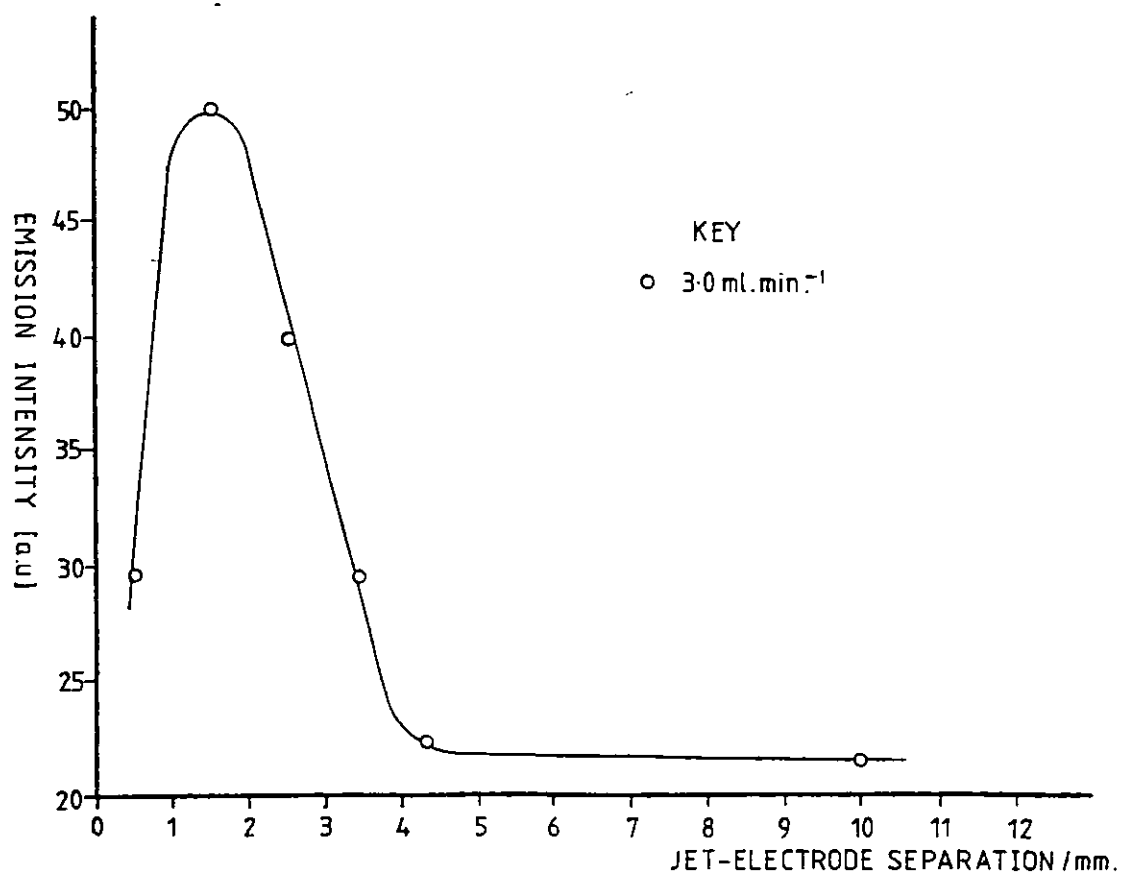
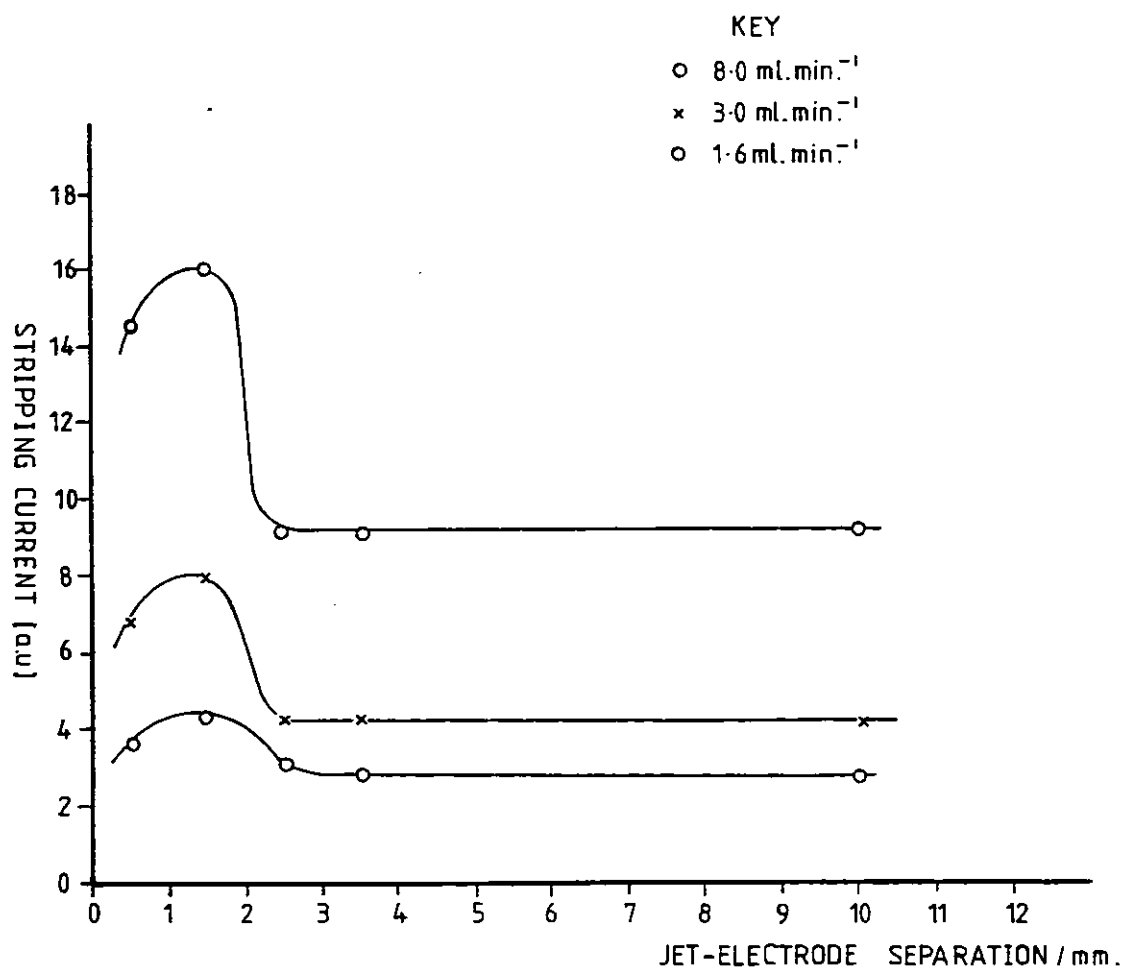


FIGURE 5-6: Effect of jet nozzle-electrode separation using stripping current (top) and plasma (above).

following manner:

$$M(t) \propto i_d = SV^{3/4} \dots\dots\dots(5.2)$$

where: $M(t)$ Mass analyte plated at electrode as a function of time.
 i_d Limiting diffusion current.
 S Proportionality constant.
 V Volume flow rate of solution.

Taking logs to both sides, equation 5.2 becomes,

$$\begin{aligned} \text{Log } M(t) &= \text{Log } S + \frac{3}{4} \text{Log } V \dots\dots\dots(5.3) \\ (\text{Log } i_d) \end{aligned}$$

If the Yamada equation is true, a plot of $\log M(t)$ or $\text{Log } i_d$ versus $\text{Log } V$ will be linear with a slope of $\frac{3}{4}$. Such a plot, constructed from experimental data, obtained using identical solutions and plating times as for the optimisation of jet-electrode separation, is shown in figure 5.7. For both ICP emission intensity and stripping current plots, the volume flow rate dependence is linear for flow rates between 2.0 and 8.0 ml./min. which suggests that the cell is operating under Yamada hydrodynamics. However some slight discrepancy is apparent, for both cases, between the volume flow rate exponent (0.80-0.84) as determined experimentally and that predicted by the Yamada equation. Two reasons may be proposed to account for this: (1) the Yamada equation is based on the assumption that volume flow over the electrode surface is laminar; but this might not be the case for the experimental system used and would lead to a deviation from the predicted flow rate behaviour. (2) the volume flow rate dependence may differ from that predicted because the previously optimised jet-electrode separation (1.5mm.) might not be where Yamada hydrodynamics are rigorously obeyed.

Although these considerations may be of significance for

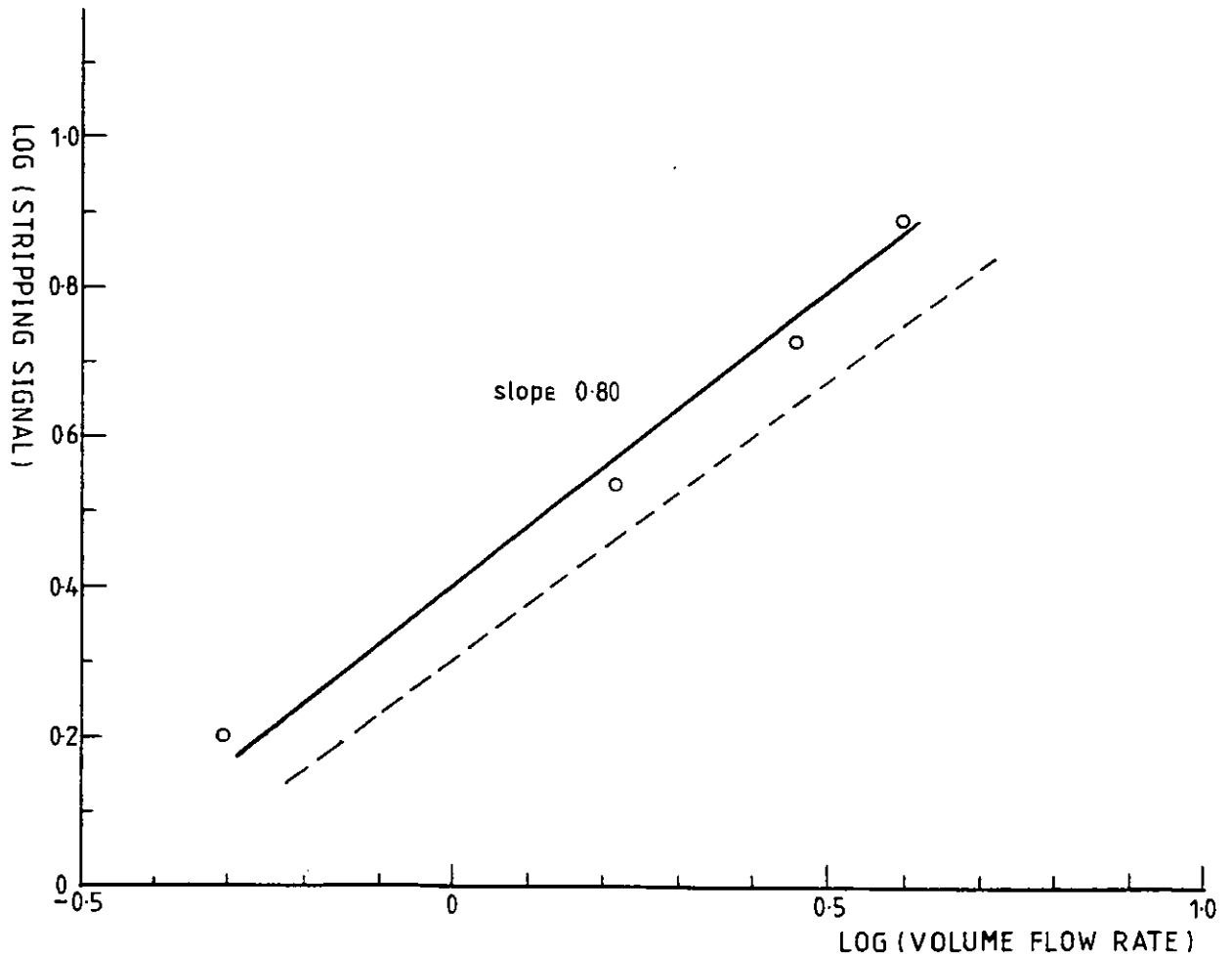
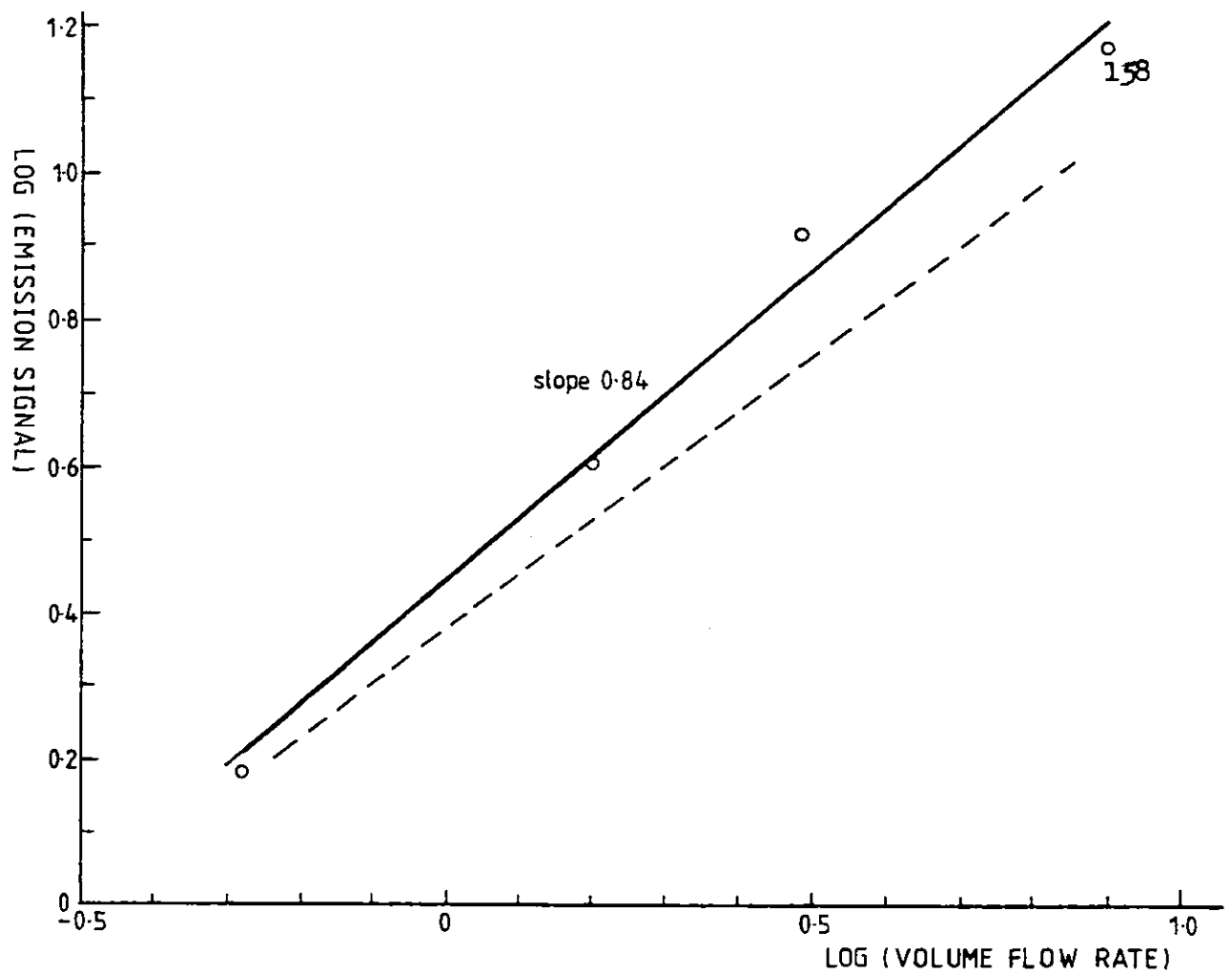


FIGURE 5.7: Volume flow rate plots for wall-jet cell using plasma (top) and stripping current (above).

electrochemical studies, they are relatively unimportant in preconcentration for the ICP, because the main criterion is to obtain the best overall mass transport. The optimum flow rate selected was 3.0ml./min. to ensure compatibility with the natural uptake rate of the nebuliser.

Effect of pH.

Assessment of the optimum pH for deposition of electroactive species at the working electrode cannot be rationalised to a direct comparison of electrode response as the pH is varied. The alteration of the chemical environment resulting from a change in pH will modify the positions of the deposition and stripping potentials and the shape of the stripping profile. This has been well illustrated by Štulíková and Vydra (233) in their study of the cyclic voltammetry of copper (II) at the glassy carbon electrode.

For selection of optimum pH with stripping of the collected species into the ICP, the main criterion adopted was the pH value producing the maximum amount of deposited material with minimal interference. In this study, buffer systems were used covering the range pH 2-10, table 5.3.

Table 5.3: Buffer solutions for the optimisation of pH.

pH	Buffer System
2.0	0.2M KCl/0.1M HCl
4.0	0.2M PHP /0.1M KCl
6.0	0.2M PHP /0.1M NaOH
8.0	0.025M Borax/0.1M HCl
10.0	0.025M Borax/0.1M NaOH
* PHP Potassium hydrogen phthalate.	

Deposition from these buffer solutions, each containing 10ppm. copper, was effected for 5mins. after which the collected metal was stripped and pumped to the ICP for determination. In each case the deposition potential was selected to be on the diffusion controlled region of the current/voltage curve, determined by previously recording each curve polarographically. The possibility of matrix effects occurring in the ICP source itself was also considered, but an investigation of the emission properties of copper in the presence of the buffer reagents revealed no significant interference.

A plot of deposition efficiency, as determined by the area under each emission profile, against pH is shown in figure 5.8. The optimum pH was found to be 4.0, and consequently 0.1M KCl (pH4.3) was retained as the supporting electrolyte after finding similar deposition behaviour to the pH 4.0 buffer system.

Collection Characteristics of the Wall-Jet Electrode.

Having established the optimum operating conditions for the wall-jet cell for use as a preconcentration device, calibration experiments were carried out to determine the range of concentrations and deposition times for which the cell response remained linear with respect to the mass of analyte plated onto the electrode. Deposition curves for copper concentrations 0.01-50ppm. are reproduced in figure 5.9. For high concentrations viz. 50ppm., linearity is observable for a total deposition time of 200s. For a concentration of 10ppm., linearity is observable up to 1000s. The point of curvature for both of these is equivalent to a total mass of plated copper of 500 μ g. One possible reason for the curvature, is that the copper deposited upon

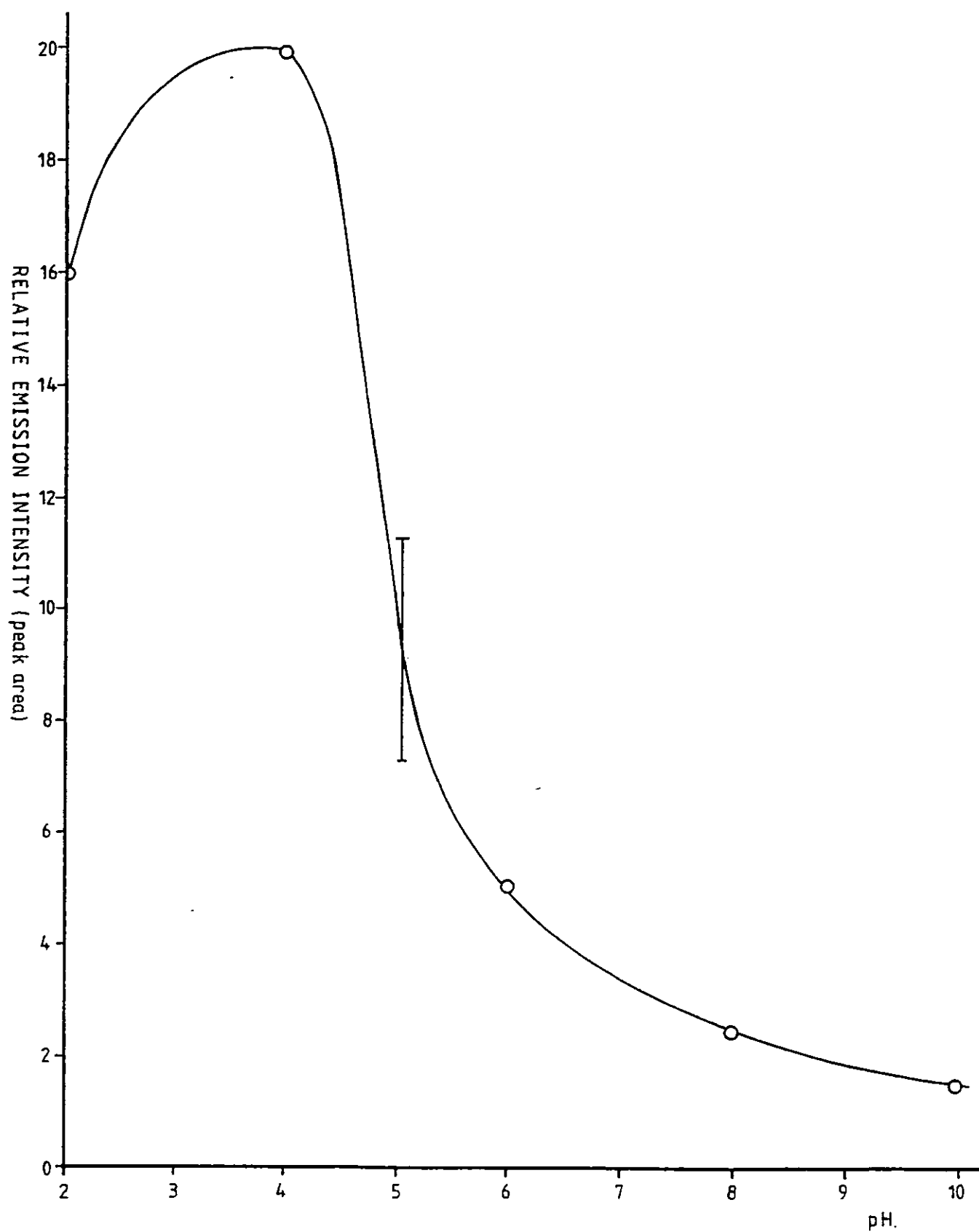


FIGURE 5-8 : Effect of pH on the deposition efficiency of copper.

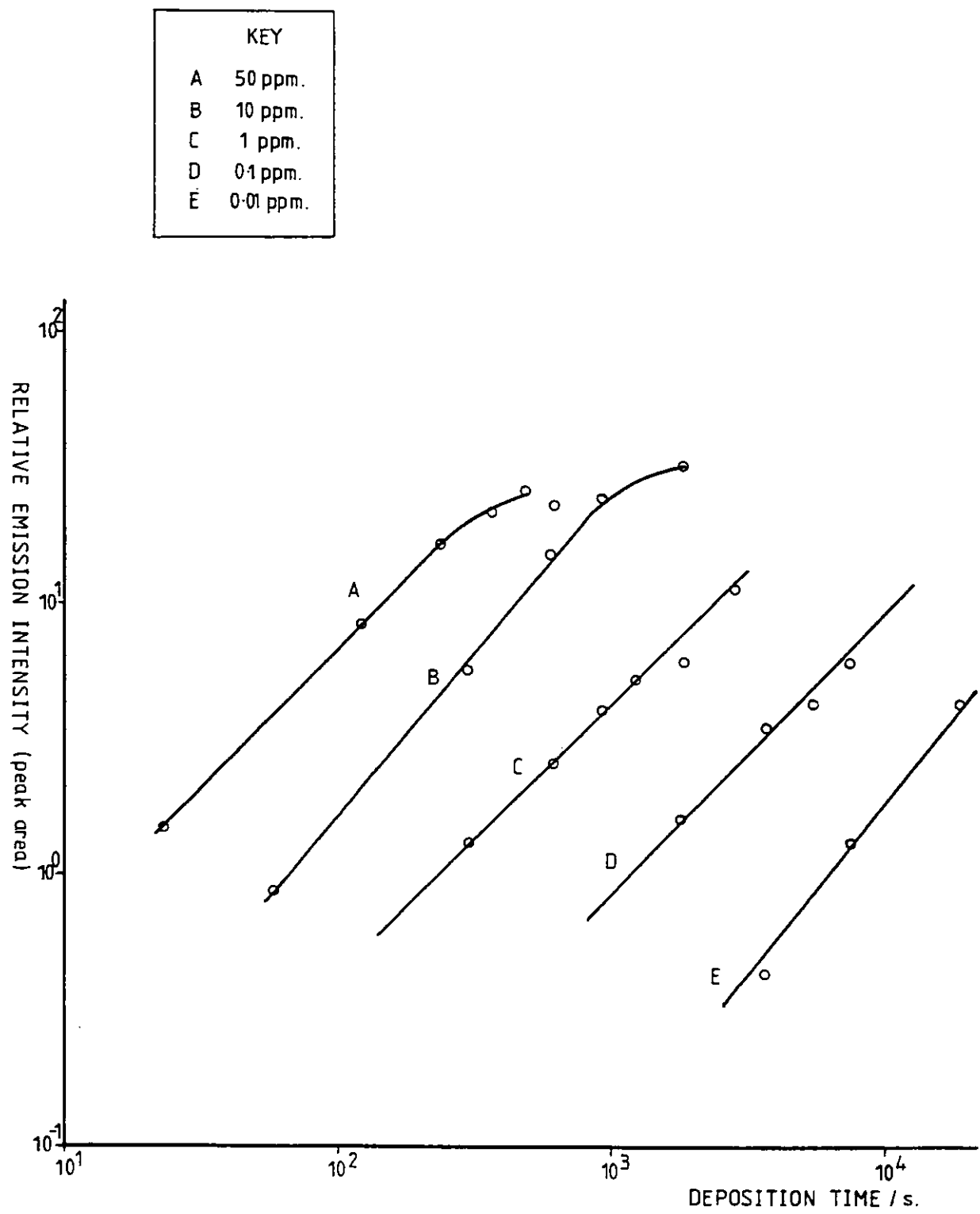


FIGURE 5-9 : Deposition characteristics of electrode as a function of deposition time for various concentrations of copper.

the electrode reaches a level where the current demand for further deposition exceeds that which the potentiostat used is capable of delivering. If this is the case, a larger capacity potentiostat would extend the calibration range, although this should not normally be necessary for preconcentration analysis in view of the low concentrations likely to be encountered.

The plating efficiency of the wall-jet cell was determined by selecting optimised conditions and observing the emission intensity at the 324.75nm. Cu(I) line when a 1ppm. copper solution was nebulised into the ICP after being pumped through the cell, and measuring the drop in emission intensity when copper was removed at the electrode upon application of the deposition potential. The deposition efficiency determined in this way was 8.5%, a figure not untypical for this type of electrode system. The stripping process was found to be quantitative with no memory effects observed in subsequent stripping cycles using only a solution of the background electrolyte, 0.1M KCl. The quantitative nature of the deposition and stripping processes is reflected in the deposition time calibrations of figure 5.9 which, within experimental error, exhibit the same slope over a wide range of concentrations and deposition times.

Possibility of Multi-Element Determinations.

The possibility of multi-element analysis was investigated in this study for determination of lead, cadmium and copper. Multi-element analysis using the wall-jet cell as an electrochemical detector, is only possible in a sequential manner, by applying an

anodic potential scan and measuring the sequential appearance of each stripping current at the individual stripping potential of each element. However, when used for preconcentration with the ICP this is not a limitation because a multichannel detector system can be used to record all analyte emission signals simultaneously.

To assess the possibility for multielement determination, lead, cadmium and copper were deposited from a solution containing 1ppm of each element in 0.1M KCl for 5min. by applying a potential of $-0.80V$ (vs. Ag/AgCl). A rapid anodic scan to a potential ($+1.0V$) more positive than the individual stripping potentials (table 5.4) was used to strip all three elements back into solution simultaneously and ^{these} were determined with the ICP operating under compromise conditions.

Table 5.4 Multielement analysis-Operating potentials.

Element	Half-wave pot.	Stripping pot.	Emission line
Copper	$+0.20V$	1. $+0.33V$ 2. $+0.54V$	324.75nm.
Lead	$-0.42V$	$-0.15V$	283.31nm.
Cadmium	$-0.50V$	$-0.33V$	228.80nm.
Plating potential $-0.80V$; Stripping potential $+1.0V$.			

Unfortunately, assessment was restricted because the spectrometer used was only of the single channel type and a multichannel spectrometer was not available. It was therefore necessary to perform this experiment in triplicate at the wavelength of each element. With a multichannel spectrometer these determinations could be performed simultaneously. The optimum conditions previously established for the element copper were found to be fairly compatible for the elements cadmium and lead, but deoxygenation of solutions was necessary because severe interference with lead deposition was observed. Deoxygenation

was accomplished by purging the solution with argon for several minutes before analysis.

Analytical Application.

For operation of the flow cell as a preconcentration device, it is desirable to have some quantitative relationship which can be used to calculate the concentration of analyte in the original sample. The preconcentration efficiency, η , may be defined as:

$$\eta = \frac{V_s \times \omega}{V_c} \quad \dots\dots\dots(5.4)$$

where: V_s is the volume of solution passed through cell.
 V_c is the volume of the cell chamber.
 ω is the optimised deposition efficiency.

In theory therefore, the concentration of analyte in the sample solution may be computed from the relationship:

$$C_s = \frac{C_c}{\eta} = \frac{C_c V_c}{\omega V_s} = \frac{m_c}{\omega V_s} \quad \dots\dots\dots(5.5)$$

where: C_c is the concentration of collected analyte in the cell chamber after stripping.
 m_c is the mass of collected analyte after passing V_s through the cell.

The limitation of using equation 5.5 for quantitative applications, is that it assumes that the optimised deposition efficiency will stay constant. This may not always be true if the sample contains significant quantities of other matrix species which could give rise to enhancements or suppressions. If this is the case, the efficiency factor must be determined for each sample type or alternatively standard additions and internal standard methods may be used.

Equation 5.4 illustrates that the best preconcentration gain will be achieved when V_c is minimised and when ω is maximised. The design of the flow cell is therefore of crucial importance to the usefulness of this sample introduction method. Also the preconcentration efficiency is not in principle limited because the amount preconcentrated will depend on V_s . Clearly however, the penalty for using large volumes of sample solution, V_s , is the time taken to pump through the cell chamber.

Unfortunately, the flow cell used for these studies was not specifically designed for this preconcentration application and was not easily adapted for such purpose. Although the efficiency of collection was acceptable, the fluid dynamics were such that the effective concentration of analyte presented to the plasma was lower than theoretically predicted, owing to dispersion of analyte in the carrier stream. The analytical performance of this prototype cell was therefore relatively poor.

The calibration linearity of the electrode was established for the range 0.01-10ppm copper, figure 5.10, indicating that the deposition efficiency stays constant for this concentration range. Assessment of the suitability of electrochemical preconcentration for analysis with the ICP was attempted by choosing a domestic tap water sample. The concentration of copper in this sample was determined by depositing the copper from 90cm³ of the sample, at a flow rate of 3ml./min. and using the previously optimised conditions. A deposition efficiency of 8.5% was assumed and the copper collected was determined after stripping, by viewing emission at the 324.75nm. line. The concentration of copper in the sample was then computed by calculating the mass of copper collected at the electrode from the emission/time

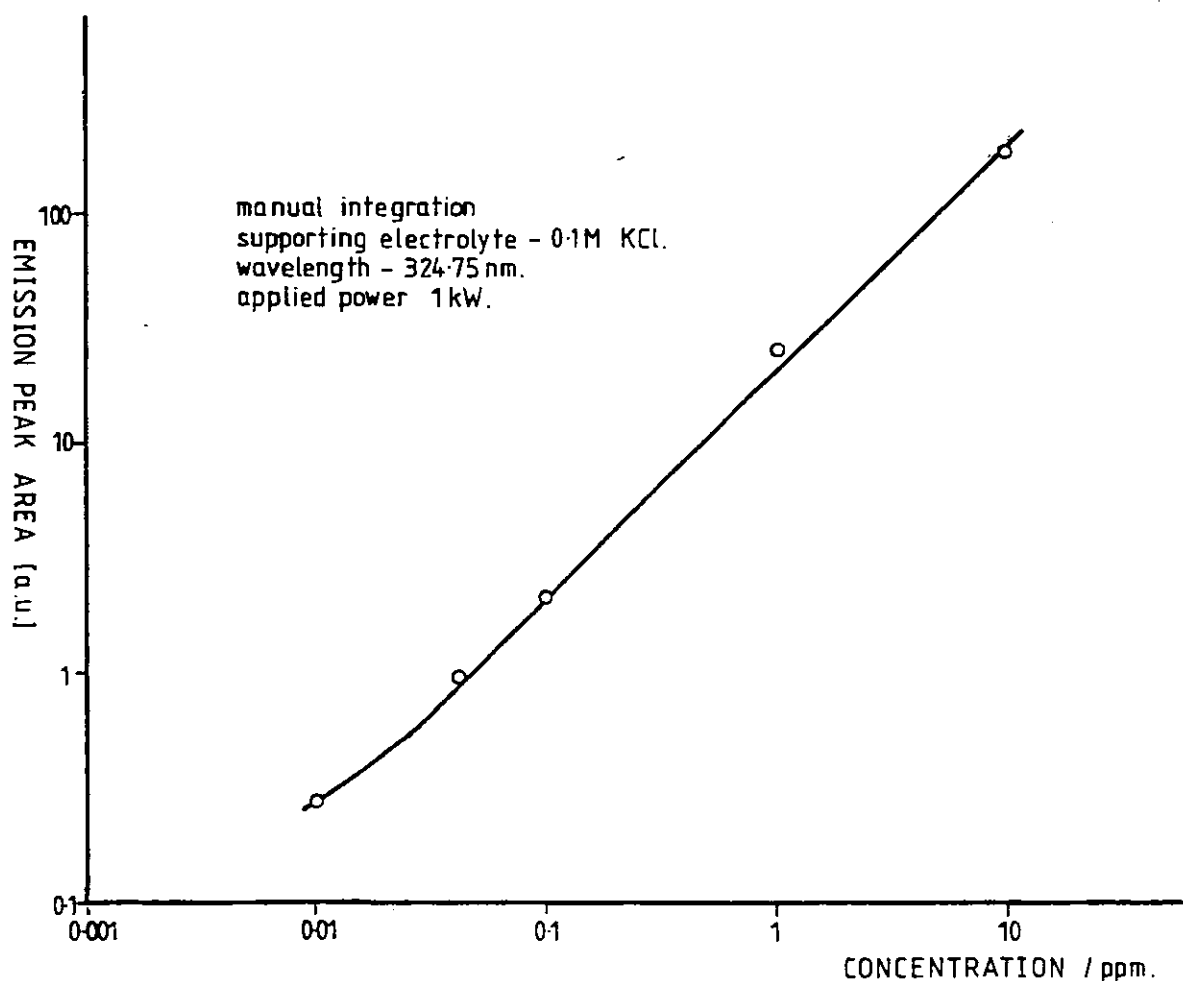
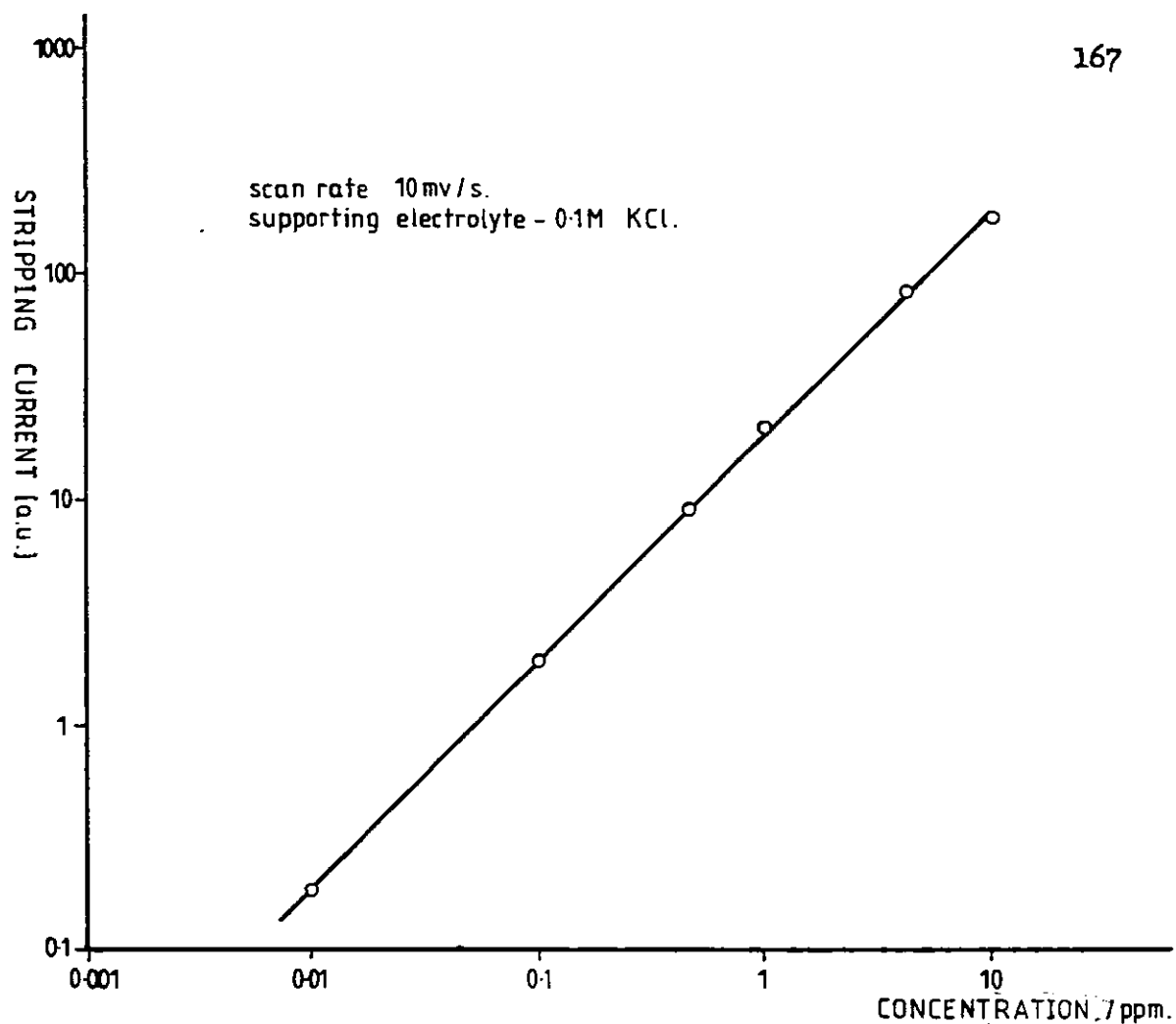


FIGURE 5-10 : Concentration calibrations for copper at glassy carbon electrode.
Top - using stripping current. Above - with connection to ICP.

profile after stripping, and using equation 5.5. The method of standard additions was also used, figure 5.11, to check for the presence of matrix effects at the electrode. The results of this determination are listed in table 5.5.

Table 5.5: Determination of copper in domestic tap water sample.

$\lambda = 324.75\text{nm}$.
 Plasma conditions-compromise.
 Sampling time-08.00.hrs.
 Base electrolyte-Aristar KCl.
 Cell conditions-as optimised.
 Sample A Copper water supply pipe.
 B Lead water supply pipe.
 Deposition time A 30mins.
 B 50mins.

RESULTS

Sample introduction method	Sample A	Sample B
Wall-jet cell (Eqn. 5.5)	0.045(± 0.004)	0.010(± 0.003)
Wall-jet cell (Std.Add.)	0.048(± 0.003)	-
Pneumatic nebuliser	0.040(± 0.008)	a
Electrothermal Vap. ^b	0.041(± 0.004)	0.008(± 0.0008)

All results expressed in ppm.

a Below detection limit.

b See chapter 6.

These results appear to suggest that matrix effects are not significant for analysis of tap water samples. The agreement between the various sample introduction methods is quite good. Also of note is the concentration of copper in the sample supplied through copper tubing, which is some four times higher than that supplied through lead tubing in the same building. Presumably some of the copper in sample A must originate from dissolution of the supply pipe.

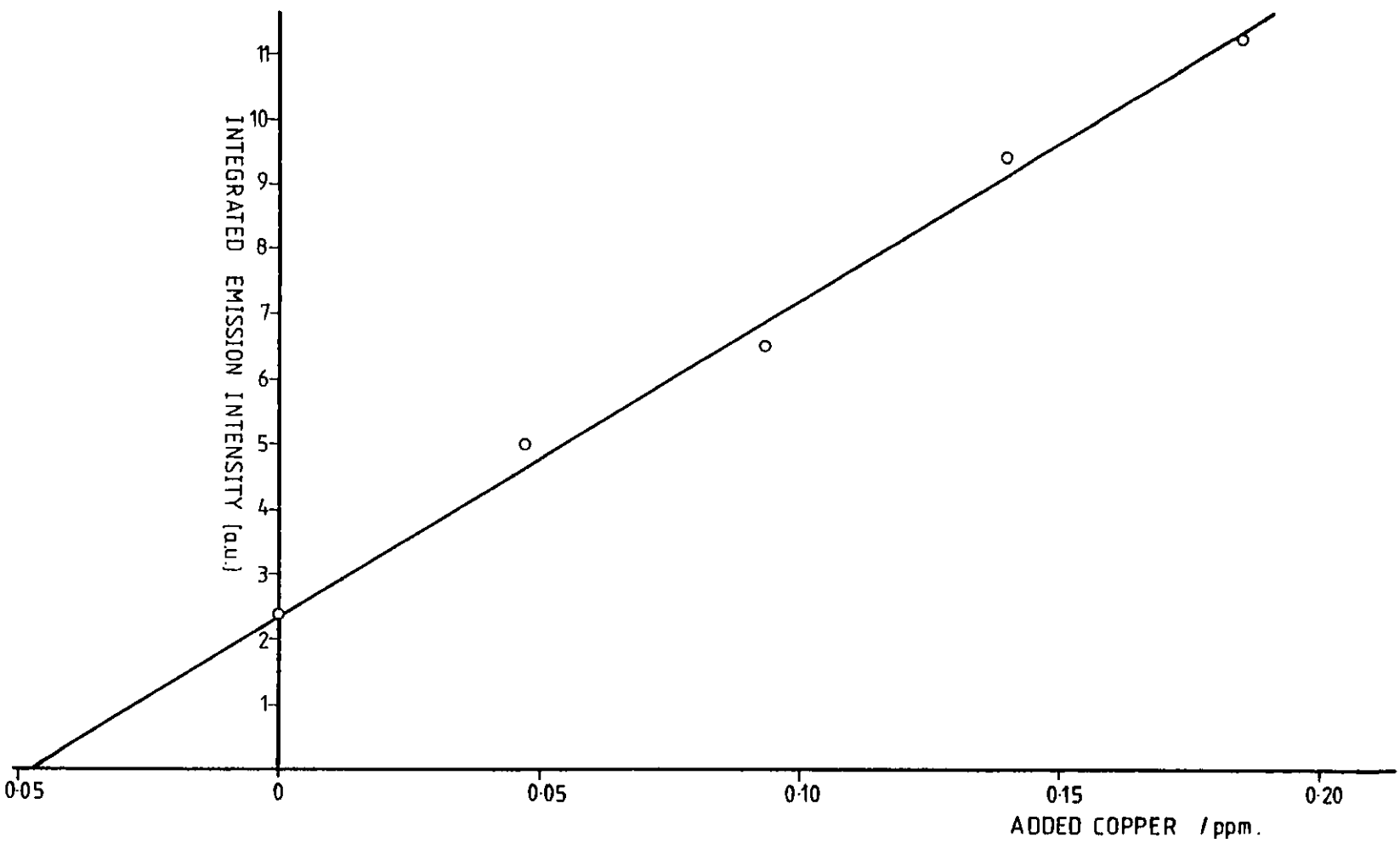


FIGURE 5-11 : Standard additions plot for the determination of copper in domestic tap water by electrochemical preconcentration and sample introduction into the ICP. Flow rate 3.0 ml/min., Emission line 324.75 nm.

New Cell Designs.

The main limitation of the wall-jet cell used for these preconcentration studies was the high dispersion of analyte during the stripping cycle in the cell. This produced severe tailing of the emission profiles obtained and introduced errors into the measurement of the mass of analyte deposited on the electrode, because integration of the emission/time profiles becomes more difficult as the profile is distorted along the time axis, that is, the background noise becomes more significant. On the basis of these studies the ideal cell would have a small sample chamber and would therefore produce a high concentration of analyte after stripping. A prototype cell which was designed to incorporate this feature was constructed and briefly evaluated for this application. The cell design, which was called the "concentric cup cell" is shown in cross section in figure 5.12. The main feature of this cell is the cup, into which fits a probe containing a Pt. ring working electrode of the same radius of curvature, to give a total volume of 30 μl . At the bottom of the cup is a drain hole which is connected to the nebuliser intake of the ICP. In operation, the analyte deposited at the working electrode is stripped off and is trapped in the cup. There is little opportunity for dispersion processes to occur.

The performance of this cell was optimised for flow rate and electrode cup separation using the element copper and these are shown in figure 5.13. As this particular cell design is new, no theory has yet been developed to predict the limiting diffusion current dependence of the electrode, but preliminary studies indicate that behaviour can be modelled on a tubular electrode configuration, the

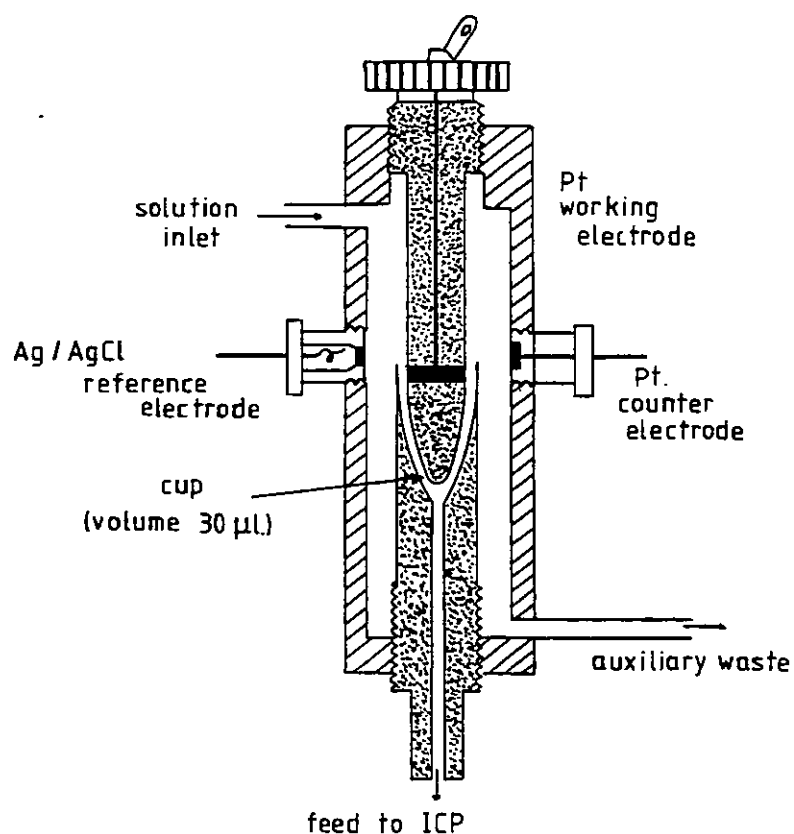


FIGURE 5-12 : Cross sectional view of concentric cup flow cell.

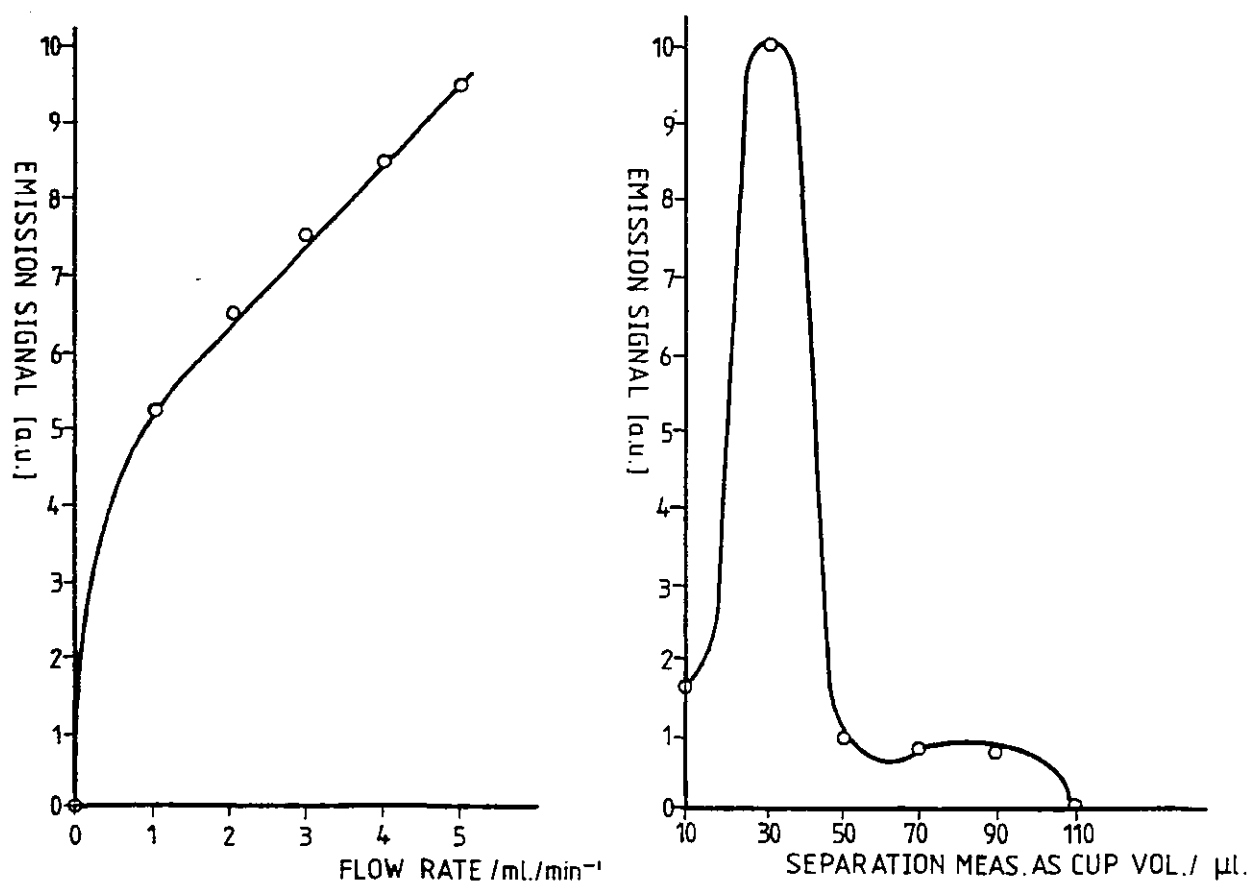


FIGURE 5-13 : Flow rate and electrode separation optimisations for the concentric cup flow cell. Species - Cu. deposition time - 5min. level - 2ppm.

properties of which are well known. The properties of the new cell are summarised in table 5.6.

Table 5.6: Properties of concentric cup flow cell.

Reference electrode Ag/AgCl
 Working electrode Pt.
 Potential excursion +1.0V.anodic ; -0.6V cathodic.
 limits.
 Half wave potential (copper) -0.30V. (see
 Stripping potential (copper) -0.10V. figure 5.14)
 Base electrolyte 0.1M KCl.
 Cell volume 30 μ l.
 Flow rate selected 3ml./min.

Connection and operation of the cell with the ICP, produced the type of emission profile depicted in figure 5.15. (copper concentration 2ppm; deposition time 10mins.). It may be observed that the profile is much sharper than that produced with the wall-jet cell. The half-width of the profile is equivalent to an effective volume of 300 μ l. Although this is larger than the physical volume of the cell it seems likely that the dominating dispersion mechanism is now that in the nebuliser intake chamber (100 μ l.) and diffusion in the spray chamber. Emission profiles sharper than that in figure 5.15 are unlikely to be obtained without modification of the nebuliser/spray chamber system. The prototype flow cell appears to be well suited for preconcentration, with the exception that the deposition efficiency of the Pt. electrode is poor ca. 1% (cf. wall-jet cell 8.5%), and future designs with more efficient electrode systems would be beneficial.

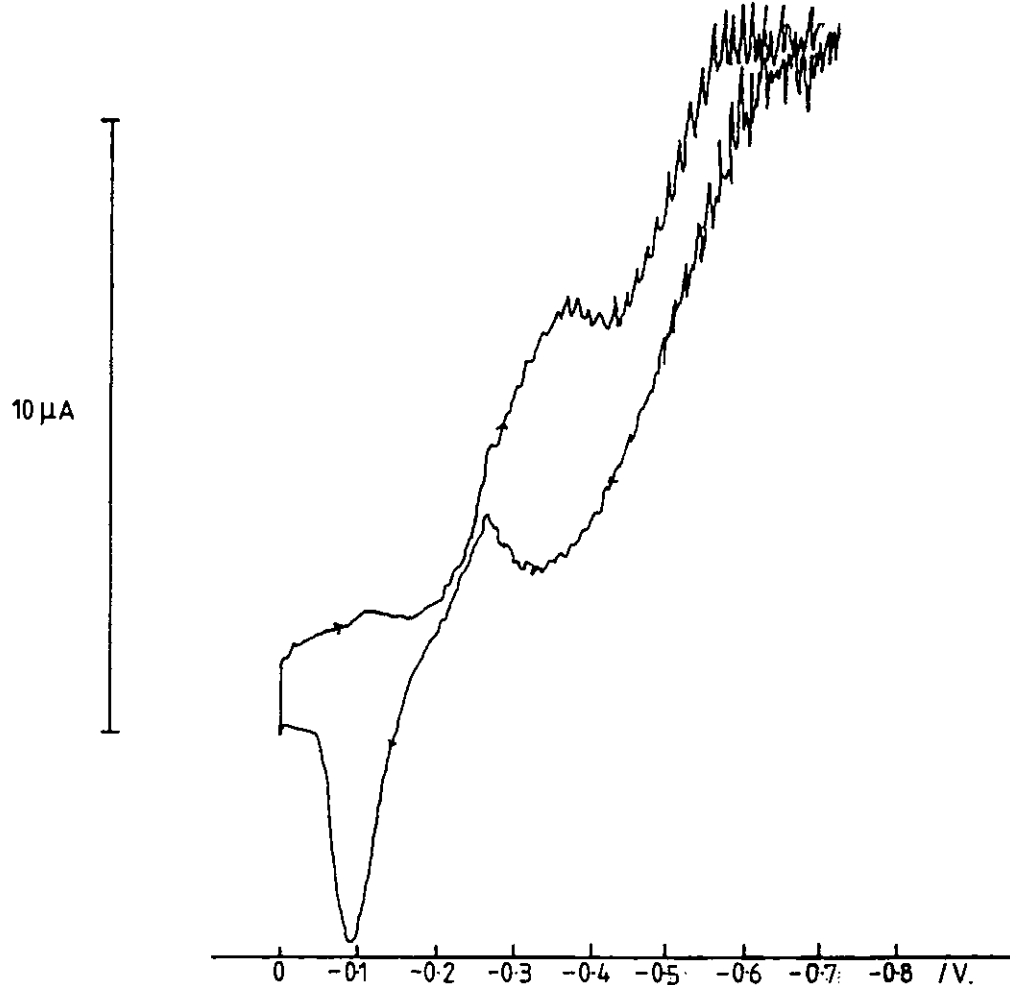


FIGURE 5-14: Cyclic voltammogram of copper with concentric cup electrode. 4ml/min. flow rate. Concentration 5ppm. 10mv/s.

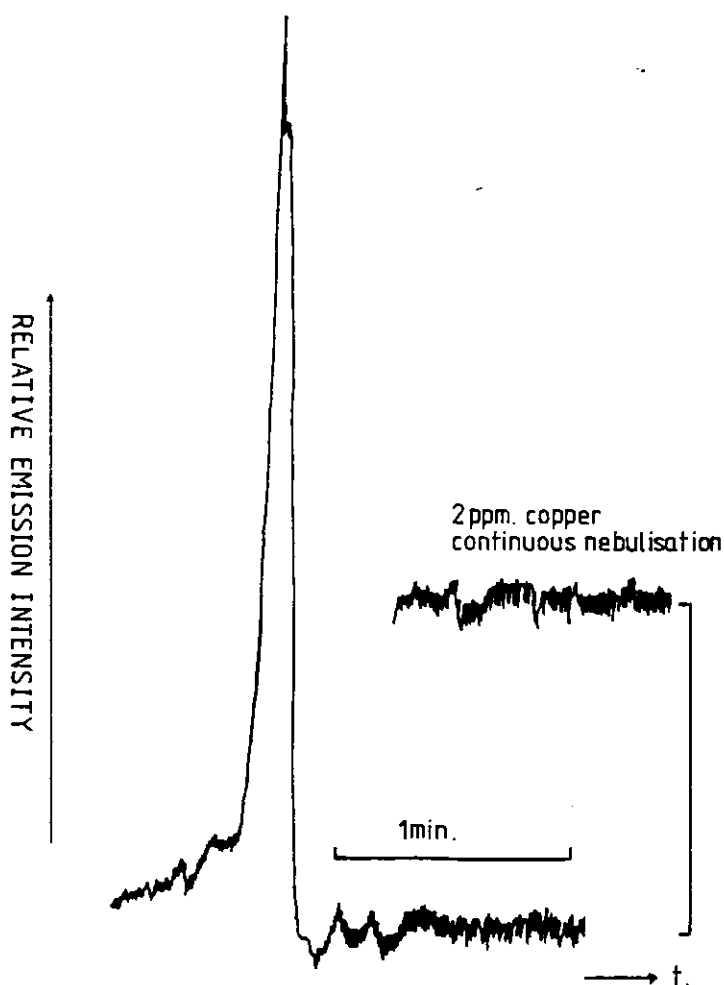


FIGURE 5-15: Emission profile from plasma after stripping from concentric cup electrode. 2ppm copper deposited 10mins. Flow rate 3ml./min. λ 324.75 nm.

5.4 Conclusions.

The design and implementation of an electrochemical preconcentration device has been assessed to modify the sample presentation for trace/ultra-trace analysis with the ICP. Presently long preconcentration times are necessary to realise any significant advantage compared with continuous nebulisation sample introduction. However this could be improved by careful design and optimisation of the flow cell and electrode configuration, preferably without relinquishing hydrodynamic control of the deposition process. The possibility of multi-element analysis has been investigated. It is envisaged that such an electrochemical preconcentration technique will be useful for the multi-element determination of ultra-trace elements in a variety of samples. One such application that shows great promise is the analysis of sea-water as the bulk concentration of salts, which causes so many problems with conventional spectroscopic analysis, is high enough to preclude the addition of a depolariser. Moreover the unwanted salts can be separated from the analyte before passage into the plasma.

It is also envisaged that automation of the entire process would be possible, a step which represents a significant advantage in comparison with other preconcentration techniques, which require more extensive manipulation of apparatus and are therefore difficult to automate.

CHAPTER 6
DEVELOPMENT OF ELECTROTHERMAL VAPORISATION TECHNIQUES
FOR SAMPLE INTRODUCTION INTO THE ICP.

6.1 Electrothermal Sample Introduction.

Electrothermal atomisation (ETA) techniques have become extremely popular for sample presentation in atomic absorption and fluorescence spectroscopy, a situation which has led to the appearance of several commercial systems. In contrast, electrothermal sample introduction (ET) for the ICP has, surprisingly, received little interest despite the potential that such a sample introduction technique has to offer.

Conceptually, the ET technique for the ICP might be expected to have the same characteristics as ETA introduction in AAS and AFS, namely the ability to handle microsize samples and the increase in sensitivity which accrues from the rapid generation of a transient collection of atomic species and these properties are usually observed. However, in other respects, the ET introduction process for the ICP is fundamentally different to that for AAS and AFS. The main characteristics are summarised and contrasted in table 6.1. ET sample introduction for the ICP involves the efficient desolvation, pyrolysis and vaporisation of all the sample, including the analyte, which is then transported to the plasma discharge in a carrier stream of argon. To maintain the efficiency of the sample transport process, a completely enclosed sampling and transport system is necessary. The ET approach can therefore be regarded as a true sample introduction method in which the analyte is presented to the plasma discharge as a "dry aerosol."

Table 6.1: Electrothermal Sample Introduction Techniques.

AAS/AFS.

1. Rapid handling of microlitre samples.
2. Increase in sensitivity up to two orders of magnitude higher than nebulisation based systems. (nebuliser efficiency ca. 10%).
3. Separation of components achievable by controlling heating ramp rate.
4. Electrothermal device becomes the atom cell on which measurements are made.
5. Requirement for efficient production of atomic species.
6. Interference by matrix species necessitates background correction techniques.
7. Sensitivity determined by kinetics of atom production and diffusion time of these away from the atom cell.

ICP

1. Rapid handling of microlitre samples.
 2. Increase in sensitivity up to two orders higher than nebulisation based systems (nebuliser efficiency ca. 2%).
 3. Separation of components achievable by controlling heating rate.
 4. Electrothermal device does not become the atom cell, but is used to generate an aerosol of sample suitable for transport to plasma.
 5. Requirement for efficient vaporisation of sample; atomisation produces interference effects in transport process.
 6. Matrix interference minimal, as final measurement performed in high temperature source.
 7. Sensitivity determined by efficiency of sample vaporisation and transport to plasma discharge.
-

In this chapter, various methods for the introduction of samples into the ICP by electrothermal vaporisation are assessed, particularly for the routine application to analytical samples.

6.2 FILAMENT-IN-FURNACE-VAPORISATION (FIFV).

6.2.1 Introduction.

Filament-in-furnace-atomisation (FIFA) was developed by Garnys and Strythe (63) at the University of New South Wales UNSW, Australia, to facilitate rapid accurate analysis of lead in microlitre volumes of blood at environmental levels. These authors had previously concluded that commercially available graphite tube atomisers were not suitable for routine measurement of large numbers of blood samples for lead, reasoning that significant variations in tube and atomisation performance were greater than variations in solution dispensation, producing poor reproducibility.

The apparatus used for FIFA was based on a tungsten filament which passed through a conventional graphite furnace as used for flameless AAS. 5 μ l. volumes of the blood were conveniently located on this filament by application with a microsyringe to several small coils of tungsten wrapped around the filament at regular intervals. Each sample was desolvated and oxidatively ashed outside the furnace, by passing a small current through the filament, after which each small coil was located inside the furnace in sequence, by electromechanical programming, for the atomisation cycle. Several advantages can be realised with this arrangement compared with static location of samples-

1. Sample matrix can be oxidatively ashed prior to analytical measurement, unlike static measurement where pyrolysis is the dominant mechanism. Matrix can therefore often be broken down more effectively.
2. All samples are subjected to the same desolvation and ashing conditions because more than one sample may be applied to the filament.
3. Semi-automated multi-sample operation enables more rapid sample analysis.
4. Sample passed into furnace suspended on tungsten and therefore does not come into intimate contact with the graphite constituting the furnace. Formation of undesirable compounds and interference effects can be avoided.
5. Rapid comparison of standards and samples.

Although FIFA was initially designed for the analysis of lead by AAS, it would also seem to have some potential as a sample introduction method for the ICP. Some of the potential attractions are: rapid sample turnover through automated sample introduction, ashing of matrix outside plasma sample introduction feed (precluding severe plasma impedance changes often caused by some matrices and non-aqueous solvents) and the ability to handle microsize samples.

For application as a sample introduction technique for the ICP, the requirements are slightly different to those of AAS in that vaporisation of analyte and efficient transfer to the plasma for excitation is necessary rather than atomisation. For this reason the technique was reclassified as filament -in-furnace-vaporisation (FIFV) for the purposes of these studies.

6.2.2 Experimental.

Apparatus.

The apparatus used in this work was obtained on loan from UNSW. The filament supported approximately six small helical coils of tungsten wire of 3-4mm. in length which were crimped in position at intervals of approximately 1cm. The filament passed horizontally through a Perkin-Elmer graphite furnace tube into which each small coil could be brought, in sequence, by a filament travel mechanism consisting of a 5mm. pitch, double archimedean screw and spring loaded ratchet. Transverse movement through the furnace was made possible by drilling two small holes (diameter 0.9mm.) in the furnace walls perpendicularly to the toroidal axis of the furnace, which is shown in figure 6.1 together with a typical FIFV coil. The filament could be electrically heated by passing a small current (2-5A) through it from a purpose built power supply. The graphite furnace was also electrically heated using a modified Shandon Southern A3370 high current, low voltage power supply.

Furnace Temperature Measurements and Calibration.

Prior to using the graphite furnace for the final stage heating of the tungsten filament, it was calibrated for temperature with respect to the power supply voltage. The temperatures attained at each setting were measured with a previously calibrated chromel-alumel thermocouple, possessing one reference junction, supported approximately 0.5-1mm. away from the furnace to avoid contamination

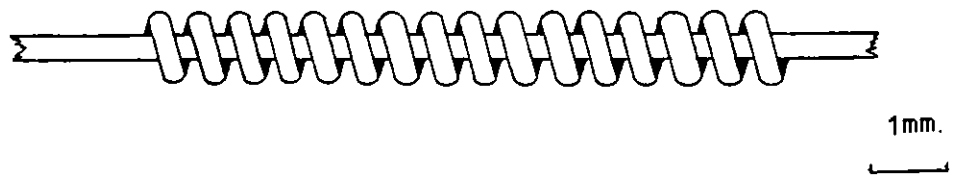
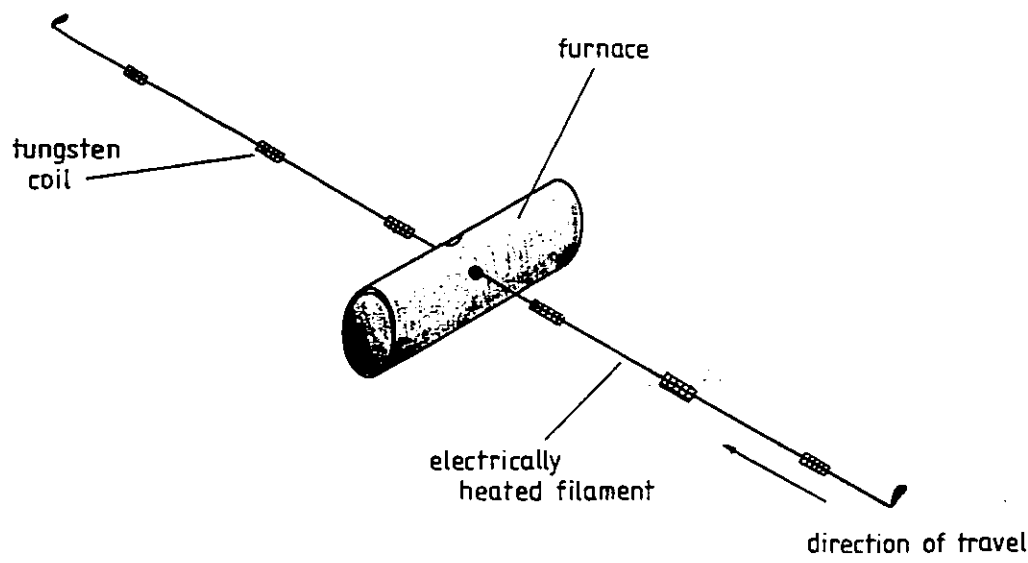


FIGURE 6-1 : Normal arrangement for filament-in-furnace analysis and close up of tungsten coil.

effects. Temperature measurements above 1500°C could not be measured with this thermocouple owing to the proximity of its melting point. Instead, temperatures above 1500°C were measured with a disappearing filament optical pyrometer (Leeds and Northrup model 8622-C). Calibration curves obtained for the furnace are illustrated in figure 6.2, for the case where no gas flow was directed through the furnace and also for the case where a gas flow of 4l./min. was established. It was observed that the maximum temperatures achievable for these two cases were markedly different. With no gas flow, the maximum temperature possible was in excess of 2200°C whilst for a gas flow of 4l./min., this temperature dropped to 1300°C. In subsequent studies where the furnace became part of the ICP sample introduction circuit, flow rates of approximately 4l./min. were necessary to establish the injector channel (toroidal plasma) in the plasma. Consequently, the forced convective cooling effect observed effectively limited the maximum working temperature of the FIFV furnace to 1300-1350°C.

6.2.3 Results and Discussion.

FIFV Configuration.

For effective sample introduction into the ICP, a gas tight transport system is required to ensure that all analyte passes through the plasma for excitation and not through some other point in the system to the external environment. Two configurations were used for adapting the FIFV apparatus for this purpose, figure 6.3. The first system was based on argon gas entry at both ends of the graphite furnace and exit to the plasma via a graphite chimney inserted in the

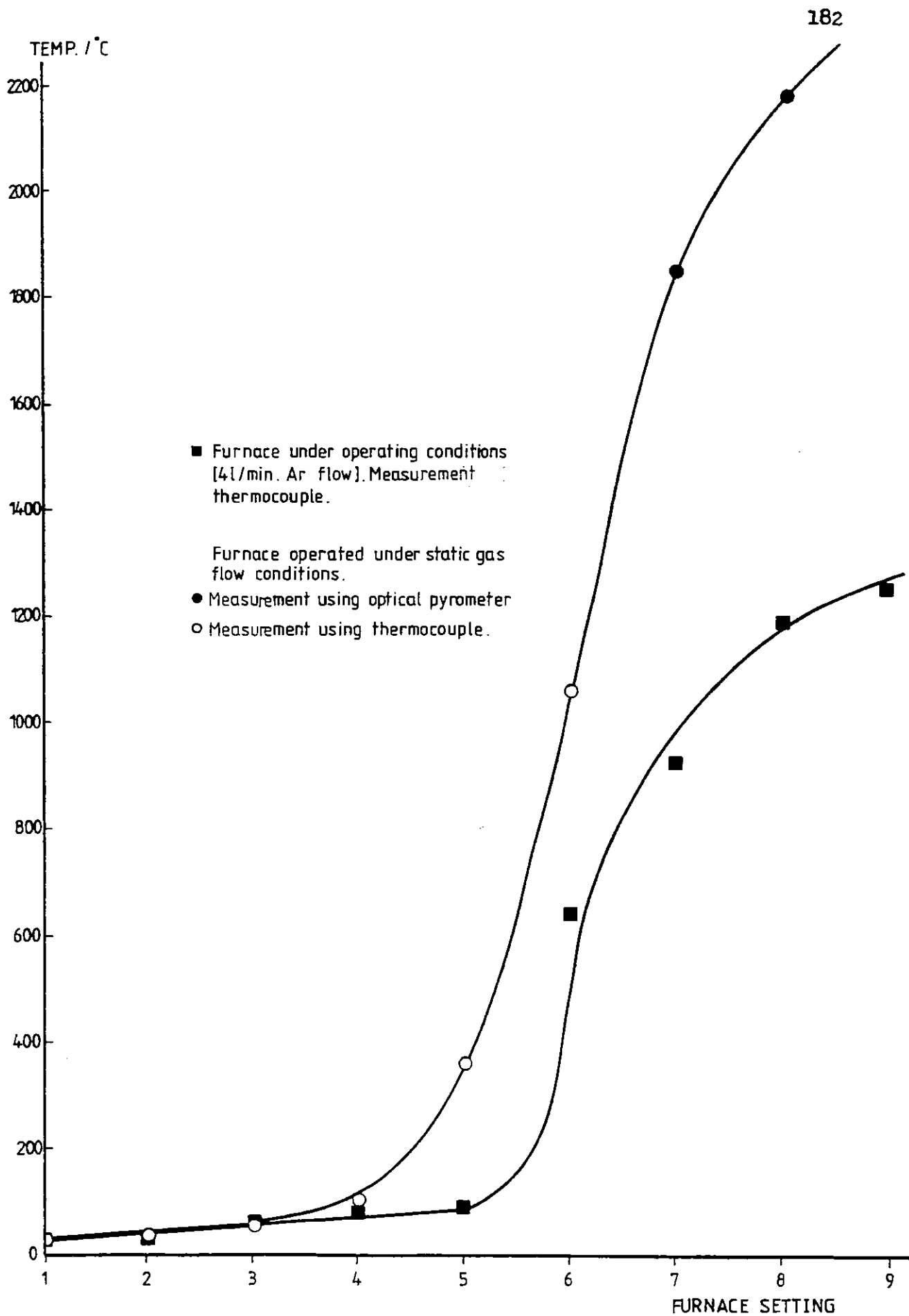
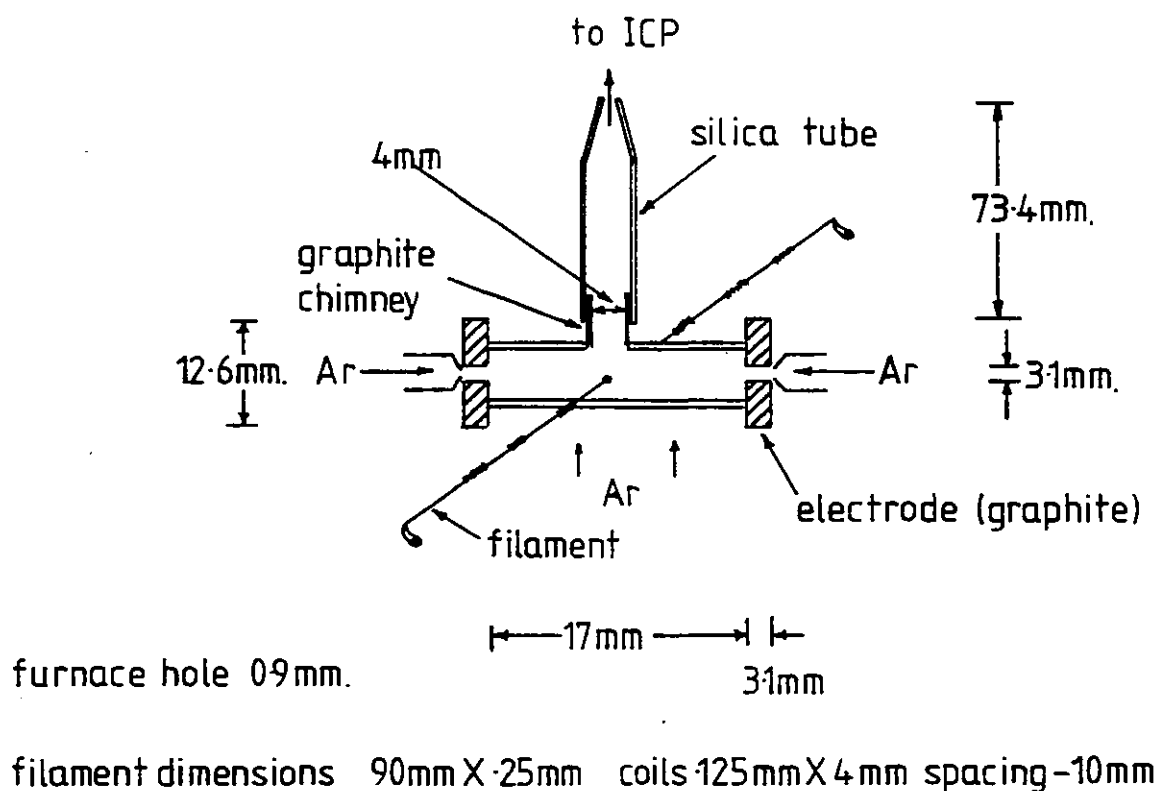


FIGURE 6-2 : Temperature calibration curves for FIFV graphite furnace using Shandon southern A3370 atomiser.

ARRANGEMENT 1 SIDE VIEW FURNACE



ARRANGEMENT 2 TOP VIEW FURNACE

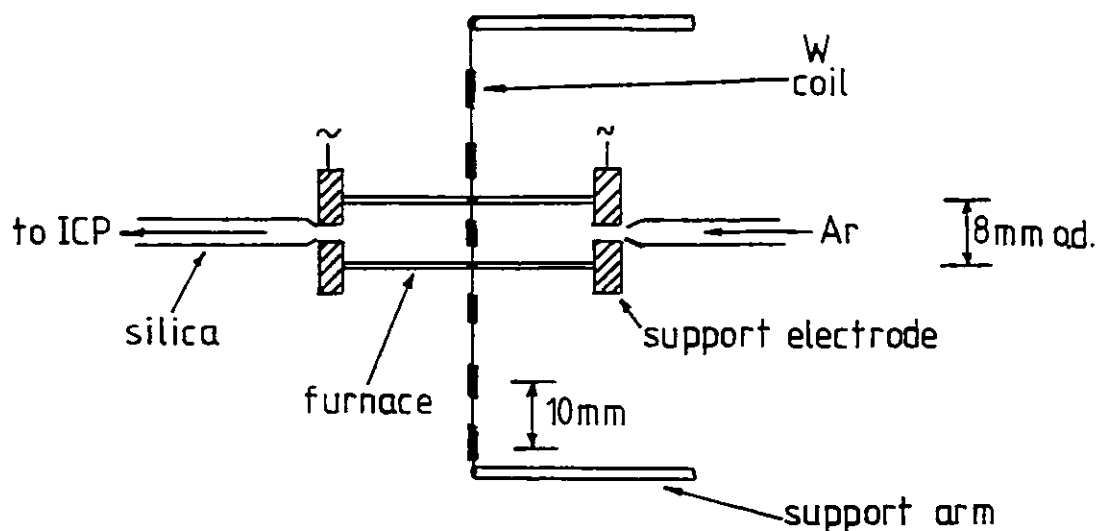


FIGURE 6-3 : FIFV arrangements for sample introduction into the ICP.

top of the furnace, thus presenting three junctions where analyte could be lost to the external environment. In operation, this resulted in irreproducibility and poor sample transport efficiency ranging from 6-60% with argon flow rates of 4-5 l./min. The high flow rates were necessary (cf. 11 l./min. nebulisation) to overcome the pressure loss through the FIFV system, producing the minimum pressure necessary for forming the toroidal configured plasma.

The secondary arrangement consisted of argon transport gas entry at one end of the furnace and exit to the plasma at the other end, producing transport efficiencies ranging from 11-75%. Further studies revealed that the majority of the remaining sample loss was through the filament transport holes in the side of the furnace but little could be done to prevent this.

Sample Application to Filament.

Small coils of tungsten wire, wrapped at intervals along the filament, were originally devised for precisely locating small volumes of liquid samples, preventing movement along the filament and presenting a high surface area for the rapid drying, ashing and vaporisation of the sample.

In the prototype apparatus, sample application to the filament coils was found to be quite difficult but much easier after the filament had been subjected to several heating cycles (producing more amenable surface characteristics). In all work, 10 μ l. aliquots of sample were applied with an adjustable micropipette fitted with a disposable polypropylene tip. Using this device, the best precision for aqueous samples was 0.033 rsd on ten successive deliveries.

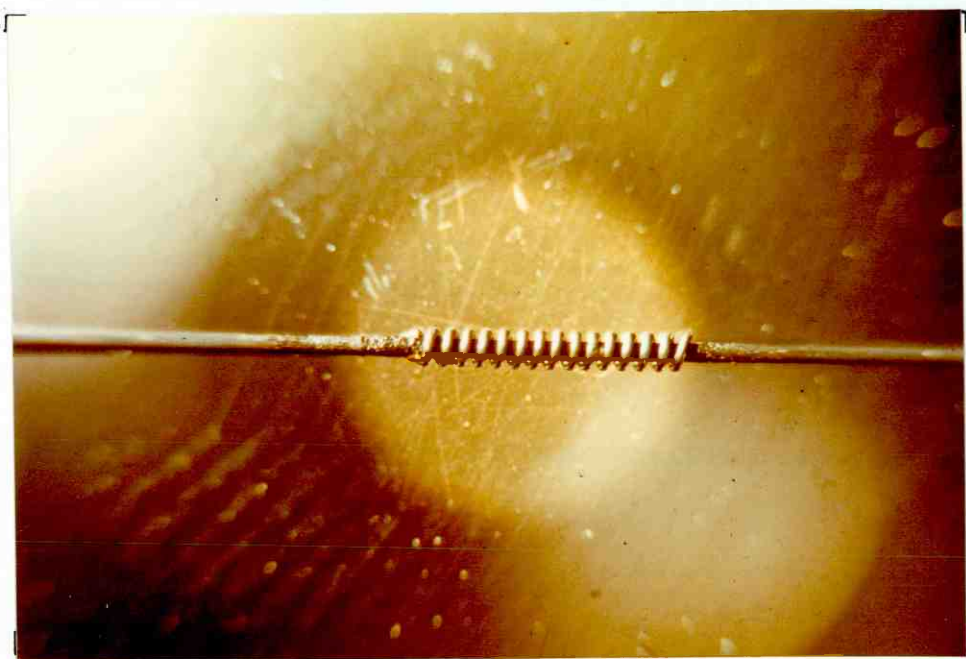


PLATE 1 DISTRIBUTION OF CHROMIUM ON FILAMENT $\times 10$.



PLATE 2 FORMATION OF TUNGSTEN OXIDE ON FILAMENT $\times 30$.

Studies were conducted to find the distribution of sample within each individual coil, by evaporating 500ppm. samples of chromium (VI) in distilled water on each coil and inspecting the coil with a low power microscope (Vickers Instruments Ltd.). The chromium was found to concentrate at the ends of each coil, plate 1., and in some extreme cases to have partially crept along the adjacent filament body. These effects were attributed to the lower heat dissipation at the ends of the coil and evidently produces bifurcation of sample to each end of the coil. Precise location of the filament on subsequent travel into the furnace would therefore appear to be necessary if the sample is to be heated uniformly.

Properties of Tungsten as Filament Material.

From preliminary experiments, it was observed that after a few heating cycles, the tungsten filament became extremely brittle. This was attributed by Garnys and Smythe to the macrocrystalline structure of tungsten and to the formation of tungsten carbide eutectic mixtures when in contact with the graphite furnace, thus lowering the melting point of tungsten from 3400°C to 2500-2800°C. Degradation of the filament would also be expected to occur outside the furnace because the oxygen rich atmospheres which promote the true ashing of samples will also promote oxidation of the tungsten. Therefore besides mechanical limitations, several chemical effects are expected.

The most important of these is the tendency to produce WO_3 at red heat. In the presence of water and U.V. radiation this appears as a blue compound and was actually observed on the filament (plate 2.) after it had been electrically heated for sample pretreatment. WO_3

sublimes fairly readily and it is therefore conceivable that during operation of the furnace some tungsten will be introduced into the plasma. In practice, intense emission at the tungsten (II) 239.709nm. line was observed which provided evidence for this. Several spectral interferences may therefore occur when the FIFV system is used for sample introduction especially as the tungsten spectrum is extremely complex. Also, since tungsten oxide species are generated, some increase in the background continuum emission from the plasma might be expected in addition to simple line overlap. A careful study of this potential effect however, revealed no significant contribution to the overall spectral background and it is evident that the high temperature of the plasma produces effective dissociation of the oxide.

Of more importance is the severity of overlap of tungsten emission lines with those of analyte species introduced into the plasma by the FIFV system. Harrman⁽²³⁴⁾ has recently drawn attention to spectral interferences caused by tungsten and predicted that severe interference could occur for several of the best lines of Al, B, Cd, Ca, Hg, Mn, Mo, Ni, Si, Pb and Zn. Careful line selection is necessary such that these potential interferences do not occur.

Additional evidence for the formation of WO_3 was provided by examination of the graphite furnace after approximately 50 heating cycles. A blue compound was found to have concentrated in the furnace near the support electrodes and near the filament transport holes and was probably the "tungsten blue" produced by heating WO_3 under reducing conditions. Removal of WO_3 also accounts for the shiny appearance of the tungsten coils after passage through the furnace, leaving a fresh pitted surface of tungsten, plate 3., which is

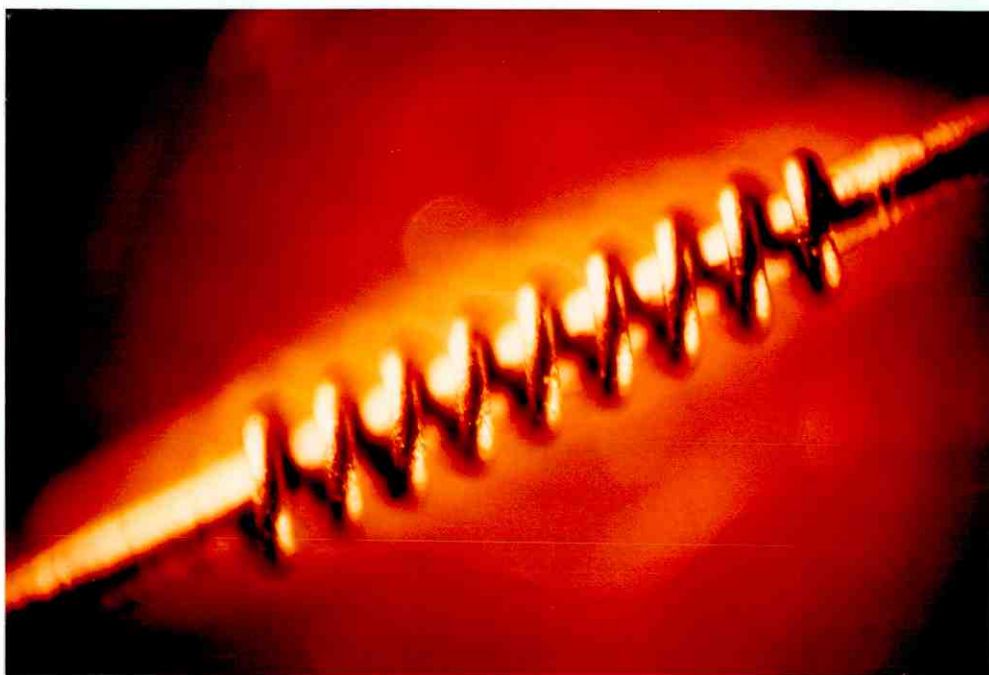


PLATE 3 PITTED SURFACE OF COIL AFTER HEATING CYCLE. x 30.

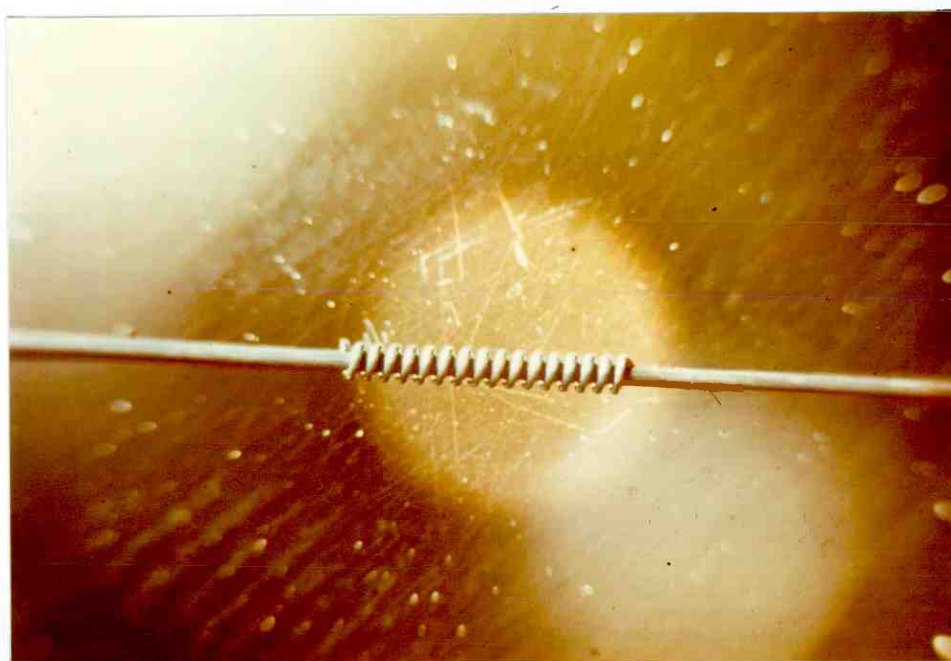


PLATE 4 SURFACE OF NEW FILAMENT COIL BEFORE USE x 10.

compared with the original surface of a new coil, plate 4.

Application to Analytical Samples.

To establish the potential of FIFV for the analysis of real samples, a preliminary investigation was conducted using three standard test elements- silver, chromium and nickel. 10 μ l. aliquots of the element under test were applied to the coils, desolvated at 125 °C and passed into the furnace for vaporisation at 1350 °C. to produce a transient emission signal on the chart recorder. Both chromium and nickel produced severe memory effects when analysed in this way, that is, some of the metal was retained on the coil after the vaporisation cycle. This was attributed to the relatively low maximum furnace temperature that could be attained. Detection limits for chromium and nickel were 5ppm using a 20 definition (chapter 4). The reproducibility was poor giving an rsd of 0.2 on ten samples.

Satisfactory results were obtained for silver but close control of furnace temperature was critical. If the final temperature was too low, inefficient vaporisation resulted, whilst if too high, subsequent samples on next consecutive filaments waiting for transport into the furnace were found to produce low results, that is, analyte loss was occurring. Such analyte loss could only have resulted from partial vaporisation of analyte before transport into the furnace, initiated by thermal transmission down the tungsten filament during the vaporisation cycle of a particular coil. This phenomenon was investigated by plotting the temperature profiles along the filament as a function of distance from the furnace whilst heating the furnace at different temperatures. These plots are reproduced in figure 6.4.

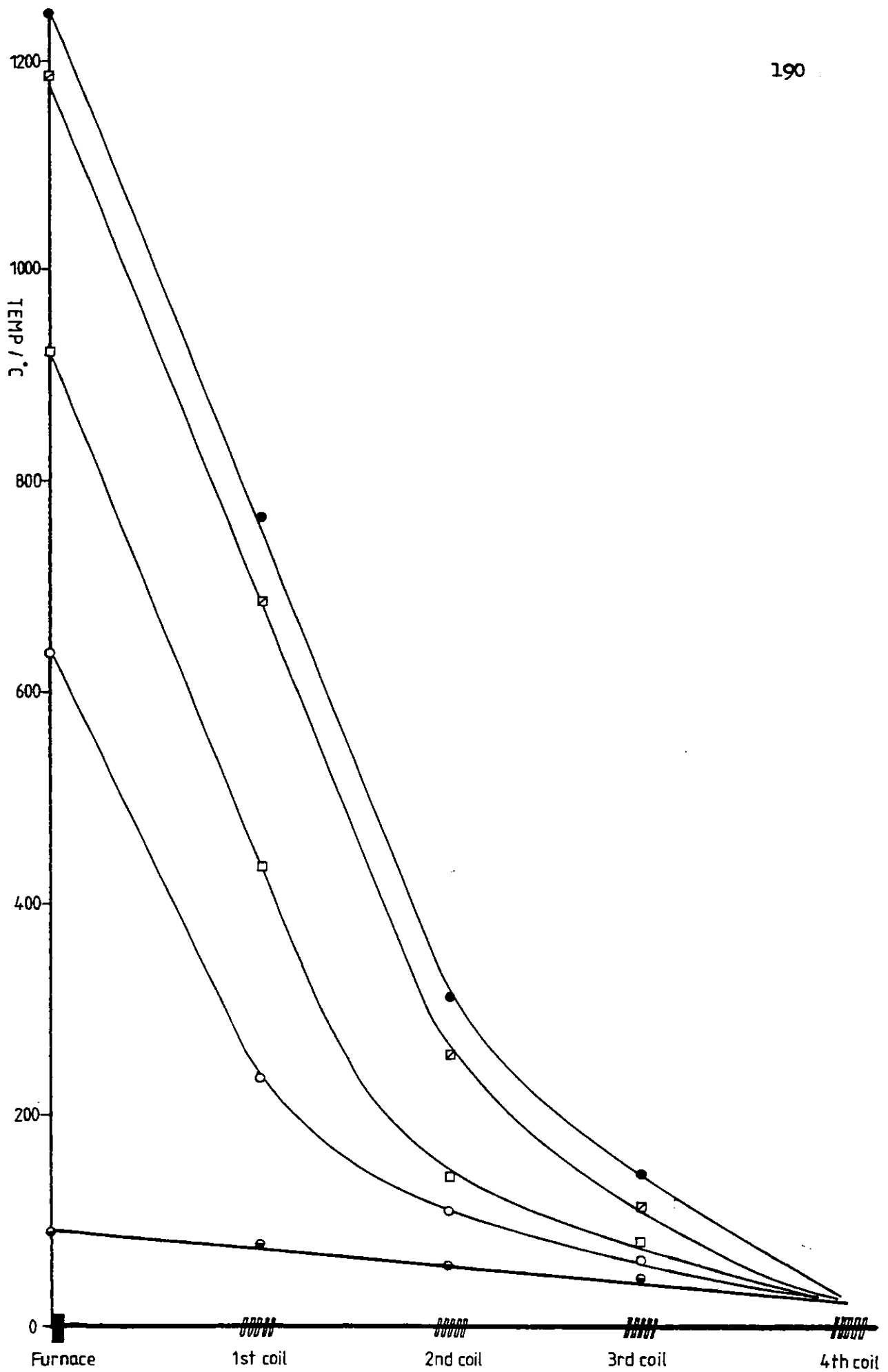


FIGURE 6-4 : Temperature distributions along FIV filament for various initial furnace coil temperatures. All temperatures obtained under operating conditions.

In all cases, ambient temperature is reached at the 4th. coil outside the furnace, but the heating effect is severe for other coils; at an initial furnace temperature of 1250°C., analyte species experience a temperature of nearly 800°C. on the first coil and 300°C. on the second coil. Although the temperature rise effect is less severe at lower initial temperatures, severe prevaporisation interference losses would be expected to occur for many volatile elements when analysed by this method.

The optimum temperature for analysis of silver was found to be 1200°C. A calibration graph for aqueous solutions of silver was rectilinear with unity slope for concentrations up to 1000ppm., figure 6.5, and the detection limit was 1400pg. for a 10 µl. aliquot. The conditions for the analysis of silver solutions are given in table 6.2 compared with those of a competing electrothermal vaporisation technique (section 6.3) studied.

Table 6.2 :Comparison of graphite rod vaporisation GRV and FIFV for analysis of silver.

Condition	FIFV	GRV
Wavelength	328.07nm.	328.07nm.
Drying time/temp.(filament)	30s.125 C.	30s.125 C.
Vaporisation time	3s.	2s.
PMT voltage	1.0kV.	1.0kV.
Vaporisation temp.(furnace)	1200°C.	2200°C.
Plasma coolant flow	16l./min.	16l./min.
Plasma auxiliary flow.	1l./min.	1l./min.
Plasma injector flow	3-4l./min.	0.8l./min.
Applied power	1.0kW.	1.0kW.
Observation height	10mm.ALC	18mm.ALC
Detection limit	1400pg(10 µl)	270pg(10 µl)
Best precision(10dets.)	0.07rsd	0.03rsd
Relative speed	1	10

ALC above load coil.

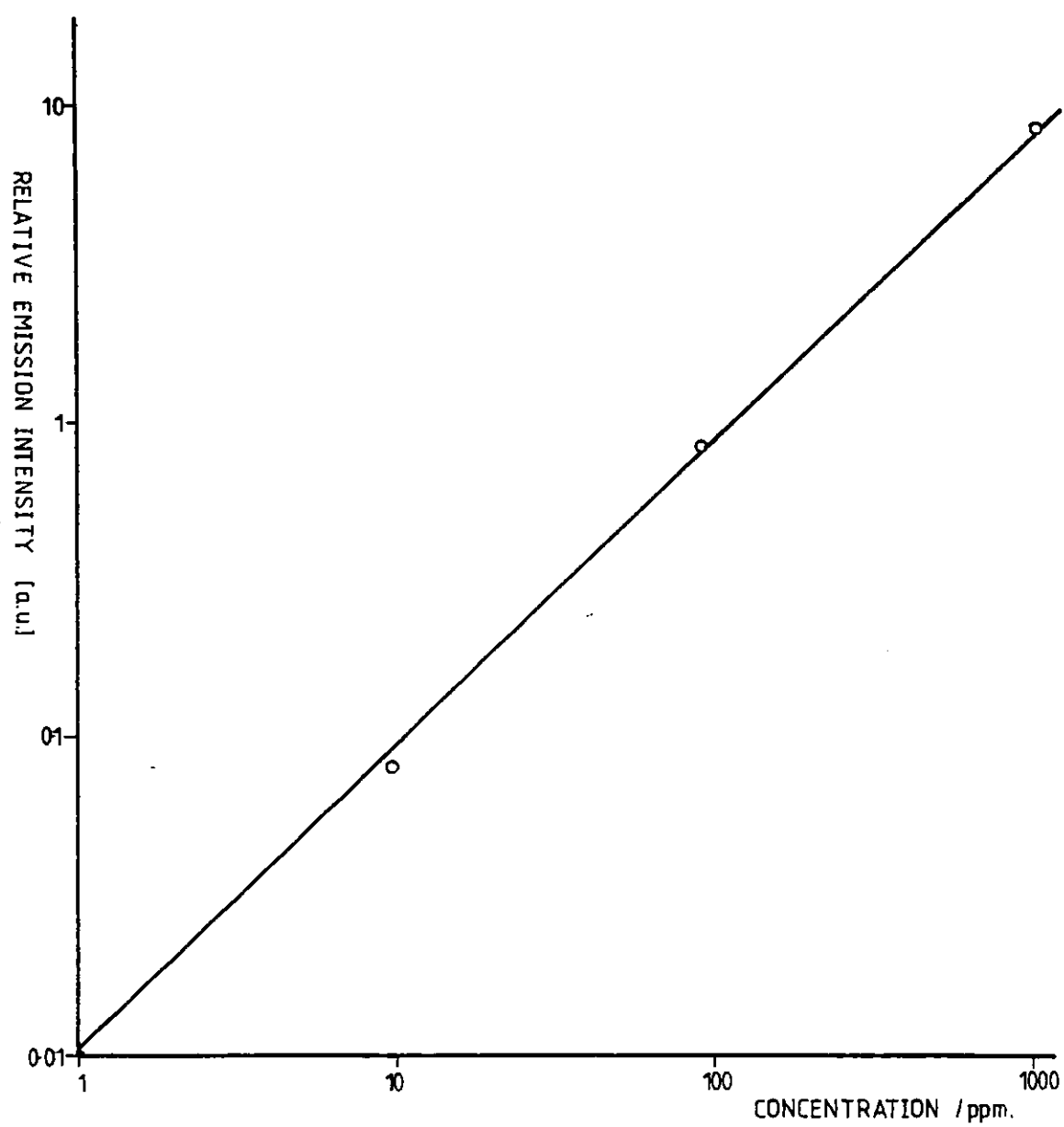


FIGURE 6-5 : FIFV calibration graph for silver using 328.1 nm. line.

The poor transport efficiency using the FIFV system is reflected in the inferior detection limit and reproducibility compared with the competing method where, for silver, the transport efficiency approaches 100%.

6.2.4 Conclusions.

In these studies, the operating characteristics of the FIFV system for use as a sample introduction technique for the ICP have been critically appraised. There is no doubt that in the FIFV mode, the system is suited for the rapid analysis of volatile elements by AAS, especially where the sample matrix may be removed by ashing; however for sample introduction into the ICP, the standard system would have to be extensively redesigned to compete with existing sample introduction systems. The main constraint is that the furnace/filament system has to be gas tight, a requirement not satisfied by the FIFV system, as analyte is able to vent through the filament transport holes. In view of these difficulties the system might be more effective if totally enclosed in a gas tight chamber containing a port through which samples could be dispensed. If this is done the furnace could be replaced by an open filament device of the West design (45).

Problems are also evident with the choice of tungsten as a material for constructing the filament because the metal is readily oxidised, promoting spectral interference and deterioration in lifetime. Selection of other materials for filament construction, such as tantalum, may prove valuable.

The main features of the FIFV system used for sample introduction

into the ICP are summarised in table 6.3.

Table 6.3: FIFV sample introduction.

Advantages.

1. Ashing of matrix and desolvation may be accomplished outside furnace so that unwanted matrix/solvents can be prevented from entering plasma.
2. Allows fast and simple analysis of samples by semi-automated handling.
3. All samples subjected to identical drying/ashing conditions.
4. Rapid running of standards.

Disadvantages.

1. Poor reproducibility when used with the ICP.
 2. Expensive—furnace life and consumption of argon.
 3. Analyte loss through transport holes.
 4. Requires high manipulative skill.
 5. Coil location in furnace critical.
 6. Toxic solvents/matrices vented to atmosphere.
 7. Possibility of volatile analyte loss by prevaporisation.
 8. Spectral interference from tungsten.
-

6.3 GRAPHITE ROD VAPORISATION (GRV).

6.3.1 Principles of Operation.

Sample introduction into the ICP employing a graphite rod has been the only electrothermal technique to have received any significant attention. Originally devised by Gunn et al. (54), it has been developed for the analysis of a wide range of sample types such as dopant levels in cadmium mercury telluride semiconductors (207),

toxic metals in biological material (205) and toxic metal content of whole blood (205).

In present form, sample introduction from a graphite rod is effected by resistively heating the rod to a temperature sufficient to vaporise the elements of interest. Matrix constituents can be selectively removed in many cases by careful programming of the temperature ramp. The vaporised species are transported to the plasma in a carrier stream of argon and passed into the injector channel in the middle of the discharge, a process which is facilitated by enclosing the rod in a glass manifold, connected to the plasma injector tube with a short length (0.5m.) of tubing. Unlike AAS, where critical design is necessary for the efficient production of free atoms and subsequent measurement of this population, the design of the graphite rod is more simple because the only requirement is to promote a rapid ramp to the selected temperature. The dead volume of the manifold enclosure is less critical than is commonly believed (235); little dispersion of the transient vapour cloud occurs because the carrier stream is directed through the manifold at high velocity. Usually a large manifold chamber is desirable to prevent excessive collisions of vaporised species with the walls of the chamber, an effect noted by Millard (236) which produces vaporisation interferences with volatile elements.

6.3.2 Experimental.

The GRV device used for these experiments is depicted in figure 6.6 and was of a similar design to that of Gunn et al. A spectrographically pure graphite rod (MCP Electronics Ltd., Alperton,

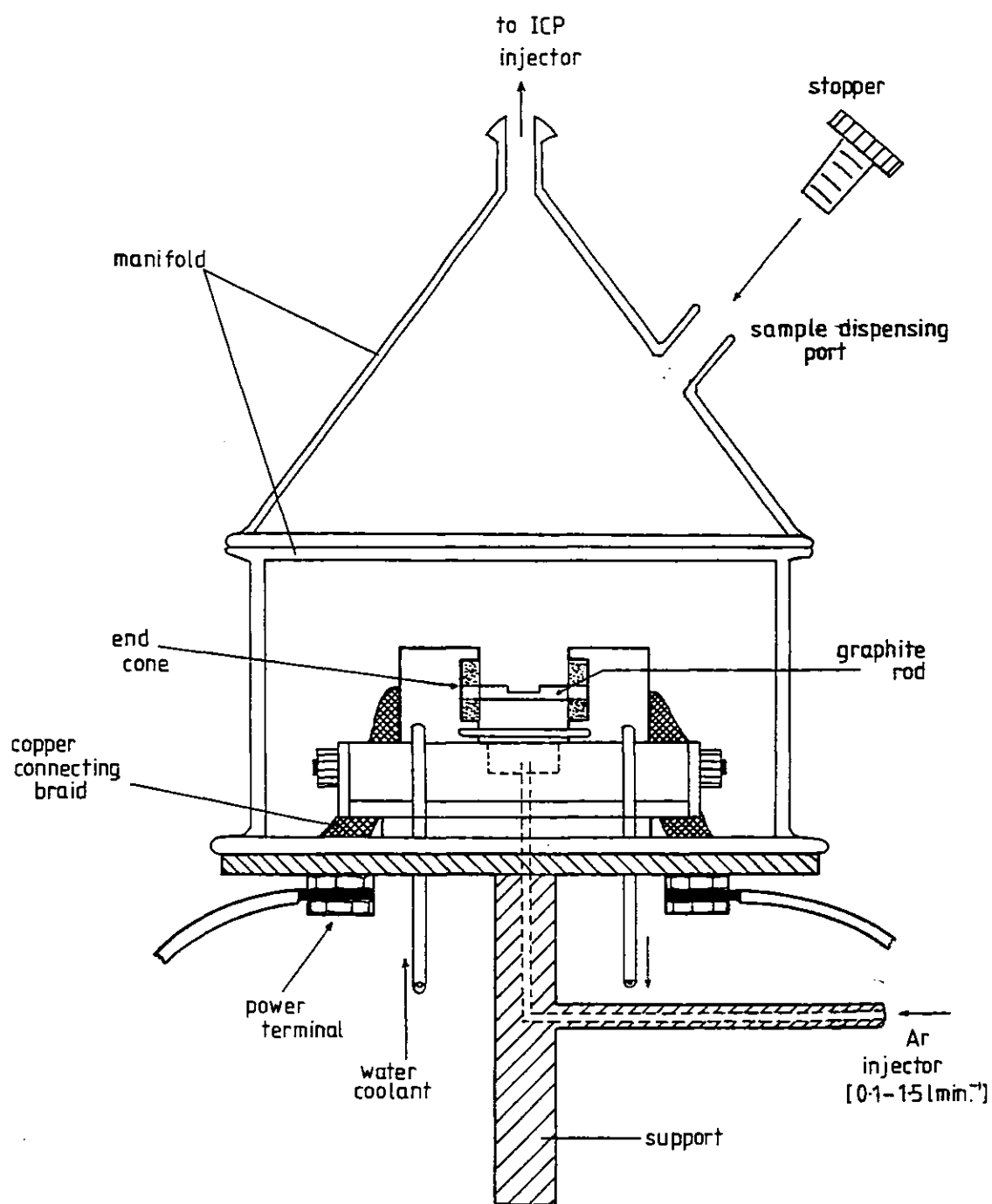


FIGURE 6-6 : The graphite rod vaporiser. Total internal manifold volume 750 ml.

Midgx.type RWO) of dimensions 25mm.X 3.10mm. was positioned between two graphite electrode discs connected to a power supply. The temperature of the rod could be varied as required by phase programming the graphite rod load with respect to the mains supply waveform. Three separate programming channels were available for desolvation, pyrolysis and vaporisation of the sample. The ramping reproducibility of the rod by this means was better than 0.045rsd.

The electrode terminals were mounted on a steel platform and furnished with water cooling ducts to dissipate excess heat in the terminals. Holes were drilled in this base for the gas inlet supply, cooling water and electrode connections. The base assembly was enclosed by a cylindrical borosilicate glass manifold of total volume 750ml., constructed in two separate pieces. The upper part of the manifold contained a small delivery port through which samples could be applied to the rod with a micropipette. This port was closed with a polypropylene stopper after application of the sample to the rod.

6.3.3 Operation of GRV.

For normal operation of the GRV, 10-20 μ l. of sample was applied to the rod with a suction micropipette. A back pressure created on removal of the delivery port stopper prevented air entrainment into the system, which would otherwise have extinguished the plasma. Samples could be applied to the rod by fabricating a depression in the rod with a jeweller's file. The rod was heated in three stages; the first, at low temperature to desolvate the sample, the second, at 300-500°C., to remove matrix and the third at high temperature to vaporise the analyte. The temperature of the rod was calibrated with

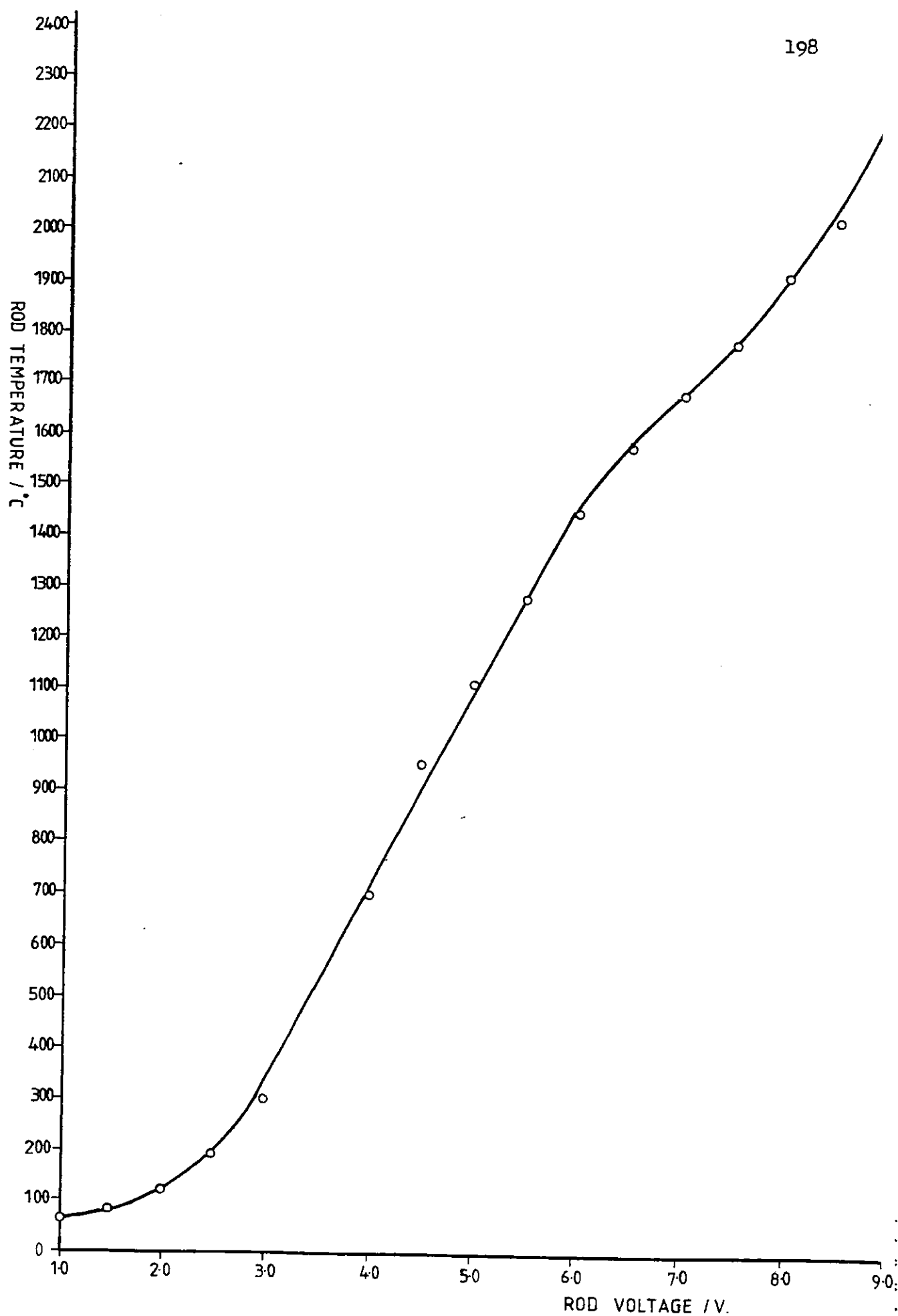


FIGURE 6-7 : Calibration curve for graphite rod using thermocouple and disappearing filament optical pyrometer sensors.

respect to the power supply using a disappearing filament optical pyrometer (Leeds and Northrup model 8622-C), figure 6.7. Operation of the third cycle caused analyte to enter the injector gas stream and subsequent emission was recorded at the chart recorder as a transient pulse. When a constant injector gas flow rate was utilised, peak height measurements were performed on the recorded signals to establish the concentration of analyte by reference to standards similarly treated. In general, detection limits achieved with the GRV unit ($< \text{ng./cm}^3$) were 1-2 orders of magnitude superior to those obtained with the pneumatic nebuliser.

6.4 DETERMINATION OF MINERAL CONTENT OF PHARMACEUTICAL SLURRIES BY DIRECT VAPORISATION FROM A GRAPHITE ROD.

Although rapid analysis of samples of high dissolved solids content would be highly desirable, this is still not routinely possible using the ICP, despite rapid progress in the design of suitable nebulisers. The alternative method is electrothermal vaporisation, which in theory would be suitable for all types of samples, liquid or solid, thus removing the need for extensive solution preparation and dilution procedures. The analysis of samples in the form of slurries, that is, stable dispersions of solids in liquids, appears to be preferable to both conventional liquid or solid analysis. For liquids of course, dissolution and dilution steps are required and for solids there is difficulty in reproducible manipulation and introduction of the sample. These problems can be successfully averted by formation of slurries, because sample handling

and dispensation is easier than for solids and the requirement for dissolution of the sample is removed.

In this work, a procedure for the determination of major and minor elements in multi-mineral, multi-vitamin capsules was assessed for direct sample introduction of slurry material from a graphite rod vaporiser. Multi-vitamin, multi-mineral capsules are widely used in the pharmaceutical market for supplementing the normal diet during adverse circumstances such as pregnancy or during the early years of life. There is therefore a need for the routine quality control of these products.

The active formulation consists of a thick slurry of the vitamin and mineral components in a vegetable oil base. This formulation is encapsulated in a soluble soft gelatin shell to facilitate peptic digestion and absorption of these components.

6.4.1 Existing Method of Analysis.

Slurry samples are normally assayed for calcium, iron, magnesium, zinc, copper and phosphorus which comprise the mineral components of most of the products marketed. At present this is accomplished by selecting one capsule or equivalent weight of filling material and dissolving in 30% v/v HCl on a steam bath for approximately 35-40 minutes. The resulting solution is then filtered through a #42 Whatman filter paper and sequentially diluted according to the element to be determined. The solution is then analysed by flame AAS with conventional nebulisation sample introduction. However, owing to several interferences which are characteristic of flame atomic spectroscopy, lanthanum chloride has to be added to solutions

containing calcium and phosphorus to prevent the formation of calcium orthophosphate, and barium chloride must be used to remove sulphates which interfere with the determination of iron. The total analysis time for the sample is usually 3-4 hours.

6.4.2 Experimental.

Instrumentation.

The ICP system used for this study was as described in chapter 4 and was used in conjunction with both a Meinhard nebuliser (T-230 A3) and the GRV device described earlier.

Samples and Reagents.

Several finished capsules and the filling material were obtained from R.P.Scherer Ltd., 216-222 Bath Rd., Slough, Berks. Flame AAS data on these specific batches was not available.

All other reagents were of analytical grade.

Experimental Procedure.

Both nebulisation and GRV sample introduction were employed for this study so that accuracy of the determinations carried out with the graphite rod could be compared with results obtained using the established method of pneumatic nebulisation, especially in the absence of alternative control data from the manufacturer.

Samples for solution nebulisation were prepared by dissolving the

formulation in a similar fashion to that used for flame AAS; 0.68-1.40g. of filling material or whole capsule was dissolved in 20cm³ of 4M HCl by heating on a hot plate at 70°C. for 40 minutes. The resulting solution was cooled and filtered through a Whatman #42 paper and made up to 100cm³ with distilled water. Filtration was necessary to remove insoluble fats and titanium dioxide present in the gelatin shell. Blanks were prepared by diluting 20cm³ of 4M HCl to 100cm³ with distilled water. These solutions were then nebulised into the ICP operating under the conditions described in table 6.4. No dilution steps were necessary owing to the wide dynamic calibration range of the ICP.

Table 6.4: Compromise conditions for the determination of elements in capsules.

Parameter	Operating Condition
Forward power	1.0kW
Reflected power	<2W
Viewing height	20mm.
Nebuliser uptake	2.5ml./min.
Injector flow rate	1.0l./min.
Coolant flow rate	16l./min.
Auxiliary flow rate	0.5l./min.
Entrance/exit slit width	35 μ m.
Photomultiplier EHT	1100V

Sample preparation for the analyses using the GRV device was very simple, merely involving the production of a slurry of reduced viscosity which was easily and precisely pipetted onto the graphite rod. Reduced viscosity slurries were produced by dispersing 0.1g. of each formulation in 100cm³ of 4M nitric acid containing 0.2% v/v Triton-X-100 and heating at 60°C. for 4-5 minutes. Because the slurry

technique has the advantage that all constituents of the capsule are dissolved or suspended, there was no requirement for filtration and therefore the possible loss of analyte with the insoluble fat and titanium dioxide was avoided. The slurries prepared in this manner were found to be stable over a period of one week. 10 μ l. aliquots of the slurries were pipetted onto the rod and dried at 100 °C. for 20s., pyrolysed at 300 °C. for 6s. and vaporised into the plasma at 2200 °C. for 4s. The resulting emission for both nebulisation and GRV sample introduction was observed at the analytical wavelength of each element.

6.4.3 Results and Discussion.

Nebulisation.

Nebulisation of the acid solutions into the ICP caused no major problems apart from a slow build up of deposits upon the injector tip after extended use. To check for the existence of possible interference effects, standard solutions of 10ppm. concentrations of each element were prepared and to these solutions a 100 fold excess by weight of all other elements likely to be found in the formulation was added. These solutions were then analysed and compared with aqueous standards of the elements of interest (Cu, Fe, Zn, P, Ca, Mg) to assess the levels of interference, but none were found.

The possibility of Ca signal suppression at the Ca(I) 422.67nm. line, in the presence of phosphate was investigated. No suppression was observed even when $\text{PO}_4^{2-}:\text{Ca}^{2+}$ mol.ratios were varied from 0-1, suggesting that stable formation of calcium phosphate in the plasma

was prevented by the high temperature. To account for possible changes in background and stray light, the continuum background level was measured 0.5nm. either side of the analytical lines and this data used in the computation of signal intensities. However no serious rise in the background was apparent. Table 6.5 shows the results of the determinations on the filling material and also on the whole capsules. These results are compared with the quality control specification supplied by the manufacturer.

GRV Sample Introduction.

No matrix effects were observed in the analysis of the slurries with the GRV apart from minor enhancements in zinc and magnesium signals attributed to an improvement in sample transport efficiency to the plasma by the mechanism described by Millard (236). Zinc and magnesium were therefore determined using the method of standard additions. An example of this method is shown in figure 6.8 for the determination of zinc in a slurry of sample number 1.

The choice of the relatively high vaporisation temperature was dictated by the thermal properties of the calcium and iron compounds present. At lower temperatures than 2200 °C., memory effects were observed owing to the inefficient vaporisation of the oxides of iron and calcium formed during pyrolysis. There was a slight (ca. 10%) degradation in the detection limits of Cu, Zn, Mg, and P at this temperature, but this was considered acceptable for the purposes of these studies and did not affect the reproducibility attainable. The results of the analyses are shown in table 6.5 and the precision of the analyses in table 6.6.

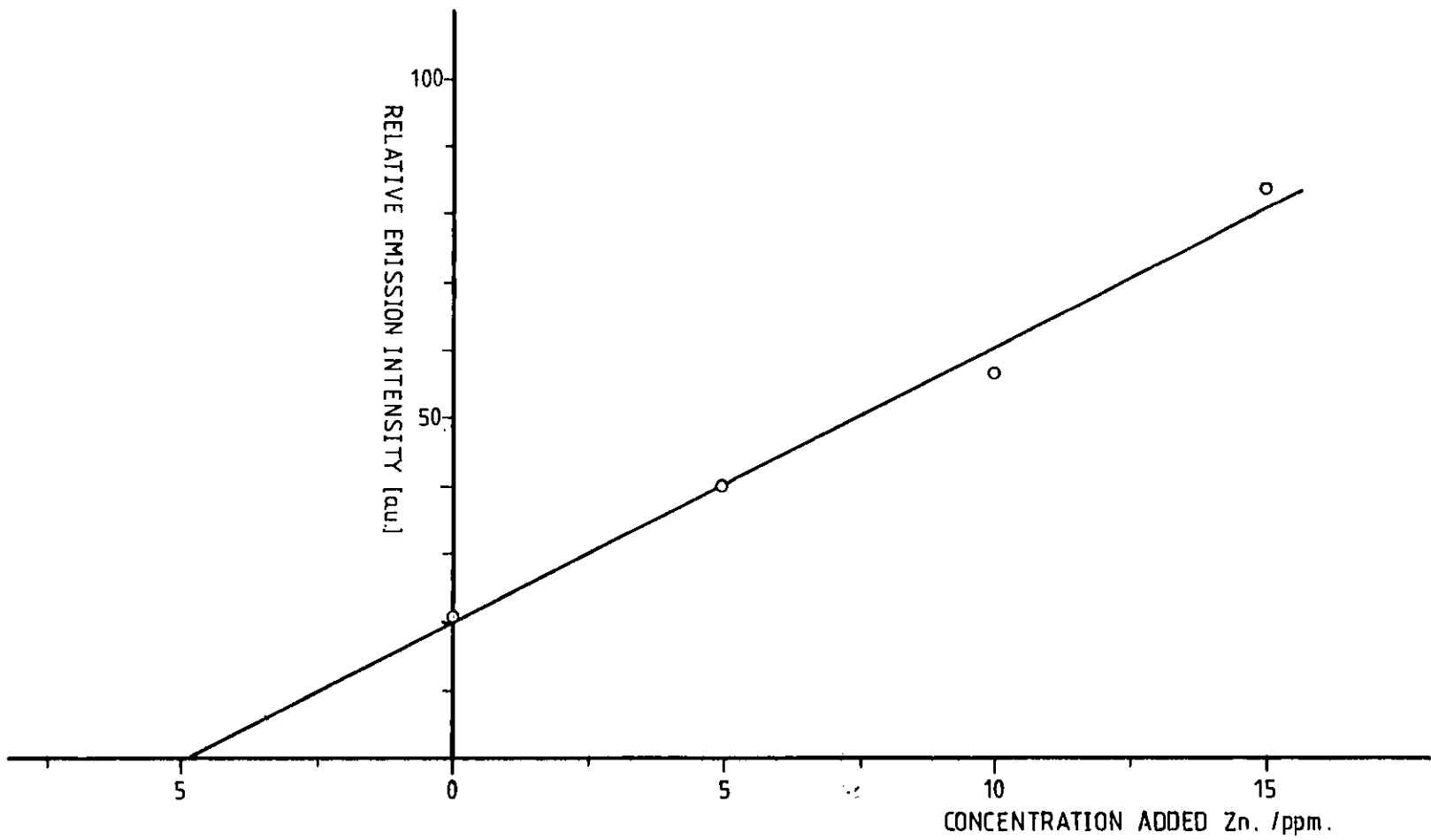


FIGURE 6-8 : Standard additions plot for the determination of zinc in pharmaceutical sample # 1. $\lambda = 213.86 \text{ nm}$.

Table 6.5: Element levels determined in pharmaceutical preparations.

Element	Whole	Cap./mg.	Fill mat./mg.	Specification/mg.	λ /nm.	
sample1	Neb.	GRV	Neb.	GRV	(FAAS)	
Cu	0.48	0.46	0.47	0.50	0.45-0.55	324.75
Fe	9.8	9.5	10.5	9.4	9.4-11.0	259.94
Zn	0.52	0.53	0.48	0.48	0.45-0.55	213.86
Ca	71.0	72.7	68.0	72.5	65-75	422.67
Mg	2.10	2.05	2.15	1.93	1.9-2.2	279.55

sample2						
Cu	0.17	0.20	0.20	0.21	0.18-0.22	324.75
Fe	7.8	8.3	7.4	6.9	6.7-7.7	259.94
Zn	0.055	0.050	0.055	0.054	0.04-0.06	213.86
P	61.4	62.5	-	-	59-71	253.57
Ca	81.0	80.0	80.0	81.0	79-88	422.67
Mg	0.80	0.74	0.83	0.85	0.45-0.55	279.55

Table 6.6: Precision of determinations expressed as rsd on ten measurements (sample2) and calibration range (GRV).

Element	Nebuliser	GRV	Calibration Range
Cu	0.03	0.02	0.0001-10ppm.
Fe	0.04	0.03	0.002-10ppm.
Zn	0.05	0.04	0.007-100ppm.
P	0.04	0.04	0.1-100ppm.
Ca	0.03	0.04	0.0002-10ppm.
Mg	0.03	0.02	0.00002-10ppm

Close agreement is observable between the results obtained for nebulisation of acid solutions and vaporisation of the slurries from the rod and the results also fall within the ranges specified by the manufacturer, with the exception of magnesium in sample 2 which is high. A possible reason for this apparent discrepancy may be contamination of the sample during sampling or sample preparation. It is also apparent from table 6.5 that there is no significant difference between the elemental levels determined on the whole capsule (including the gelatin) and on only the filling material. Apparently therefore, no interferences result from the presence of the gelatin shell or associated ingredients.

6.4.4 Conclusions.

The results obtained indicate that the technique of ICPOES is suitable for the determination of major and minor elements in multi-mineral, multi-vitamin capsules and in particular that satisfactory routine analysis may be performed using a graphite rod as a sample introduction device, which allows accurate and precise determinations to be carried out. Several advantages compared with pneumatic nebulisation and flame AAS can be realised; there is no need for elaborate dissolution or matrix separation procedures, sequential dilution stages are not necessary and simultaneous multi-element analysis is possible.

The total analysis time using the GRV device was found to be approximately 1 hour, representing a three fold improvement compared with flame AAS (3-4 hours) and the ICP employing a nebuliser (2.5 hours). It is expected that the analysis times with the ICP could be cut even further if the multi-element potential of the ICP is exploited.

6.5 INVESTIGATION OF SOME VAPORISATION CHARACTERISTICS USING A GRAPHITE ROD AS A SAMPLE INTRODUCTION DEVICE.

6.5.1 Requirements of System.

The objective when using a graphite rod as a sample introduction device is to produce a high transient population of analyte species in the injector channel zone viewed by the monochromator. Therefore unlike GFAAS, it does not particularly matter whether the species removed from the rod is composed of molecules, atoms, particulate material or aggregates, as atomisation will be very effectively produced on subsequent transport to the discharge. However, in common with GFAAS is the need to minimise the diffusion processes which result in the broadening of the recorded transient profile and a rapid heating rate is desirable to ensure a sufficiently high rate of removal of analyte from the surface into the injector gas stream. Therefore the optimal design of the graphite rod will be a balance between the minimal total mass of material to reduce the heat capacity whilst retaining a high cross-sectional area to ensure that high temperatures can be reached. The graphite furnaces commonly used for AAS are unlikely to be suited for sample introduction into the ICP because they are primarily designed to retain the atomised sample and their overall mass is relatively high. However a graphite furnace has recently been tested by Aziz *et al.* (208) for electrothermal sample introduction into a plasma.

In these studies, a graphite rod was used based on an earlier design by Gunn (237). The centre of the rod was modified to produce a thin platform on which up to 30 μl . of sample could be placed.

Vaporisation and sample introduction of analyte from this rod produced transient profiles similar to that shown in figure 6.9. In the first heating stage, the sample is desolvated and gives rise to an increase in the background continuum intensity as the solvent is dissociated in the plasma. The second stage normally used for matrix pyrolysis may again increase the background. Lastly, the rod is rapidly ramped to the selected vaporisation temperature at which point analyte is released from the rod as a discrete pulse, appearing as a sharp spike at the chart recorder. Superimposed on this is a small decrease in the background intensity caused by a temporary increase in the injector flow rate into the plasma, by a gas piston effect, as the gas is heated by passage over the very hot graphite rod. The background returns to its original level when the vaporisation cycle is complete. Fortunately, it is possible to separate the analyte peak from this pressure peak owing to the highly reproducible nature of the latter.

It would appear then, that in the absence of other effects, the transport efficiency using the GRV as a sample introduction device would approach 100% as all the sample would eventually pass through the plasma. In practice this may often be the case and detection limits are often far superior to those obtainable using conventional nebulisation (transport efficiency 2%). For some other elements this is not observed, for a variety of vaporisation interferences predominate which modify the transport process:

(a) Depression of the transport efficiency by deposition of analyte on the walls of the transport system. This appears to be more significant for volatile elements such as Cd, Zn, As.

(b) Depression of the transport efficiency caused by incomplete vaporisation of the sample. These can be resolved into three cases:

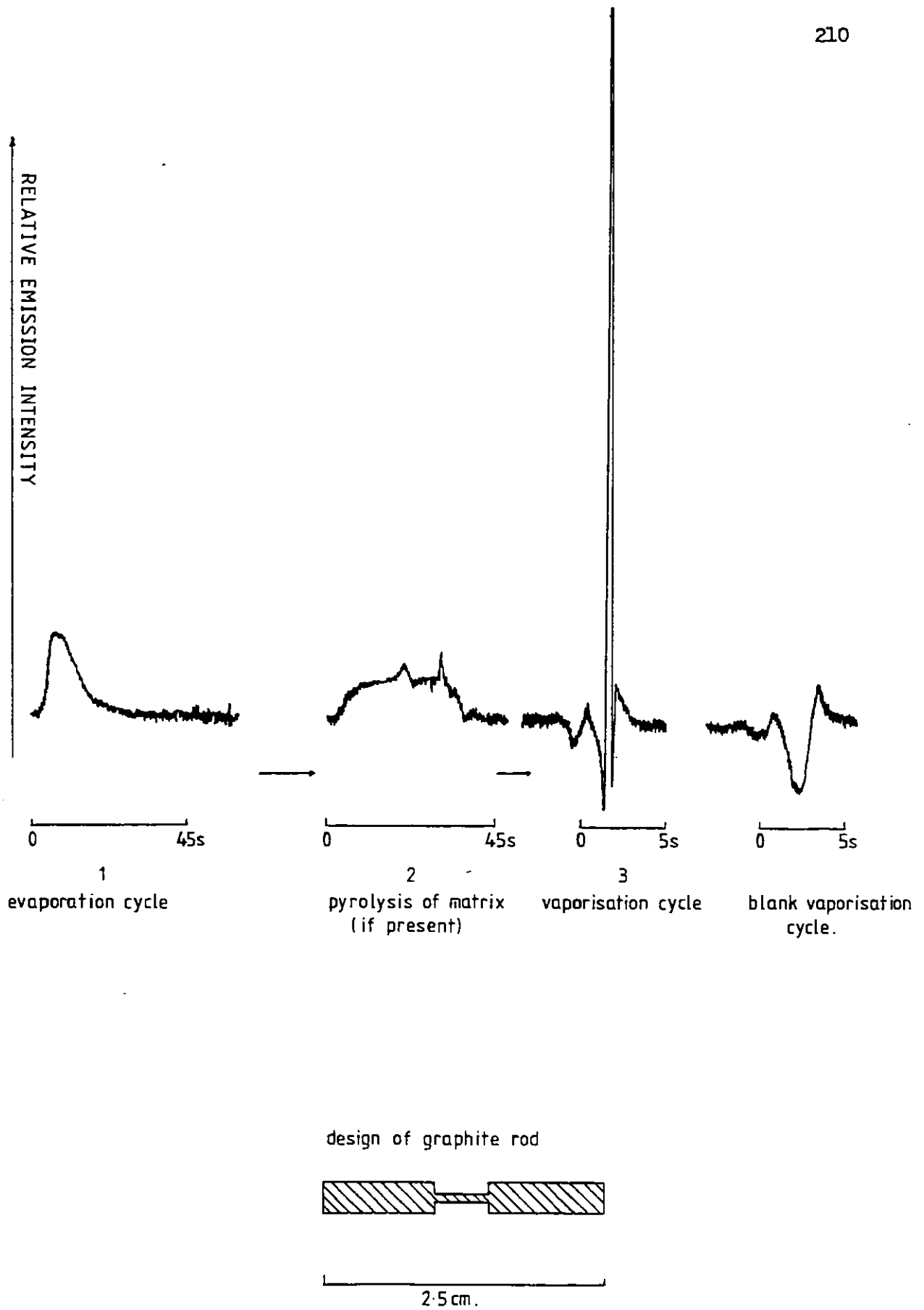


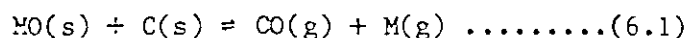
FIGURE 6-9 : Typical emission signals using a graphite rod for sample introduction
0.1 ppm lead, 283.31 nm.

(i) compounds that have too high a vaporisation temperature for determination on graphite eg. Pt compounds. (ii) compounds which decompose at high temperature to form other thermally stable species (iii) compounds which form carbides by reaction with the graphite (Cr, Zr, W, Mo, B).

(c) Prevaporisation losses of volatile elements eg. Hg.

Neglecting the formation of carbides, the graphite substrate used for the vaporisation process will participate in the mechanism of vaporisation of analyte. However the precise role is still not well understood owing to the complexity of the fast high temperature reactions. What is clearly important is the thermal chemistry of the sample applied to the graphite. For the majority of metals, oxy-anion salts such as sulphates, nitrates, carbonates and hydroxides will decompose at low temperature to form the corresponding metal oxide. Other salts including halogen salts, sulphides, selenides and tellurides remain essentially unaltered before conversion into another physical state.

It is conceivable that for those samples which can be thermally degraded to the oxide, reduction to the element by the graphite will occur at a suitable temperature. A possible route for this process has been proposed by Campbell and Ottaway (238) :

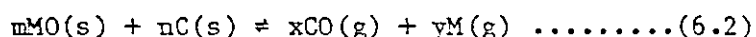


where MO is the metal oxide involved and M is the metal to be vaporised.

This model assumes that sufficient energy is released by the forward

reaction to produce metal atoms in the gaseous phase, even though the overall temperature might be below the boiling point of the metal. Whether this process will occur before the vaporisation or sublimation of the oxide and its subsequent removal from the graphite surface, can be predicted by considering the thermodynamic equilibria relevant to the system. At high temperatures the rates of reaction are extremely fast and the reactions are under thermodynamic control; a knowledge of the free energy change occurring for a particular process can therefore be a reliable indicator of the likely reactions.

Consider again the reduction of metal oxide,



where m, n, x, y refer to the number of moles of oxide, graphite, carbon monoxide and metal respectively.

The free energy change ΔG° for this forward reaction is given by,

$$\Delta G^\circ = y \Delta G_f^\circ \text{M}(\text{g}) + x \Delta G_f^\circ \text{CO}(\text{g}) - m \Delta G_f^\circ \text{MO}(\text{s}) - n \Delta G_f^\circ \text{C}(\text{s}) \dots\dots\dots(6.3)$$

where ΔG_f° is the standard free energy of formation of the species.

In accordance with the second law of thermodynamics, the reduction process will proceed when ΔG° becomes negative. If ΔG° is positive, the reverse reaction will occur such that the metal will reduce CO back to C.

Because ΔG varies with temperature, there will be a particular temperature where the reduction process will proceed. If this is below the temperature where a phase transition takes place, then reduction will proceed, but otherwise the oxide will be removed unaltered. Alternatively, spontaneous dissociation of the oxide into its

constituent elements is also possible when ΔG° for the reaction $MO(s) \rightarrow M(s) + O(g)$ becomes negative. This process is most notable for Hg, Ag, Pt and Au, the oxides of which decompose before any interaction with graphite.

If the sample is applied to the graphite surface as the halide, sulphide or other form, little change would be expected because carbon is ineffective at reducing these anionic forms. However in some cases there may be sufficient energy to dissociate these compounds into the constituent elements before they leave the graphite surface.

Although the reduction mechanism outlined here is of particular relevance to GFAAS, where production of atomic species is mandatory, it is also of importance for elucidating sample transport interferences when the GRV system is used for sample introduction into the ICP. Therefore two elements, cadmium and molybdenum which were found to have poor transport efficiencies, were investigated with the aim of characterising the vaporisation phenomena.

6.5.2 Vaporisation Characteristics of Cadmium.

In a preliminary study of the transport characteristics of analyte after vaporisation from a graphite rod, Millard (236) noted that interference was most significant for relatively volatile elements such as cadmium, zinc and arsenic, concluding that deposition on the transport system was the cause of this behaviour, which could be prevented by addition of Se(VI) to the sample as a concomitant element.

In these studies, the transport characteristics of cadmium were investigated using the apparatus previously described. The physical

properties of cadmium and some of its compounds are listed in table 6.7.

Table 6.7: Properties of cadmium and relevant compounds.

Compound	mpt./ °C	bpt./ °C	notes
Cadmium	321	765	
Cadmium chloride	568	980	not reduced by C
Cadmium oxide	sublimes	1770	reduced by C at <u>ca.</u> 800-1000 °C
Cadmium sulphide	sublimes	1000	not reduced by C
Cadmium selenide	1260	-	
Cadmium sulphate	forms oxide		
Cadmium nitrate	forms oxide		

It is expected therefore that if the halogen salt is selected, the appearance temperature of analyte would be approximately 1000 °C. and if the sulphate or nitrate is selected, the appearance temperature would be 800-1000 °C. as elemental cadmium is formed by reduction of the oxide.

The emission intensity from 10 µl. aliquots of 1ppm. cadmium, as sulphate, applied to the rod and vaporised into the plasma was optimised as a function of applied r.f. power, observation height, injector flow rate and vaporisation temperature. The optimum conditions were 900W power, 25mm. observation height and 0.4l./min. injector gas flow. The effect of vaporisation temperature on the behaviour of cadmium can be seen in figure 6.10. When the vaporisation temperature exceeded 1100 °C cadmium was removed from the rod and emission observed from the plasma. This appearance temperature is quite close to that expected from the oxide reduction model. Below 1100 °C., memory effects were observed on successive blank firings of the rod, indicating incomplete removal of cadmium from the rod. Above 1650 °C., the maximum emission intensity from cadmium occurs and presumably it is at this temperature, or above, that the optimum

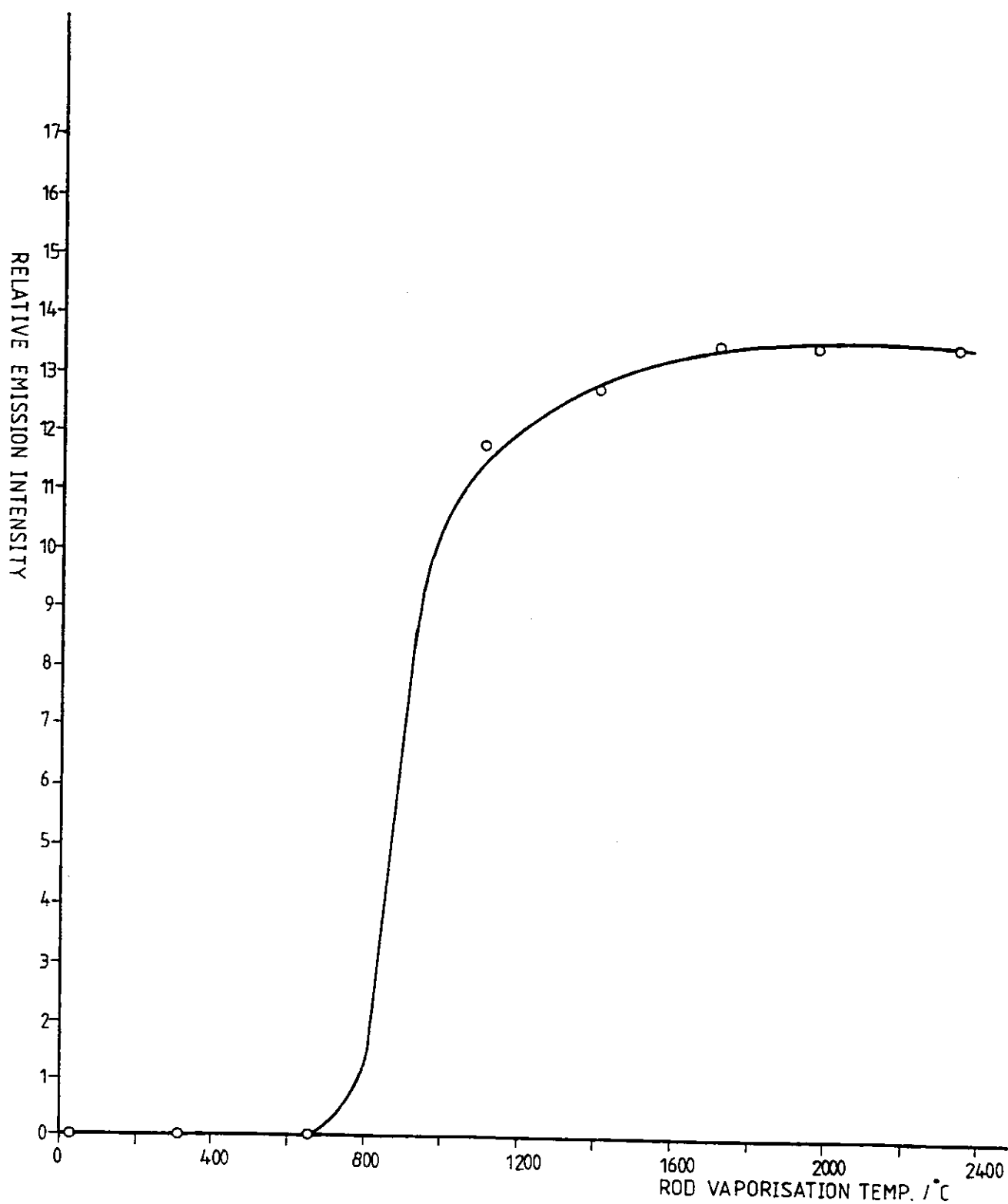


FIGURE 6-10 : Vaporisation characteristics of cadmium from graphite rod. 1ppm.
 $\lambda = 228.8 \text{ nm.}$

transport efficiency results. However the sample transport efficiency, which was measured relative to silver (an element known to have a transport efficiency close to 100%), was found to be only 11%. The residual quantity of cadmium was found to have largely deposited on the walls of the transport manifold, by analysing washings of 30% v/v HCl from the manifold and comparing against a blank. As no memory effects were observed at the optimum temperature, it was considered unlikely that any cadmium was remaining on the rod. If the oxide reduction model is assumed correct then elemental cadmium must have been deposited on the walls of the manifold.

Investigation of 10 μ l. aliquots of a solution containing 1ppm. of cadmium as its chloride revealed, surprisingly, identical thermal behaviour to the sulphate salt, with the same manifold deposition interference. Such behaviour was not expected on the basis of complete molecular volatilisation of the chloride, which would be expected to display a different transport efficiency to cadmium produced from the sulphate. A possible explanation for this is that sufficient energy is available from the hot graphite to dissociate the chloride (dissociation energy 204kJ/mol.) to cadmium and chlorine, before the boiling point of the chloride is reached. Alternatively, the presence of water of crystallisation can often promote oxide formation (239) with subsequent reduction to the element as before. If this were true, then for both sulphate and chloride salts, elemental cadmium would be the ultimate degradation product and therefore similar behaviour would be observed.

In order to investigate the effects of other reagents on the transport efficiency of cadmium 10 μ l. aliquots of 10-100X excess of the reagents by weight, were added to 10 μ l. of 1ppm. cadmium as

sulphate and chloride. The transport efficiencies are summarised in table 6.8.

Table 6.8: Effect of matrix reagents on cadmium.

Matrix reagent *	Transport efficiency $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	Transport efficiency $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$
—	—	—
Se(VI)	74%	70%
MnO_4^-	11%	11%
Cr(VI)	8%	11%
NaBH_4	11%	11%
Mg	30%	28%
S^{2-}	72%	76%
* no matrix effects in the plasma itself were observable for cadmium in the presence of these reagents.		

Inspection of table 6.8 reveals that (a) addition of Se(VI) and S^{2-} to cadmium improves the transport efficiency to an acceptable level, but strong oxidising agents (MnO_4^- , Cr(VI)) have little effect, (b) strong reducing agents (BH_4^-) have little effect , (c) both chloride and sulphate salts of cadmium have similar matrix reagent responses.

These results suggest that formation of the selenide and the sulphide of cadmium substantially alters the proportion of vaporised element transported to the plasma. Since neither of these is reduced by carbon it seems reasonable to suppose that the increase in efficiency is attributable to molecular volatilisation without formation of elemental cadmium. The three fold increase in transport efficiency in the presence of Mg could be explained by the formation of a stable CdMg alloy, which is known to exist. Interestingly, magnesium has also been observed (240) to depress the atomic vapour population of cadmium in GFAAS. Presumably a similar mechanism was responsible.

In another series of tests, the transport manifold was cleaned thoroughly and 10 μ l. aliquots of 1ppm. cadmium, as chloride, were vaporised from the rod. Immediately after recording the transient emission signal it was noticed that a large background signal was present which slowly decayed to the natural background level. The signal was found to be that from cadmium emission suggesting that the deposition process with a freshly cleaned manifold was reversible.

The desorption kinetics of this process were investigated by firstly assuming a first order process,

Let a_{cds} = Amount cadmium adsorbed at time t .

a_0 = Initial amount adsorbed.

if process is first order,

$$\frac{-da_{cds}}{dt} = k_1 a_{cds} \quad \dots\dots\dots(6.4)$$

where k_1 is the first order rate constant. Integrating equation 6.4,

$$\ln(a_{cds}) = -k_1 t + C \quad \dots\dots\dots(6.5)$$

where C is a constant.

when $t=0$, $C = \ln a_0$

$$\ln(a_{cds}) = -k_1 t + \ln a_0 \quad \dots\dots\dots(6.6)$$

Therefore a plot of $\ln a_{cds}$ against t should be a straight line of slope $-k_1$ if the process is first order. Results obtained from

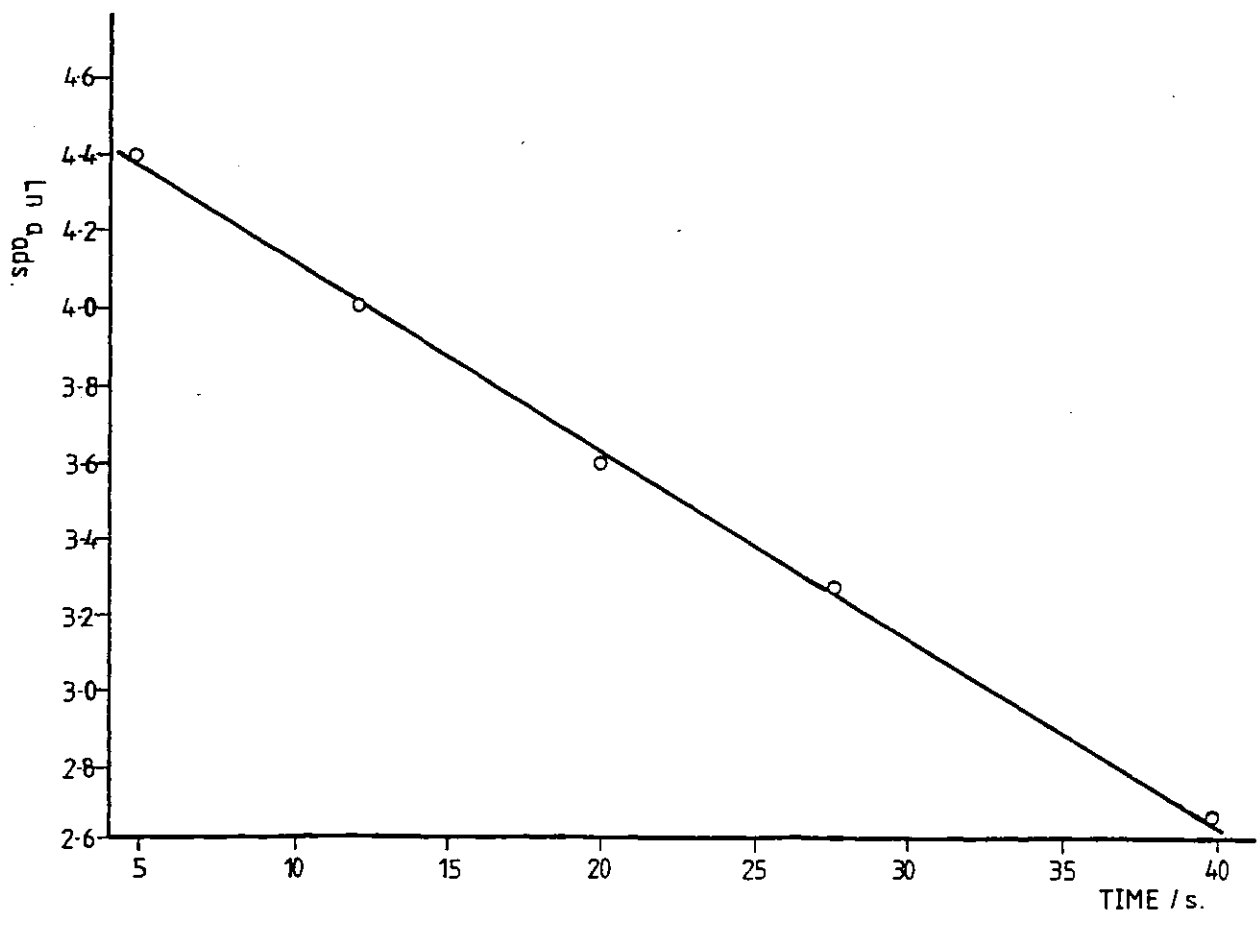
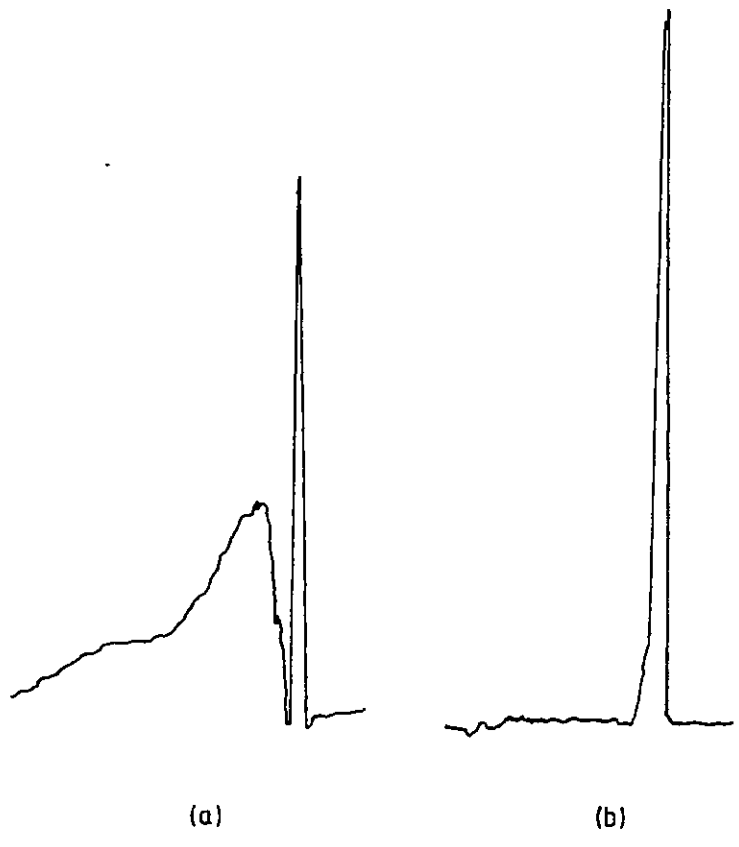


FIGURE 6-11 : ABOVE - Plot of $\ln a_{ods}$ vs. time for desorption study of cadmium 1ppm $\lambda=228.8\text{ nm}$. TOP- (a) emission profile cadmium after cleaning transport manifold (b) emission profile cadmium before cleaning.

measurements on the desorption profile are shown in figure 6.11. A straight line of negative slope indicates that the process is indeed first order and yields a rate constant of 0.049s^{-1} (± 0.003).

The reason for cadmium desorption from a cleaned manifold is not entirely clear. Although desorption could occur through collision of argon atoms from the injector gas with the adsorbed species, it is evident that the same process does not occur for a "dirty" manifold. Therefore it would seem that the presence of deposited matter has an important effect on the mechanism of cadmium deposition on the transport manifold.

6.5.3 Vaporisation Characteristics of Molybdenum.

The formation of thermally stable carbide compounds when certain elements such as Mo, Zr, W and V are heated on graphite, is well known. Sneddon *et al.* (241) used X-ray diffraction measurements to identify some of the compounds present when ammonium molybdate was heated on graphite, concluding that MoC was the predominant species formed.

In this work, stock solutions of sodium molybdate, 10ppm. in molybdenum, were prepared. The vaporisation behaviour was investigated by pipetting 10 μl . aliquots onto the graphite rod and viewing the emission after transport to the plasma. Initial studies suggested that carbide formation was taking place (MoC mpt. 2850°C .), that is, the transport efficiency was only 0.07% and memory effects were observed. To preclude the formation of a carbide, (a) the solutions were vaporised in an argon stream containing 0.1% v/v freon, which has been successfully used (294) for preventing carbide formation, (b)

solutions were prevented from coming into contact with the graphite by lining the rod with spectroscopically pure tantalum foil.

In both cases the transport efficiency remained less than 2%, but no memory effects were observable indicating that another type of interference process was operative. This process was identified when, after several analysis cycles, clearly observable deposits of a bluish-white compound appeared in the transport manifold. This was not thought to be the carbide because the phase transition temperature for volatilisation of the carbide lies well above the maximum temperature attainable with the GRV device. Instead, it seemed likely that MoO_3 was being formed (molybdates are solutions of MoO_3 in hydroxide media) and this was subliming (sublimation temperature $780^\circ\text{C}.$) with deposition onto the manifold before any dissociation of the oxide could take place. To prevent the deposition of molybdenum in the transport system, a number of matrix agents were included with molybdate solutions added to the tantalum covered rod. The effects of these reagents are listed in table 6.9.

Table 6.9: Effect of matrix agents on transport efficiency of molybdenum.*

Reagent	X excess	Transport efficiency
-	-	0.1%
Cr(VI)	1-100	0.5
Mn(VI)	1-100	0.5
NaBH_4	1-100	0.6
Mg	1-100	0.1
Na_2HPO_4	1-100	0.1
NaNO_3	1-100	0.1
Se(VI)	1-100	0.1
H^+	1-100	0.1
S^{2-}	1	19
S^{2-}	10	56
S^{2-}	100	84
S^{2-}	1000	86
* No matrix effects in plasma itself observable.		

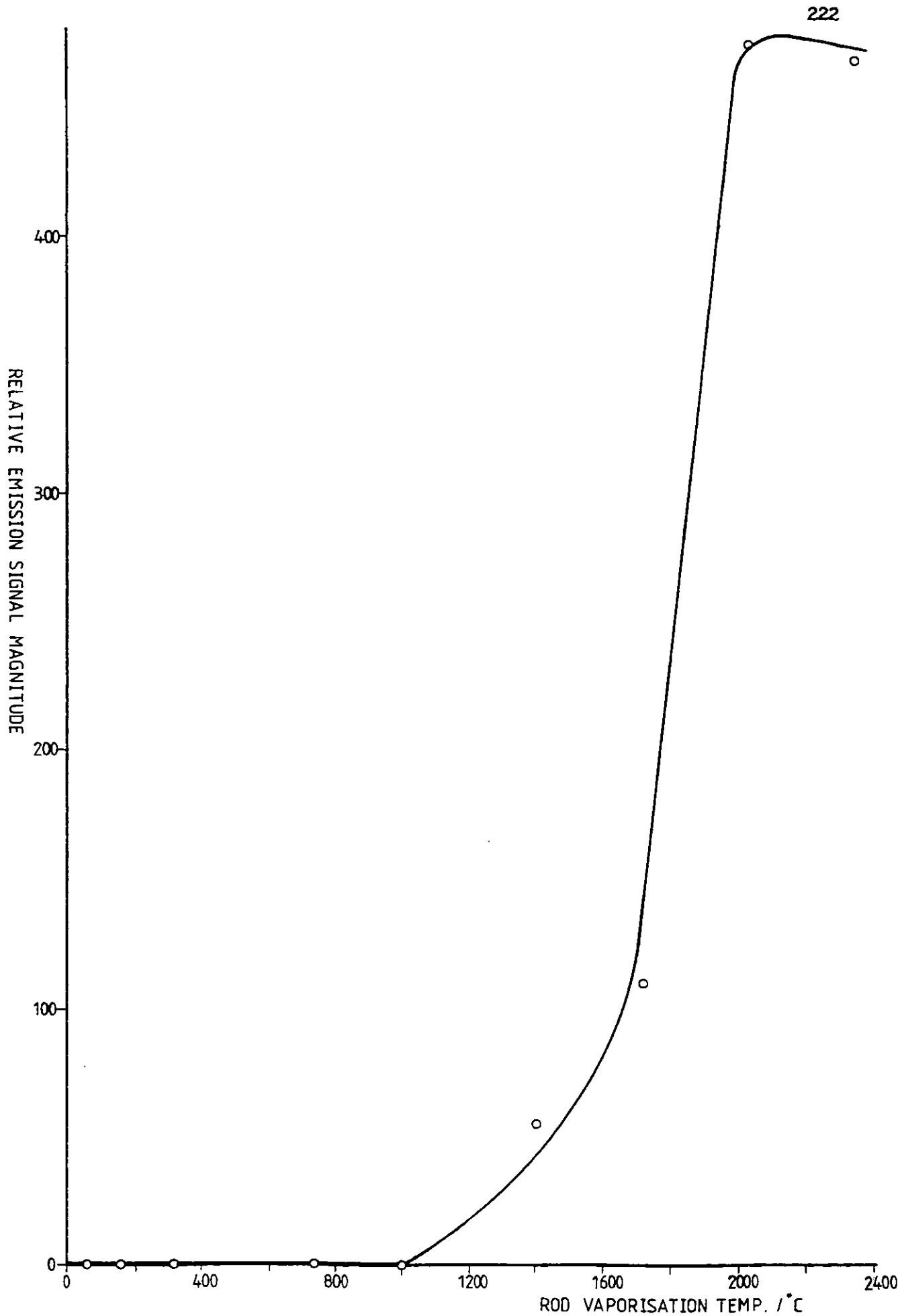


FIGURE 6-12 : Vaporisation characteristics of molybdenum with addition of S^{2-} as matrix reagent.

Of all the reagents tested, only S^{2-} was observed to increase the transport efficiency to any significant extent. Vaporisation of S^{2-} solutions alone, was also found to be effective at removing molybdenum previously deposited on the transport manifold. Formation of molybdenum sulphide is known to result from heating molybdenum (VI) oxide with S^{2-} and is fairly stable at high temperatures. Using a 100X excess by weight of S^{2-} ion, the reproducibility of sample transport to the plasma was better than 0.06rsd determined on ten successive determinations. The optimum temperature of vaporisation was 1800–1900°C., figure 6.12. A calibration graph constructed for the range 0.1–100ppm. molybdenum containing S^{2-} , was rectilinear and of unity slope which suggested that S^{2-} could be used as a matrix modification reagent for a wide range of molybdenum concentrations.

6.5.4 Conclusions.

The vaporisation characteristics of cadmium and molybdenum have been investigated on a preliminary basis. For cadmium the main interference process appears to be adsorption of elemental cadmium onto the walls of the transport manifold. This is not surprising in view of the high reactivity of atomic species and it is possible that some bond is formed between the cadmium and functional groups attached to the manifold wall. The results also indicate that this process is sometimes reversible with first order desorption kinetics.

The transport interference in the determination of molybdenum when not in intimate contact with the graphite rod is also caused by deposition onto the transport manifold. In this case, the likely cause is the formation of MoO_3 which readily sublimates, although it is not

clear why deposition of the oxide should occur.

These studies have shown that the transport process of analyte using the GRV device for sample introduction is exceedingly complex. Further studies should be oriented to the identification of the species deposited on the transport manifold, by using X-ray diffraction and surface techniques, such that a more complete picture of the vaporisation process can be obtained. Until such time as this is complete, careful consideration is necessary so that matrix interference does not distort analytical data when the GRV is used for sample introduction.

Whatever the mechanism of these interference effects, the matrix reagent S^{2-} appears to possess remarkable properties in improving the sample transport efficiency when added to cadmium and molybdenum and should be seriously considered as a universal matrix modification reagent when real samples are analysed. Alternatively, it is likely that if sample transport interferences are expected, the best approach for reliable analysis remains the method of standard additions.

CHAPTER 7

THE ROLE OF WATER IN THE ICP
AND ITS SIGNIFICANCE FOR SAMPLE INTRODUCTION.7.1 Introduction.

One of the propensities of electrothermal sample introduction for the ICP is the production of a "dry" aerosol, that is, any water is removed from the sample before the analyte is vaporised. Therefore it is reasonable to suppose that the excitation processes in the ICP, resulting from introduction of the dry aerosol, will be different to those following sample introduction with a pneumatic nebuliser, where analyte and water simultaneously enter the discharge. A study of these phenomena is necessary so that the operating criteria for nebulisation and electrothermal sample introduction can be established. This is of particular importance if electrothermal sample introduction is to be widely accepted as a mainstream technique for the ICP.

Neglecting any possible chemical effects which may occur between water and analyte in the injector channel of the discharge, the presence of water would be expected to have a fundamental influence on the physical characteristics of the injector zone. Boumans and DeBoer (1986) proposed that the water entering the central channel of the plasma would consume approximately 20% of the total power supplied to the injector gas itself, which would imply that the temperature in the central injector zone would decrease when water is present. In addition there would be a substantial variation in the composition of the plasma gases when water is present. If a nebuliser with an uptake rate of ca. 2.5ml./min. and an overall efficiency of 2.0% is

considered, a simple calculation shows that the molar ratios of argon, hydrogen and oxygen in the injector channel will be 84.0:10.7:5.3, Ar:H:O, neglecting any impurities in the argon or entrainment of atmospheric gases, and assuming a gas flow rate of 1.01./min. The ionisation energies of hydrogen and oxygen (13.598eV;13.618eV) are over 2eV less than that of argon (15.759eV) and therefore at the normal temperatures experienced in the plasma injector, a substantial increase in the electron density would be expected, ensuing from ionisation of the hydrogen and oxygen. This increase in the electron density will affect the attainment of the LTE state as explained in chapter 4, but will also affect the ionisation equilibria of analyte species introduced into the plasma and therefore will modify the emission properties of these species.

The aim of this study was to assess the role of water in the ICP and to ascertain whether significant deviation occurs when electrothermal vaporisation is used in preference to pneumatic nebulisation for sample introduction.

7.2 Determination of Electron Density.

Several traditional spectroscopic methods are available for the measurement of electron density, n_e , although laser and microwave techniques are now very popular. Of the established techniques, the two most used are measurement of the background bound-free and free-free continuum emission from the plasma, and measurement of spectral line broadening by charged particles as a result of the Stark effect. Estimates of n_e can also be obtained from Saha equilibrium calculations, but these have been found (242) to give much lower n_e

values than those using line broadening methods. A possible explanation for this (243) is the assumption made in Saha estimations, that the LTE state exists, when this is probably not true. On the other hand, the line broadening methods do not assume the existence of LTE.

For the studies reported here, the electron density was determined from measurements on the Stark broadened Balmer $H\beta$ line at 486.133nm. This line was chosen because extensive Stark broadening information is available (158) and the broadening processes have been thoroughly studied (244, 245) ; the $H\beta$ line is also spectrally isolated, so that measurements of the line profile can be performed with little interference from other species.

The hydrogen atom is subject to a linear Stark effect, that is, the perturbation is directly proportional to the electric field and the energy levels are symmetrically split. This is not the case for other atoms with more than one electron which exhibit a quadratic Stark effect and are difficult to treat mathematically. Assuming that all the collisions are elastic, the halfwidth of the $H\beta$ line, $\Delta\lambda_{1/2}$, is proportional to $n_e^{2/3}$ if quasi-static (ionic) broadening is accepted as the best model for the broadening process. The value of n_e can be obtained from the relation,

$$n_e = C(n_e, T) (\Delta\lambda_{1/2})^{3/2} \dots\dots\dots(7.1)$$

where C is a weak function of n_e and T.

Values of C have been tabulated by Griem (158) and n_e values can be estimated with an accuracy better than $\pm 10\%$.

Measurement of the half-width of the H_{β} line was facilitated by a slow wavelength scan across the line using 15 μ m. spectrometer entrance and exit slits. The background under the line was measured at 485.5nm. Unfortunately, the half-width of this experimental profile was not the Stark half-width because further broadening by the Döppler effect and by the spectrometer itself takes place, the half-widths of which have to be deconvoluted from the experimental profile to yield the Stark half-width. To facilitate this, the instrumental half-width was determined by separately scanning across the copper(I) 465.11nm. line whilst nebulising a 100ppm. solution. This line was subject only to Döppler broadening and instrumental broadening. The Döppler component was calculated to be 0.0032nm. by assuming a temperature of 6000K and using the relation:

$$\Delta\lambda_D = 7.16 \times 10^{-7} \lambda_o \sqrt{T/M} \dots\dots\dots(7.2)$$

where, $\Delta\lambda_D$ is the Döppler half-width.

λ_o is the spectral wavelength.

T is the temperature.

M is the mass number of the species (Cu=64).

The difference between the measured experimental half-width, 0.0138nm. and the Doppler half-width represents the instrumental half-width. However, the Döppler profile has a Gaussian type dispersion and the instrumental profile a Lorentzian dispersion (157), both of which fold together to produce a Voigt profile. The Voigt profile cannot be resolved analytically and to determine the relative contributions of the Döppler and instrumental components in the experimental Voigt type profile, computer constructed tables of the Voigt profile (246) were consulted. By this means the instrumental half-width was determined to be 0.012 nm.

The broadening process by the Stark effect can also be defined by a Lorentzian profile. The Döpler half-width (Gaussian) of the H_{β} line, which was calculated to be 0.0269nm. (6000K), was removed from the experimental profile, again using tables, and the instrumental profile subtracted from the half-width so obtained to give the Stark half-width of the line. The Stark half-width was translated into the corresponding electron density by using the Griem tabulations interpolated to give values for $C(n_e, 6000K)$ and inserting all values into equation 7.1.

7.3 Determination of the Excitation Temperature.

The excitation temperature T_{exc} , is the term used in Boltzmann's law to define the relative population densities of an atom or ion. If the Boltzmann formula is written,

$$I_{21} = \text{constant} \frac{g_2 A_{21}}{U(T)} v_{21} \exp(-E_2 / kT_{exc}) \dots\dots\dots(7.3)$$

where I_{21} absolute emission intensity.
 g_2 statistical weight upper level.
 $U(T)$ partition function.
 A_{21} transition probability for emission.
 v_{21} frequency of emission line.
 E_2 excitation energy to upper state.
 k Boltzmann constant.
 T_{exc} excitation temperature.

then knowledge of the absolute values of I_{21} and A_{21} enable a value for T_{exc} to be calculated. However, the errors normally associated with this approach are prohibitory and instead equation 7.3 can be rewritten,

$$\text{Log} \frac{I_{21} \lambda_{21}}{g_2 A_{21}} = \text{constant} - \frac{E_2}{kT} \dots\dots\dots(7.4)$$

A plot of $\log I\lambda/gA$ against E for several spectral lines should therefore be a straight line of slope $1/kT$. If E is expressed in cm^{-1} , the slope becomes $-0.625/T_{\text{exc}}$ from which T_{exc} can be computed. This type of plot is termed an atomic Boltzmann plot. Any deviations from the straight line will be caused by deviations in the Boltzmann distribution of the energy levels. The main error in this type of T_{exc} determination is caused by the uncertainties in the values of A_{21} which are rarely known to better than $\pm 25\%$.

For these studies, the temperatures were estimated by scanning over three argon lines and measuring the relative intensities of each. Transition probability data for these lines which were assumed to be optically thin, was taken from Malone and Corcoran (247) and is shown in table 7.1. The argon lines selected were within a narrow spectral range, so that the wavelength dependent response of the spectrometer could be reduced to negligible proportions. T_{exc} values were calculated by plotting $\log I\lambda/gA$ against $E_2 \text{ cm}^{-1}$ and finding the best linear fit between the data points using a Z80 computer program.

Table 7.1: Argon spectral data.

$\lambda/\text{nm.}$	E_2/cm^{-1}	g_2	$A_{21} 10^7 \text{ s}^{-1} \text{ . (a)}$
430.01(I)	116999	5	0.0318
426.63(I)	117184	5	0.0265
425.94(I)	118871	1	0.3665
(a) data from Malone and Corcoran.			

Although other thermometric species than argon can be used for the determination of T_{exc} , such as Fe, Ti, V, these have to be introduced into the plasma in aerosol form. The selection of the plasma forming gas, argon, for the determination of T_{exc} was necessary for objectively assessing the effects of water in the plasma, because it was independent of the sample introduction system.

7.4 Excitation Processes in the Plasma.

7.4.1 The Role of Water.

In order to investigate the effect of water on the plasma properties, a system for generating precisely defined quantities of water had to be devised. Two methods were considered for achieving this; the first consisted of varying the input pressure to the nebuliser so that the uptake rate and therefore the amount of water injected into the plasma could be varied. This method was rejected because the pneumatic nebuliser used (Meinhard T-230 A3) was designed to work at a constant input pressure and uptake rate with only a narrow tolerance band. Variation of the input pressure would also have altered the overall injector gas flow rate, an undesirable event since this has a dramatic influence on the properties of the plasma. The second method involved passing argon through a flow meter and over a constant surface area of water, heated to different temperatures such that the vapour pressure could be varied. The apparatus for achieving this is shown in figure 7.1, argon was passed over water contained in a Dreschel bottle, at a fixed flow rate of 1.0 l./min. The temperature of the water was controlled between 10 and 60°C. to give a vapour pressure according to the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \dots\dots\dots(7.5)$$

where dP change in vapour pressure.

dT change in temperature.

ΔH enthalpy change on vaporisation (assumed independent of T).

ΔV molar volume change on vaporisation.

Although the vapour pressure could be predicted from this equation, it

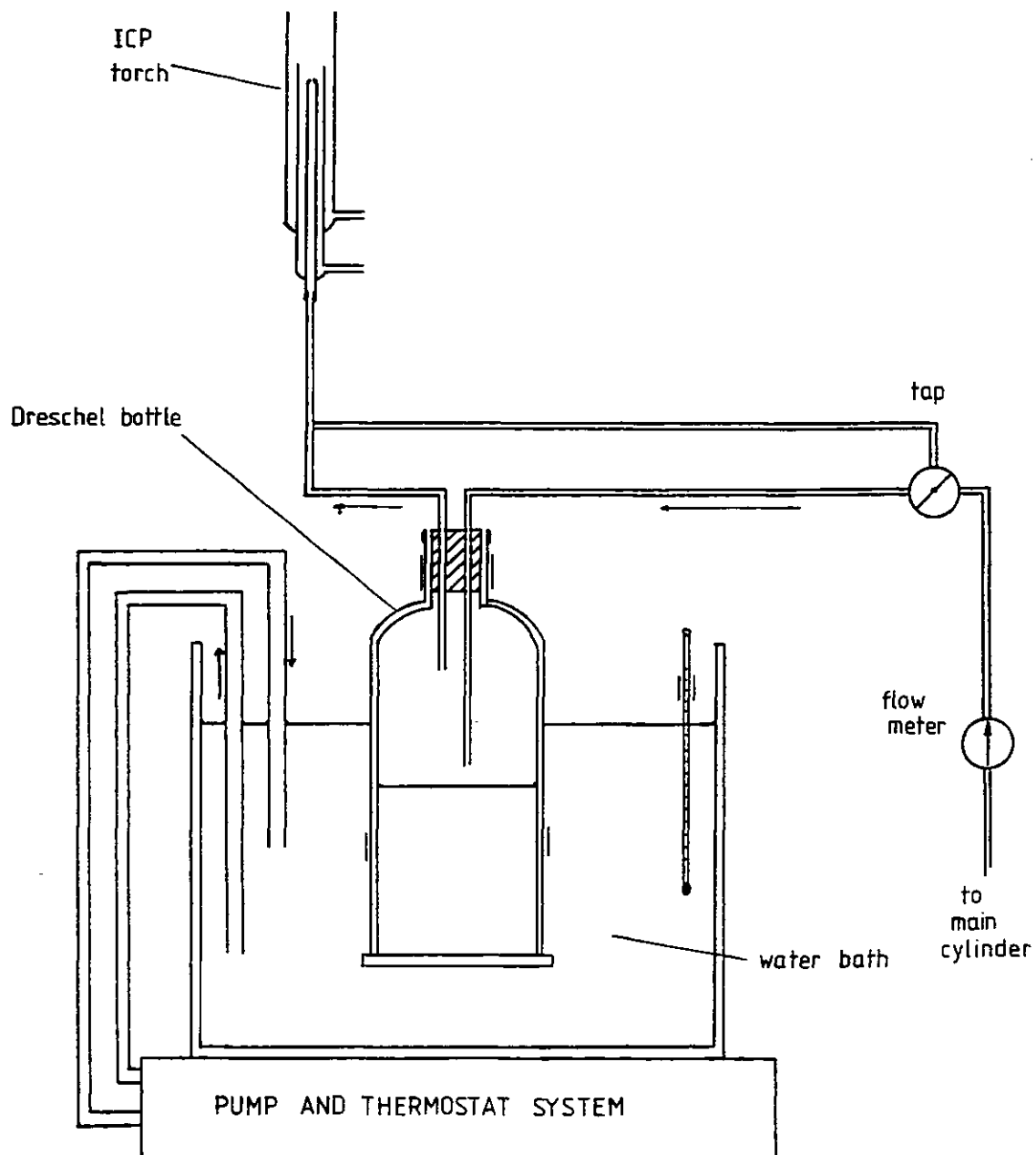


FIGURE 7.1 : System for water vapour generation at a fixed argon injector flow rate 1.0 l/min.

was decided to calibrate the system empirically, since water vapour would be generated under dynamic rather than static equilibrium. Accordingly, a CaCl_2 drying tube was fixed to the apparatus outlet such that the amount of water per litre of gas stream could be gravimetrically determined. The calibration graph for dynamic equilibrium is shown in figure 7.2. The dashed line on this graph represents the quantity of water normally present in the injector gas stream when the pneumatic nebuliser is employed. A tap system built into the apparatus was used for injecting dry argon without passage over the water surface.

Measurements of electron density in the plasma as the amount of water entering the injector channel was varied, were performed at an observation height of 10mm. and the results are shown in figure 7.3. It can be seen that the electron density increases from an initial value of 1.30×10^{21} to $1.65 \times 10^{21} \text{ m}^{-3}$ as the amount of water increases, which represents a 27% rise. Curves were also constructed for the variation of electron density with observation height above the load coil at different applied powers with and without the presence of water in the injector gas and these curves are presented in figure 7.4. The electron density clearly decreases as the observation height increases and as the power coupled to the plasma decreases. The maximum value of n_e obtained at 5mm. observation height and 1.2kW applied power is $2.3 \times 10^{21} \text{ m}^{-3}$. For the establishment of the LTE state an electron density $\geq 1.0 \times 10^{22} \text{ m}^{-3}$ (159) is required and consequently the results obtained seem to support the general contention that the analytical ICP is not in fact in LTE, although LTE could be approached in the core of the plasma, where the highest temperatures are experienced.

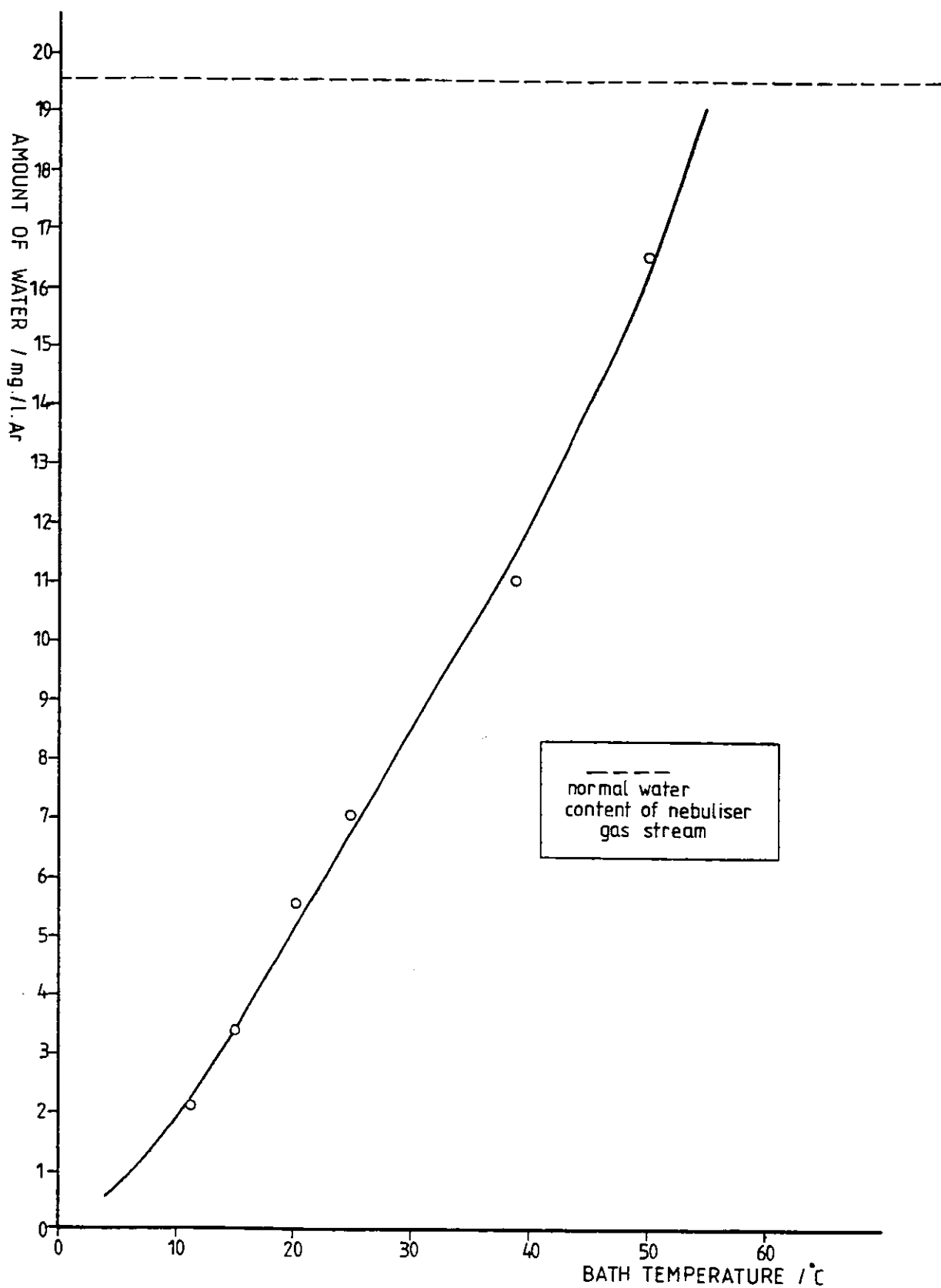
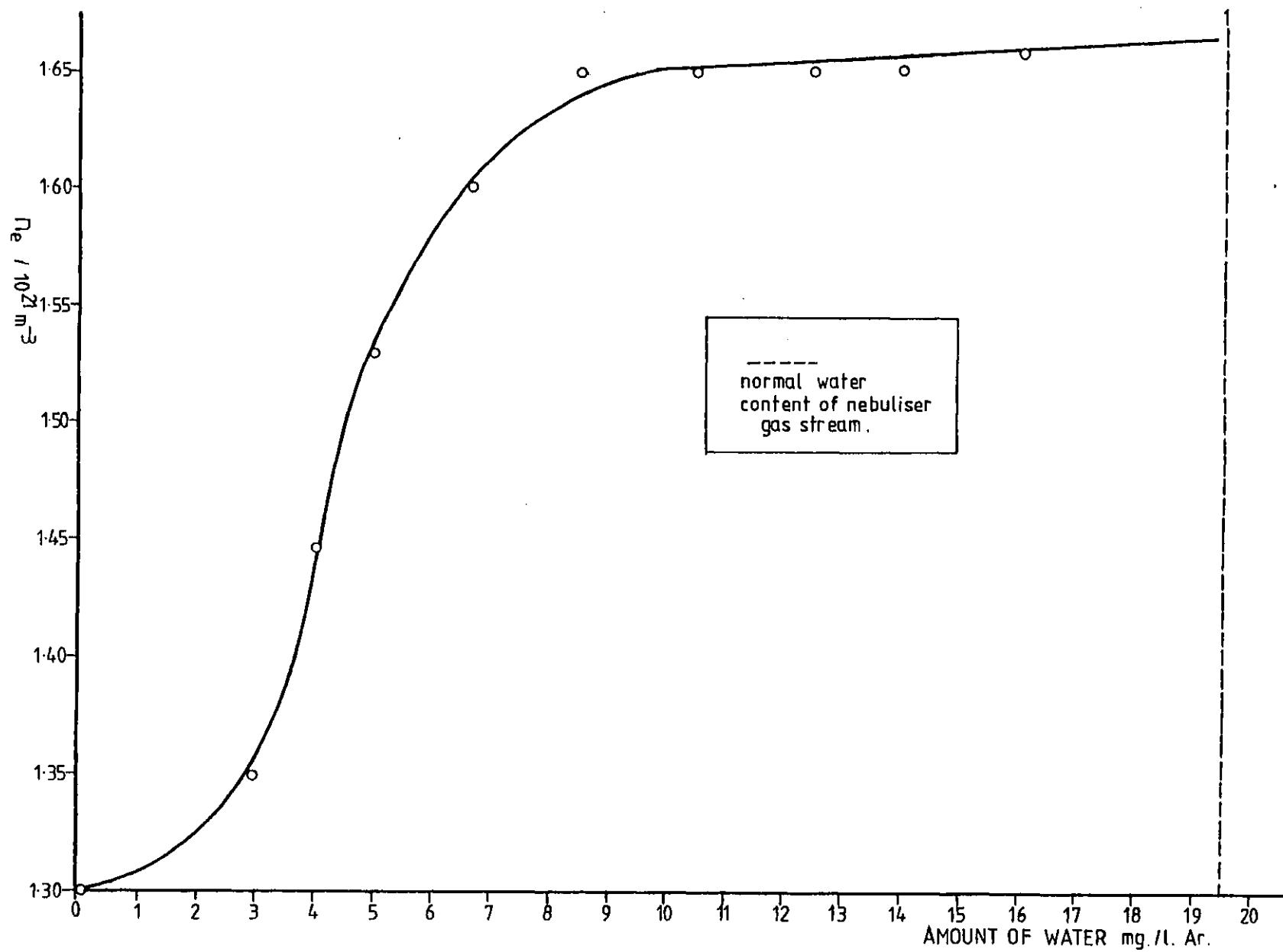


FIGURE 7-2 : Calibration for water vapour generation apparatus at a fixed gas flow rate 10 l/min.

FIGURE 7-3 : Variation of electron density with amount of water entering injector channel of plasma. Stark half-width increases from 0.250 to 0.287 nm.



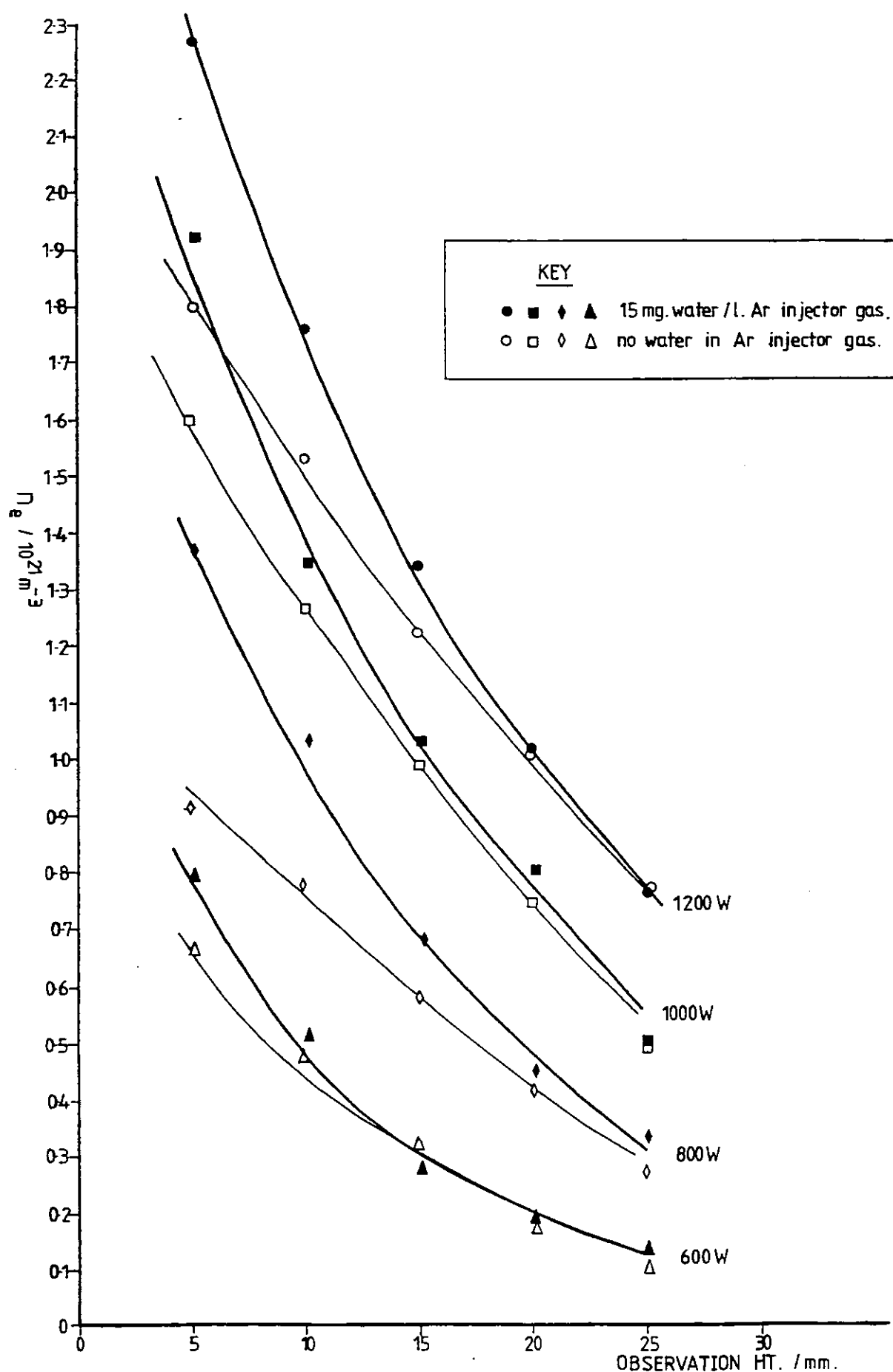


FIGURE 7-4 : Electron density curves for large plasma with and without the presence of water in the injector gas stream.

The effect of water on the electron density curves is interesting; at low observation heights the presence of water increases the electron density, while at high observation heights ($> 20\text{mm.}$) the electron densities with and without the presence of water are comparable. Obviously then, the effect of water at low observation heights is to bring the plasma nearer to LTE, but little effect would be expected when the observation height increases to the values normally used for analytical purposes.

A similar trend is observable if the temperature distributions in the plasma are examined, table 7.2,

Table 7.2: Temperature distributions in the ICP.

Power/W.	Observation Ht./mm.	T _{exc} /K.	
		19mg. H ₂ O/l.Ar.	no water.
600	5	5581	5641
	10	5392	5577
	15	5209	5394
	20	4866	4836
	25	4555	5920
800	5	5692	5912
	10	5342	5841
	15	5196	5729
	20	5013	5521
	25	5974	6141
1000	5	5589	6132
	10	5817	5936
	15	5983	6183
	20	5335	6192
	25	5860	5501
1200	5	5800	6298
	10	6436	6389
	15	5573	6262
	20	5709	6090
	25	5264	6183
All temperatures $\pm 250\text{K}$, PMT 800V, Coolant flow 19l./min.			

Although the temperatures obtained are only accurate to $\pm 250\text{K}$, the underlying trend is an increase in temperature with applied power and

decreasing observation height. If applied power and observation height remain constant, a decrease in temperature when water is present in the injector zone, is evident when compared with the corresponding temperature without water. This would imply a decrease in electron density when water is present, because the lower temperature would effectively reduce ionisation in the discharge. A lowering of the temperature when water is present in the discharge is probably caused by a reduction in the amount of applied power coupled to the argon injector column, because some of the power is consumed in raising the temperature of the water, and water has an order of magnitude larger specific heat. For the case of a pneumatic nebuliser working at 2% efficiency and an uptake rate of 2.5ml./min., the amount of power required to convert the water to steam is approximately 12W (plus a further 13W if dissociation of the water is included) compared with approximately 90W required to heat the injector gas itself. It is apparent then that some 13% of the power normally consumed by the argon injector gas is diverted into the water. At this point it must be remembered that the electron density increases when water is present, which would not be expected from the overall decrease in the temperature. The most reasonable explanation for this is that the number of ions and electrons produced through ionisation of the water in the plasma must be greater than the decrease in the number of electrons from argon, as the temperature decreases. Rough calculations suggest that some 30% more electrons would be available overall when both processes are taken into consideration, a figure which agrees quite well with the experimentally observed rise of 27%.

7.4.2 Excitation Characteristics of Calcium.

In order to compare directly the excitation phenomena when an analyte is introduced into the plasma, with and without the presence of water, the spatial and power characteristics of calcium, chosen as model element, were investigated using (a) the Meinhard nebuliser for sample introduction and (b) the GRV device described in chapter 6. For both of these, a 4ppm. solution was used, prepared from analytical grade calcium chloride dissolved in distilled water. Signal to background ratios (S/B) as a function of observation height and applied power for the calcium ion line Ca(II) 393.37nm and the atom line Ca(I) 422.67nm. are shown in figures 7.5 and 7.6 respectively using nebulisation sample introduction. For the ion line, depressions were observed as the power increased from 600-1200W and the optimum observation height decreased slightly from 25mm.-21mm. above the load coil. The atom line showed a similar trend, but the optimum observation height remained at 26mm. above the load coil. It was also observed that the atom S/B attenuation, as the power was increased, was far higher than that of the ion line, which is not unexpected if the excitation and ionisation energies of the atom and ion are compared. If the corresponding plots for sample introduction using the GRV, figures 7.7 and 7.8 are examined, a similar trend is apparent; the best S/B ratios were observed at 24mm. for the ion line and 26mm. for the atom line.

Of more significance are the ion/atom (I^+/I^0) intensity ratios with water and without water. For sample introduction using the nebuliser, the ratio ranged from 21 at 600W to 47 at 1200W at 10mm. observation height whilst for sample introduction with the graphite

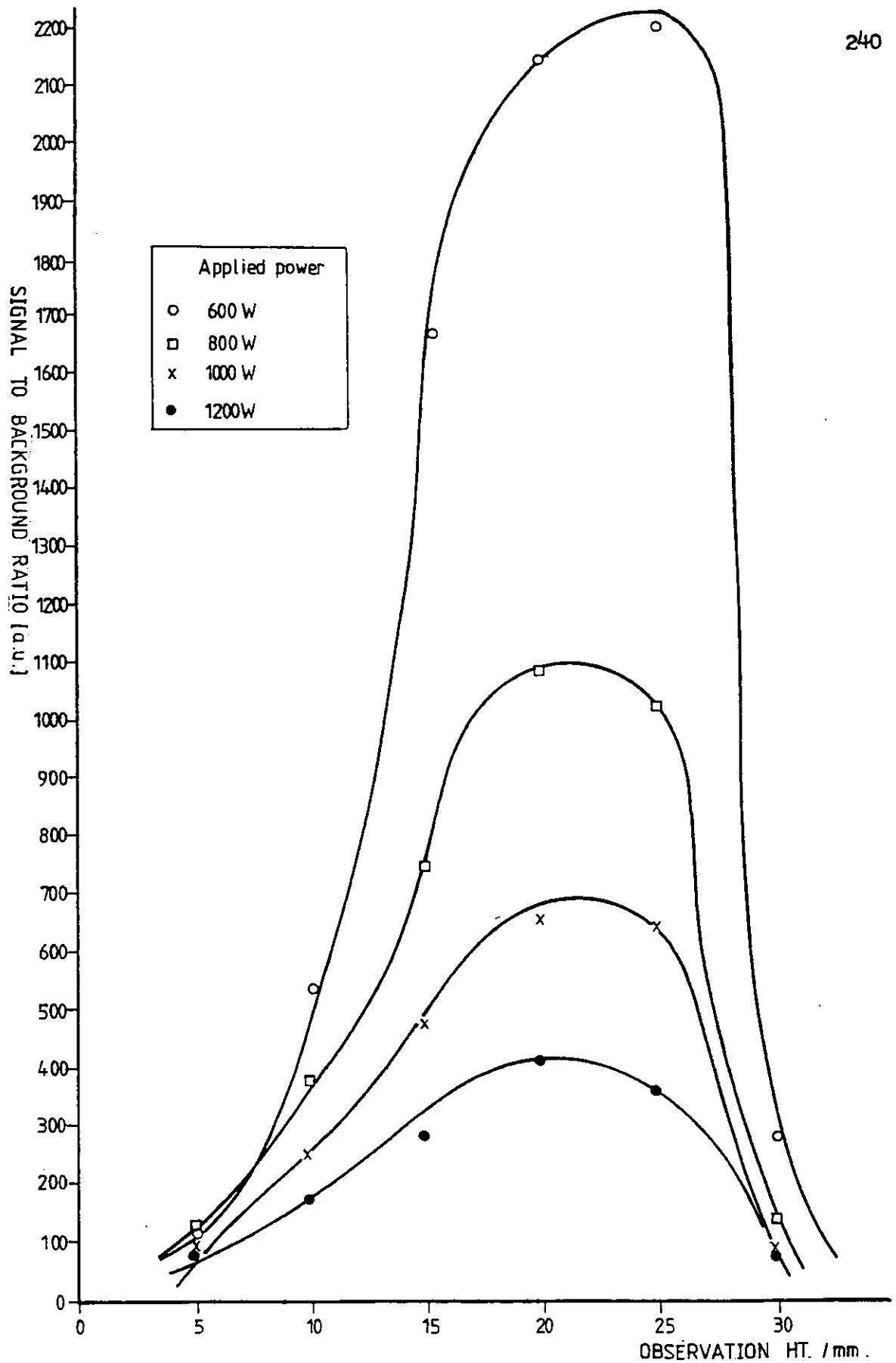


FIGURE 7-5 : Emission characteristics of calcium as a function of observation height using pneumatic nebuliser. Concentration 4ppm.

CALCIUM (I) 422.67nm.

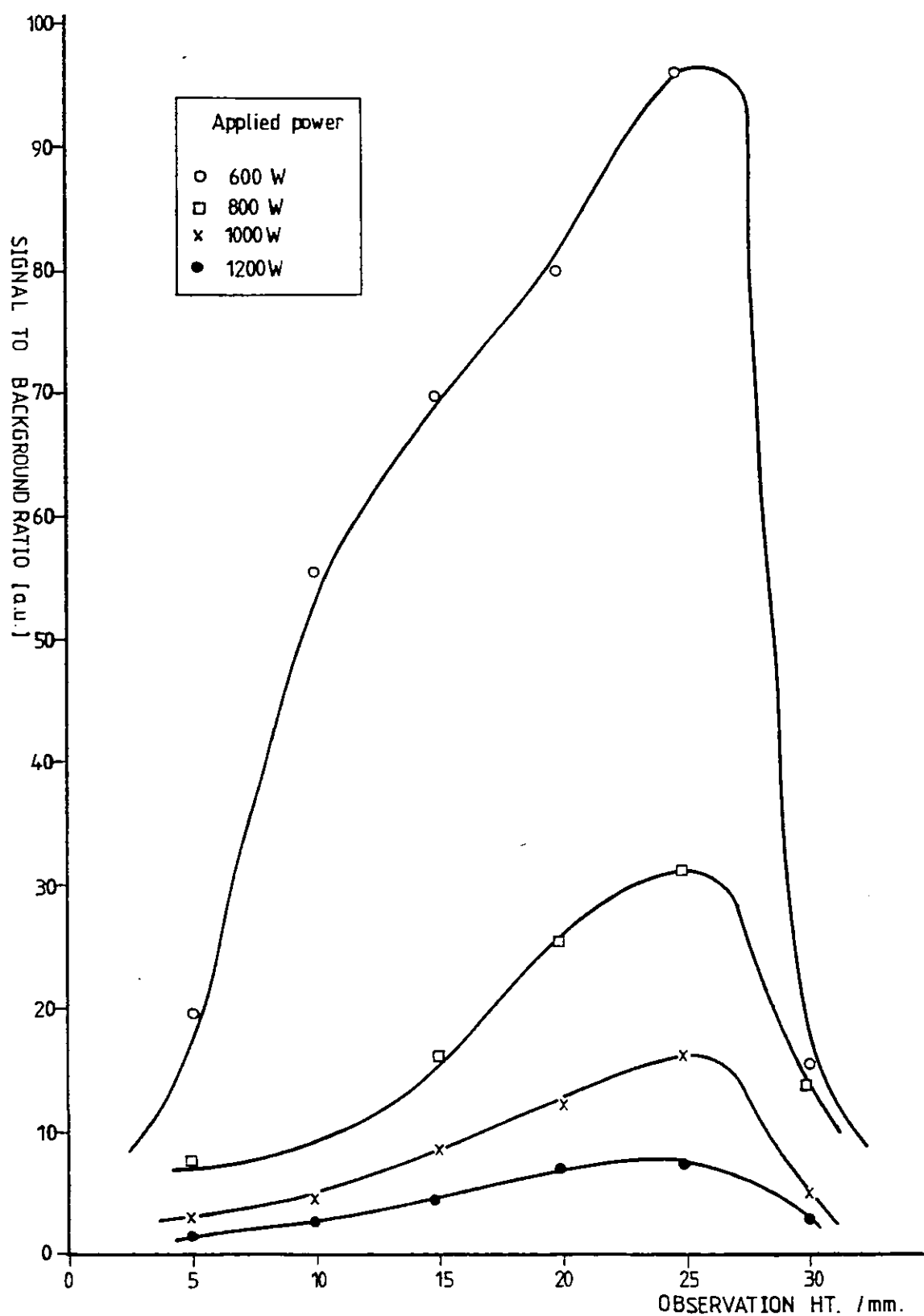


FIGURE 7-6 : Emission characteristics of calcium as a function of observation height using a pneumatic nebuliser. Concentration 4ppm.

CALCIUM (II) 393.37 nm.

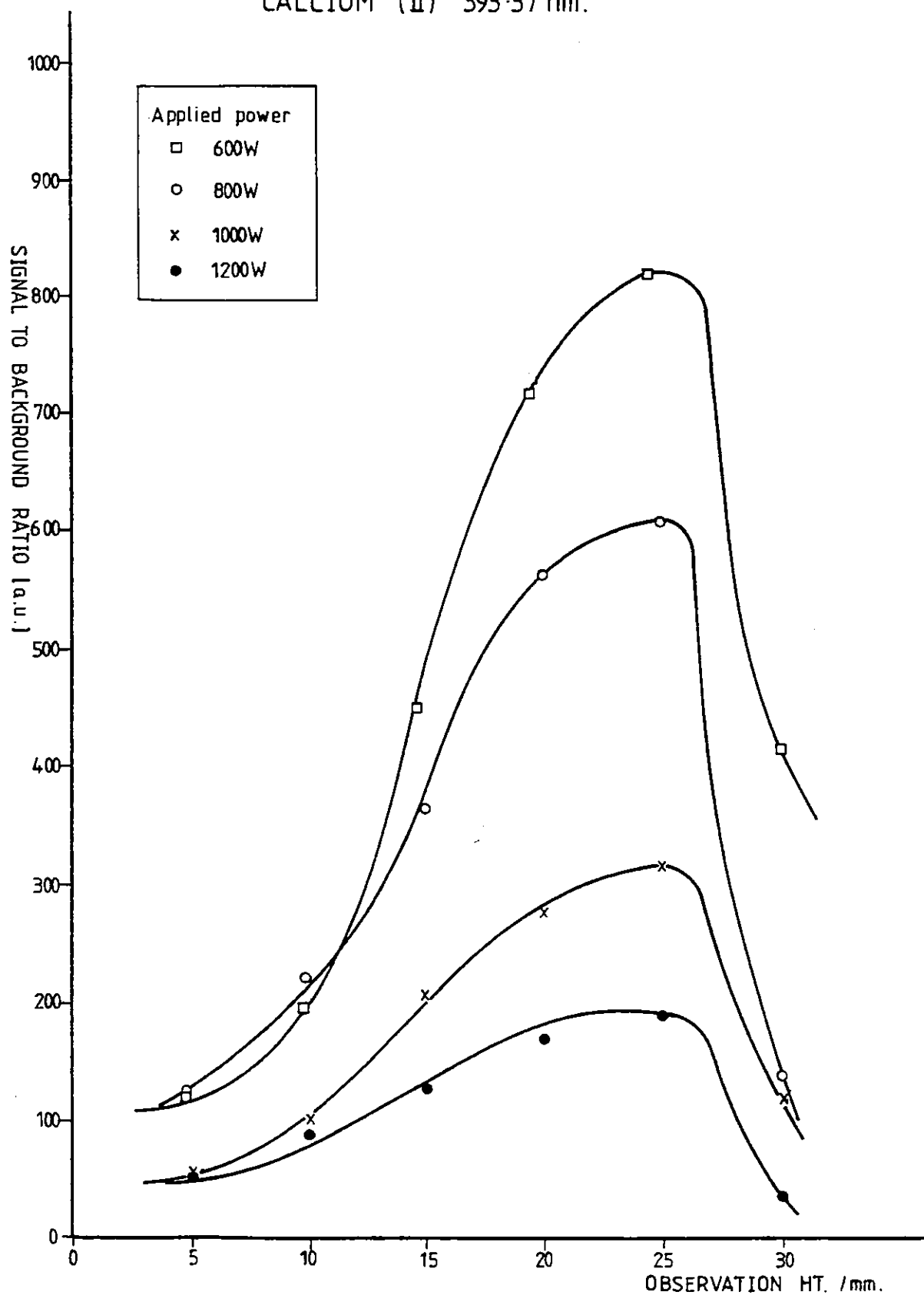


FIGURE 7-7 : Emission characteristics of calcium as a function of observation height using dry aerosol sample introduction. Vaporisation temp. 1950 °C. concentration 4ppm.

CALCIUM (I) 422.67 nm.

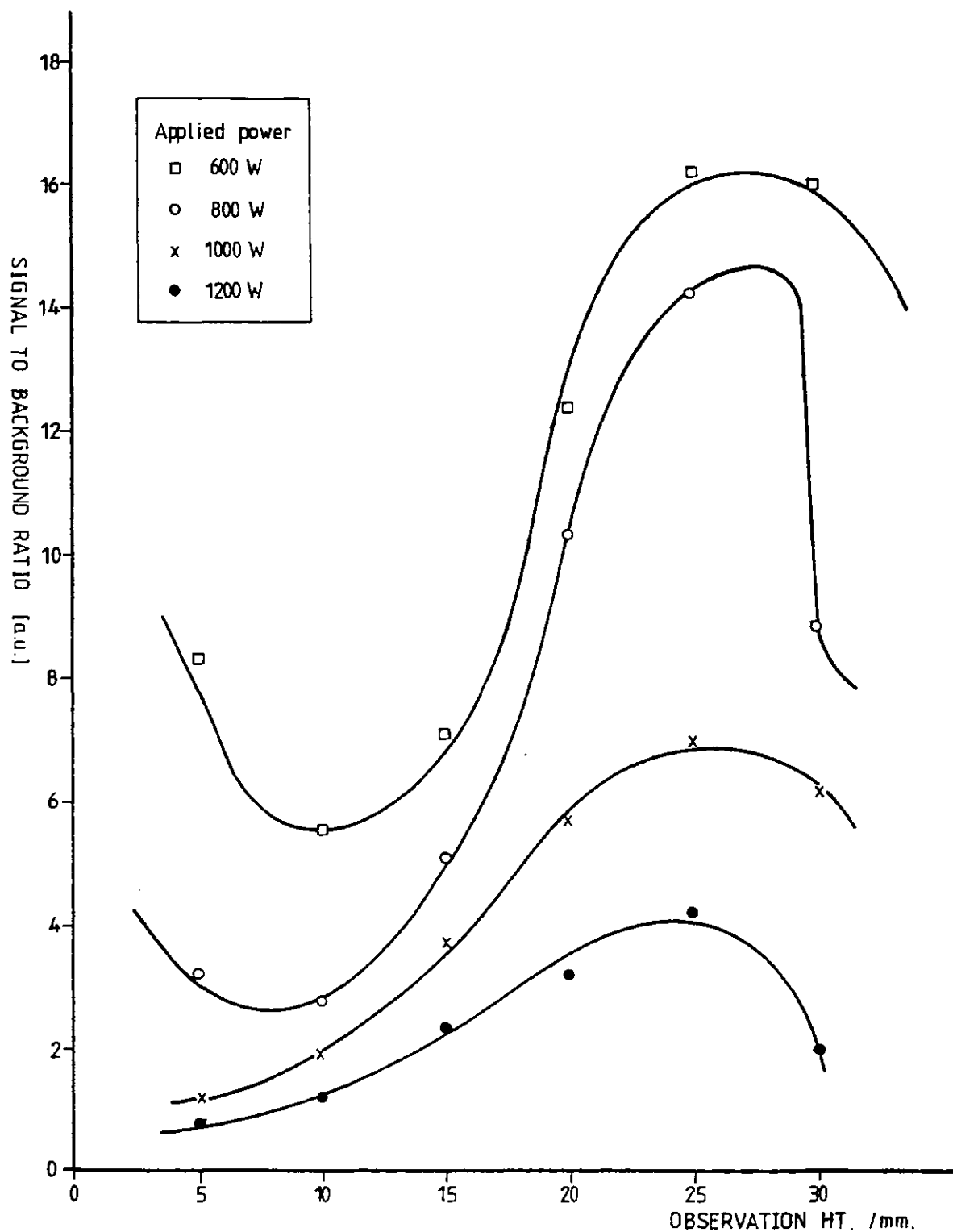


FIGURE 7-8 : Emission characteristics of calcium as a function of observation height using dry aerosol sample introduction. Vaporisation temp. 1950°C concentration 4ppm.

rod, these ratios were respectively 74 and 89. At viewing heights greater than 15mm., the ion/atom emission ratios were comparable to those obtained with the pneumatic nebuliser. In the presence of water then, the ion/atom population for calcium is possibly decreased, in accordance with the expected shift in ionisation equilibrium as the electron density increases, thereby increasing the relative atom population.



Although this is the most reasonable model for this effect, other workers (248) have found that the ionisation shifts, when large quantities of a concomitant easily ionised element (which would be expected to increase n_e) are added to the analyte, are much lower than expected if ionisation shift is the exclusive interference process, and suggest that other interference mechanisms must contribute. At present, the precise effect of species which should contribute to the electron density in the plasma is not well understood and much work is required in this area.

7.5 Excitation Measurements in a Miniature Discharge.

7.5.1 Experimental.

Impetus for the development of torches and plasma discharges smaller than those popularly in use, has resulted from the lower gas consumption and smaller r.f. generation equipment needed, with attendant savings in running costs. Such a "miniature" plasma was

conceived by Allemand and Barnes (212), but only Savage and Hieftje have made any systematic studies (216,249,250).

For these studies, a miniature torch was designed and constructed for maintaining a plasma 30% smaller than that of the conventional design. The miniature torch was constructed in the same demountable arrangement as described in chapter 4 and is shown to scale in figure 7.9. The torch was supported in a machined brass base to provide tangential gas entry, and radiofrequency power was coupled via an 18mm.i.d. 1.5turn water cooled load coil constructed from 3mm. copper tubing. This provided a flux density calculated at 2.1mT when using the IPC 27.1 MHz. power generator.

In operation, the discharge was essentially similar to the conventional type except that power levels as low as 200W could successfully be used for sustaining the discharge and gas flow rates between 5 and 10 l./min. were sufficient for operation. Preliminary comparisons between the working properties of this miniature plasma and the conventional plasma indicated that similar detection limits were attainable and calibration curves had the same wide dynamic range as their conventional plasma counterparts.

7.5.2 Excitation Temperatures.

Excitation temperatures obtained using the atomic Boltzmann plot for the miniature plasma with and without the presence of water are given in table 7.3. If these temperatures are compared with those of the conventional plasma, they are some 500-600K lower, but do not exhibit as much spatial variation with observation height. However, in common with the conventional plasma is the decrease in

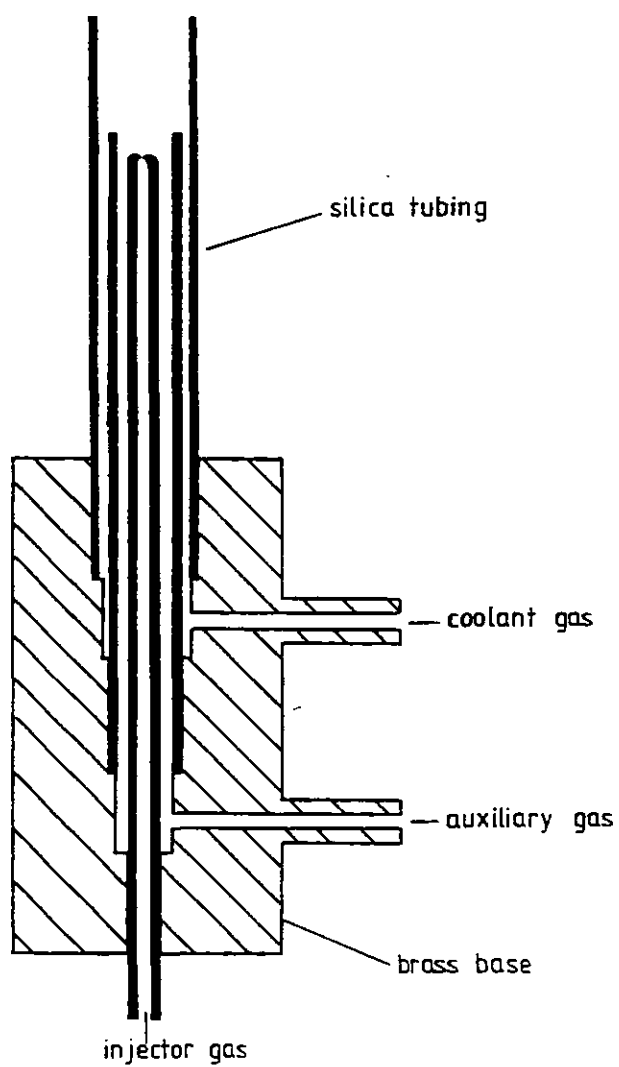


FIGURE 7-9 : Miniature torch assembly (to scale.)

temperature associated with the presence of water in the injector gas, although this is not as significant at higher powers.

Table 7.3: Excitation temperatures in the miniature ICP.

Power/W.	Observation Ht./mm.	Excitation temp./K.	
		19mg.H ₂ O/l.Ar	no water
600	5	4843	4920
	10	4514	4939
	15	4566	5038
	20	4976	5257
800	5	4635	5203
	10	4662	5189
	15	5451	5057
	20	4587	5142
1000	5	5103	5196
	10	5196	5156
	15	5573	5422
	20	5070	5058
All temperatures $\pm$ 250K. Coolant flow 9l./min. Injector 1.0l./min.			

It is perhaps not surprising that the temperatures in the miniature plasma are lower than those of the conventional plasma, if the overall sample injection velocities are considered. For both plasmas, the volume flow rate of injector gas remained the same, largely enforced by the standardised conditions adopted. For the miniature plasma however, the injector tube orifice was only 0.8mm. compared with 1.5mm. for the conventional plasma, resulting in overall sample injection velocities of 13.1 and 9.4 m./s. respectively. The higher axial velocity in the miniature plasma would successfully explain the lower temperatures measured. Although a reduction in sample injection velocity, by careful design of the sample introduction system would seem to be a good idea, relatively high injection velocities are apparently necessary in miniature plasmas (251) on account of the higher magnetohydrodynamic pressure in the core of the discharge compared with the conventional plasma.

7.5.3 Electron Density Measurements.

Electron density measurements were performed on the miniature plasma discharge in the manner previously described. Curves for the variation of electron density as a function of observation height, applied power and the presence of water, can be observed in figure 7.10. As expected from the temperature distributions, the electron density increases with applied power and decreases with increasing observation height. Interestingly, the electron density is greater with the presence of 10mg. water/l. injector gas than without, at low observation heights but not at high observation heights, a trend similar to that obtained with the conventional plasma. What is also observable is the absolute magnitude of the electron density values in the miniature plasma which are some five times higher than the equivalent values for the conventional plasma. Since the temperatures in the miniature plasma are not greater than those of the conventional plasma, the higher power density in the miniature plasma, owing to its smaller dimensions, must contribute.

A study of the effect of water on the electron density in the miniature torch is presented in figure 7.11 for the range 0-19.5mg.H₂O/l.Ar using the water vapour generation apparatus. In common with the conventional plasma, the electron density increases some 37% from 3.8×10^{21} to $5.2 \times 10^{21} \text{ m}^{-3}$ although the rate of increase is not as high as for the conventional plasma. Again a plateau region is observable where additional water does not contribute to the overall electron density in the injector channel at that particular viewing height.

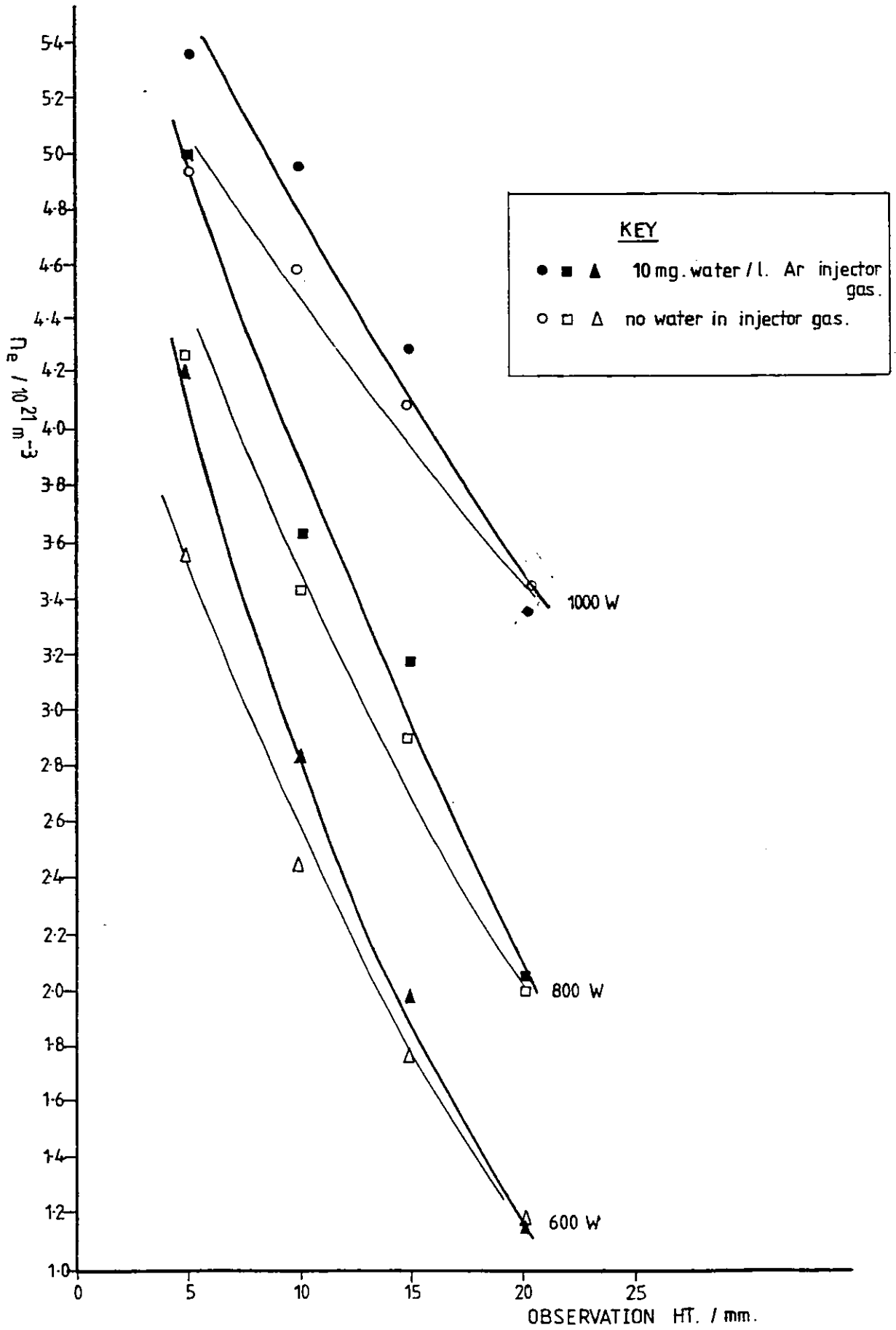


FIGURE 7-10 : Electron density curves for mini plasma with and without the presence of water in the injector gas stream.

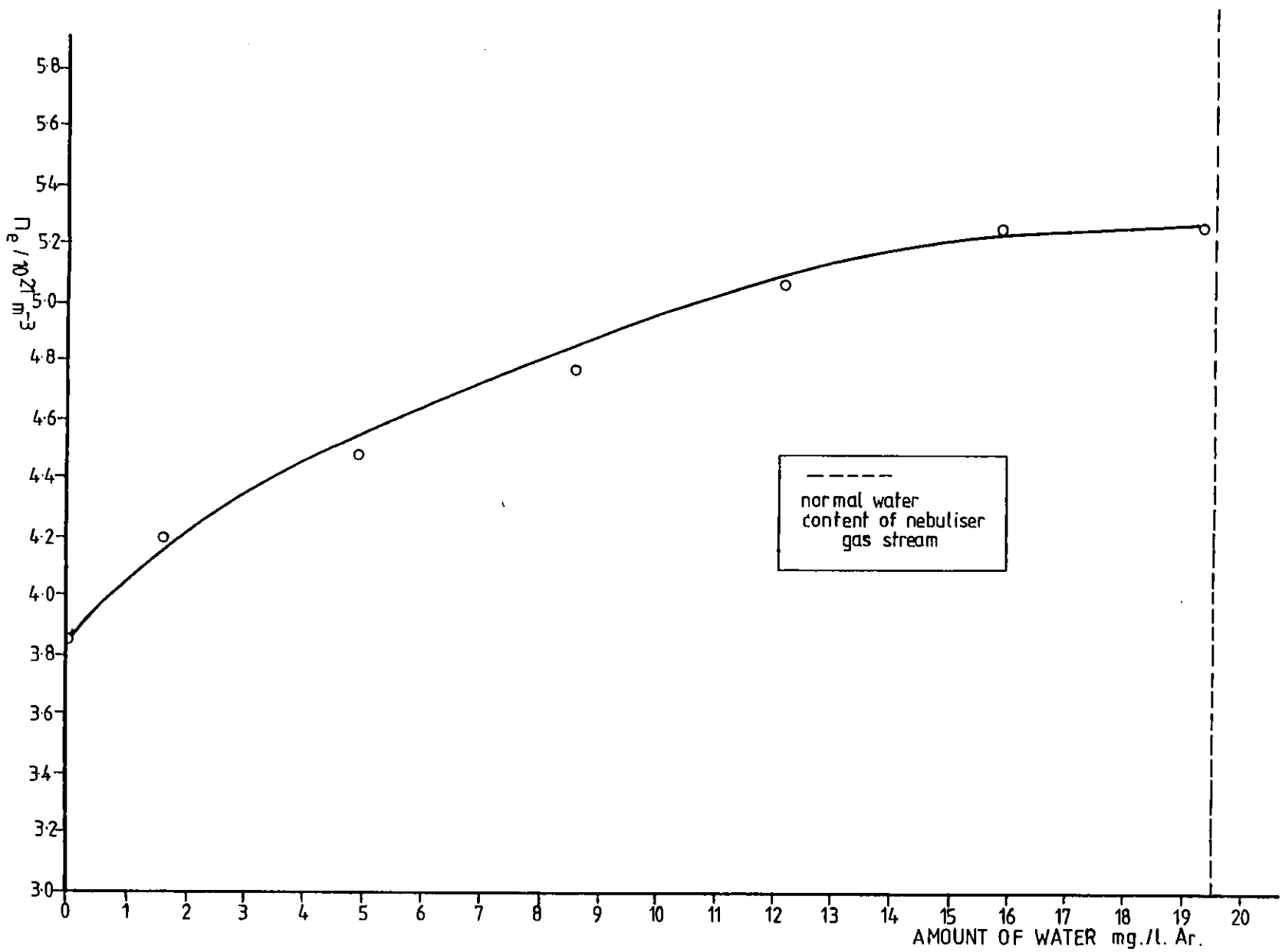


FIGURE 7-11 : Variation of electron density with amount of water entering injector channel of plasma sustained in miniature torch. Stark half-width increases from 0.500 to 0.617 nm.

7.5.4 Emission Characteristics.

The behaviour of calcium in the miniature torch was investigated using a 4ppm. solution. With the pneumatic nebuliser, the best S/B ratios were at 28mm. observation height for the Ca(I) 422.67nm. line and 17mm. observation height for the Ca(II) 393.37nm. line.

Identical optima were observed for dry-aerosol sample introduction with the GRV device. These observation height maxima were similar to the expected values; the higher excitation potential of the calcium ion relative to the atom means that most intense emission would be expected to occur lower down in the plasma tailflame where the temperatures are higher, whereas atomic emission would be expected high up in the tailflame where the temperatures are lower and less ionisation takes place. Ion/atom ratios, I^+/I^0 determined for the calcium species in the miniature plasma were entirely unexpected. With the presence of water, these ratios were 126 at 600W and 163 at 1000W at 10mm. observation height, increasing to 150 and 182 respectively when dry-aerosol sample introduction was used. If these values are compared with those of the conventional plasma, 21/89, ion emission in the miniature plasma appears to be more dominant than for the conventional plasma. Such behaviour is not expected, because the apparently higher electron density in the miniature plasma should enhance atomic emission relative to ionic emission, if an ionisation equilibrium model is correct.

To ascertain whether this observation was exclusive to calcium, the behaviour of another element, cadmium, was investigated. For the conventional plasma, I^+/I^0 ratios for the cadmium(II) 226.502nm. line and the cadmium(I) 228.802nm. line were 0.56 at 600W and 0.69 at

1000W, at 10mm. observation height, when pneumatic nebulisation was employed. For the miniature plasma the equivalent I^+/I^0 ratios were 1.30 and 1.62. All ratios were slightly enhanced when dry-aerosol sample introduction was used.

Clearly enhancement of I^+/I^0 ratios in the miniature plasma is not confined to calcium, because for cadmium the ion line is more intense than the atom line, whereas it is the other way round in the conventional plasma.

The apparently anomalous properties evident in the miniature plasma can only be elucidated when a more thorough study has been made with respect to its physical properties. In particular, electron density values as determined, appear to be higher than might be expected from the measured temperatures. Whatever the case, ionisation in the miniature plasma was significantly higher than for the conventional plasma, additional evidence for which was provided by the structure of the recorded $H\beta$ profiles. For the conventional plasma, these consisted of a central dip, produced by line reversal, with broadened wings, as is usually found. For the miniature plasma, the central dip increased to form a hump which was raised above the broadened line wings. This effect could only be attributed to much higher hydrogen excitation than for the conventional plasma.

7.6 Conclusions.

The effect of water on the physical conditions in the plasma discharge has been investigated. For the conventional plasma, water decreases the temperatures in the central injector channel whilst simultaneously, significantly raising the electron density through

ionisation of the hydrogen and oxygen from the water. The presence of water also depresses I^+ / I^0 ratios of elements introduced into the plasma. However, these effects are confined mainly to the core region of the discharge and at the higher tailflame viewing heights, water has little effect. One can therefore conclude that analytical conditions selected for analysis of elements using nebulisation (wet-aerosol) sample introduction should be similar to those for electrothermal (dry-aerosol) sample introduction. This could be substantiated by selecting a wider range of elements for comparison, and correlating the emission properties.

The physical properties of a miniature discharge have also been investigated with respect to analyte behaviour, electron density and temperature. Electron density values for this plasma indicate that it is fairly close to LTE, much more so than the conventional plasma, although the temperatures determined for this plasma, as measured, are below those of the conventional plasma. It seems likely that the temperature measurements are more likely to be in error than electron density measurements because the intrinsic assumption was made that the argon lines selected were optically thin, which may not be totally valid. The temperature determinations should ideally be checked by perhaps using another species such as helium introduced as an impurity in the plasma injector gas.

The effect of water in the miniature plasma is much the same as in the conventional plasma. However, more complete excitation of elements appears to take place in the miniature plasma such that I^+ / I^0 ratios are enhanced.

Although the direct comparison between the miniature plasma and the conventional plasma is impeded by the difference in physical

dimensions of the two cases, several interesting effects connected with the miniature plasma have been observed, which certainly warrant a more complete investigation. It is conceivable that the miniature plasma may be superior to the conventional plasma in several respects.

CHAPTER 8

CONCLUSIONS AND
SUGGESTIONS FOR FURTHER WORK.

In this thesis, results have been presented for investigations into a range of sample presentation systems in molecular and atomic spectroscopy, which have been critically evaluated. In many respects, it has been shown that attention to the problems of sample presentation enables potentially superior detection power to be obtained and often considerable improvements in sample preparation and analysis time for analytical samples.

Photoacoustic spectroscopy has been examined with respect to quantitative analysis of propranolol and fat content in milk powders. It has been shown that quantitative treatment of samples in the solid phase by PAS could replace existing methods of analysis. At present, empirical calibration systems are necessary because a rigid theoretical treatment for quantitative PAS, as pertaining to the solid phase, has not emerged. Much useful work is therefore required in this area.

For the analysis of propranolol, a linear calibration system has been obtained for the near-IR region. However, as commonly observed, the calibration function for the U.V.-vis. region deviates towards the concentration axis at high concentrations of propranolol. Two mechanisms have been proposed to account for this, based on light scattering from the sample and alteration of the thermal wave

propagation through the sample. Although photoacoustic saturation could also be responsible for this effect, this would not be expected to occur because the molar absorptivity of propranolol is fairly low. Conclusive evidence that saturation is not responsible can be obtained by studying the linearity of the calibration function whilst altering the modulation frequency. If saturation is not the cause, then the calibration graph will be unaltered by the use of higher modulation frequencies (equation 2.6).

Results for intact propranolol tablets suggest that the analysis of propranolol, at present assayed using wet chemical techniques, could be accomplished without any modification or destruction of the solid formulations. A further study of this system could be used to assess potential commercial exploitation for which a dedicated instrument could be built. This instrument would have to correct for the difference in physical size of the formulations but could be adapted for several different products.

The popularity of the ICP has been reflected by the very high growth rate in commercial sales of plasma instruments. A range of sample introduction systems for use with the ICP have been investigated. It has been shown that the detection power of the ICP could become comparable to the best analytical techniques, by retaining the simplicity of the nebuliser for sample introduction but employing electrochemical preconcentration. This process could easily be automated such that on-line ultra-trace simultaneous multi-element analysis could be accomplished. At present no other technique is available for this purpose.

Electrothermal sample introduction systems have also been

investigated. In general, these enable one to two orders of magnitude improvement in sample transport efficiency compared with the pneumatic nebuliser. For the GRV device, a number of transport interferences are observed. Studies of these effects for cadmium and molybdenum indicate that the main interference process is deposition on the walls of the transport manifold. If this method of sample introduction is to be accepted for commercial use, the mechanism of analyte deposition must be investigated further. Valuable evidence for the mechanism of the deposition process, and also the thermal chemistry of analyte vaporisation from the rod, could be gained by using analytical surface techniques, such that the chemical identities of the deposited species can be established. Once these are known, the interaction between the deposited species and the surface of the manifold could be characterised and the system redesigned to minimise these interactions.

The role of water in the ICP has been determined for both a miniature and a conventional discharge, to establish the necessary operating criteria for wet and dry-aerosol sample introduction. It has been concluded that at compromise conditions selected for analysis, little effect from water is expected, although this is not the case at lower observation heights.

Further studies should be oriented to the investigation of discharge phenomena occurring during the transient injection of analyte species with the graphite rod. Present studies have been confined to steady state phenomena. For the case of the determination of electron density this could be quite difficult because the temporal lifetime of the process is much lower than the time required to scan over the $H\beta$ line used for electron density measurements. Clearly, transient

information can only be obtained by collecting data over the total H_{β} line profile within the lifetime of the transient pulse. One way to do this would be to station over one particular segment of the line profile, measure the transient condition, move to another segment, repeat the transient pulse and measurement and so on for the rest of the profile. This approach, however, would not be particularly reliable because extremely good reproducibility of successive injection pulses is required. A better way would be to use a photodiode array or vidicon camera to take measurements over the whole profile simultaneously. Alternatively, transient measurements over the whole profile could be obtained by moving the profile with respect to the exit slit, via a rapidly vibrating refractor plate located inside the spectrometer entrance slit. The H_{β} profile could then be imaged using an oscilloscope or processed with a computer.

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