NON-DISPERSIVE ATOMIC FLUORESCENCE SPECTROSCOPY OF TRACE METALS IN STEELS

by

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ABSTRACT

The work described in this thesis was designed to investigate the practicability of non-dispersive atomic fluorescence spectroscopy for the determination of trace metals in steels. Accordingly, the format of this thesis is based upon the Scientific Method, and includes a statement of the problem to be solved, an assessment of the current status of atomic fluorescence spectroscopy and its application to metallurgical analysis, followed by a detailed description of the instrumentation designed to tackle the problem.

Six elements were examined using a simple non-dispersive atomic fluorescence spectrometer and the capabilities of the technique evaluated by its application to the determination of these elements in a range of standard steel samples.

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CHAPTER ONE

THE STEEL PROBLEM

1.1. Introduction

The analysis of steel and related materials is not a new problem but, with the requirements of the modern steelworks becoming increasingly more demanding, the methods by which it is tackled have had to advance accordingly. The traditional chemical methods which found wide application in the past have been superseded by the more sophisticated instrumental techniques which are now available. In particular, atomic spectroscopic methods are used extensively in metallurgical analysis for the determination of a wide variety of trace elements.

Why this should be so, and the part to be played by atomic fluorescence spectroscopy (AFS) will form the basis of this chapter.

1.2. Types of ferrous metals

In this and subsequent chapters, reference will be made to several types of ferrous metals so, for the sake of clarity, the principle features and properties of these will be discussed in this section.

Pig iron is the name given to the crude form of iron produced from the blast furnace and contains about 3% by weight of carbon. Two main types of pig iron are made: haematite (or acid iron) which contains 2 or 3% of silicon, but is low in phosphorus; and basic iron which has a low silicon content, but may contain up to 2½% of phosphorus. The brittleness of pig iron caused by its high carbon content means that it finds little commercial application.

Instead it undergoes a laborious refining process and is converted to wrought iron which, in so far as the absence of metallic impurities is concerned, may be regarded as almost pure iron, although it does contain about 1% of slag. Wrought iron is soft because it contains almost no carbon.

When carbon is alloyed with iron, the hardness and strength of the metal at first increases, although the ductility is reduced as the carbon content rises. High-carbon steels, which contain 1 to 1½% of carbon, exhibit still greater hardness, but the strength of such alloys diminishes to some extent. Steels with higher carbon contents are rarely encountered with the exception of cast iron which is characterised by carbon levels in excess of about 2½%. This results in an alloy of poor ductility, moderate strength and hardness but excellent castability.

It is clear that these plain carbon steels are of considerable value in a wide variety of applications. Depending upon which use the metal is to be put, the most suitable iron-carbon alloy may be selected to give the desired properties. There are, however, some serious limitations connected with the use of plain carbon steels. During the process of hardening by quenching (in which the steel is heated to red heat and quenched, usually in water, from that temperature) a small piece of steel will obtain uniform properties throughout its section. A large block of the same material, however, will not be similarly affected. The quenching effect of the water will be more pronounced on the outside, particularly near the edges, while the interior will cool much more slowly resulting in a gradual decrease in hardness towards the centre of the block.

In turn, this non-uniformity of properties may cause internal stresses to be set up and cracks may develop on drastic quenching. Such difficulties can be overcome by using alloy steels, in which uniform hardness can be obtained throughout a large block by mild quenching.

These alloy steels may be regarded as steels which contain, in addition to iron and carbon, specially added amounts of other elements which, although by themselves do not make hardening and tempering possible, may modify the effects brought about by such treatment. For example, manganese steel, which might contain about 1% carbon and some 13% manganese, can acquire an unusual degree of toughness by being heated to 1000^{o}C followed by quenching in water.

More familiar are the types of ferrous alloys known as stainless steels. These alloys can be conveniently categorised as follows:

1) The Martensitic group, which contain about 13% of chromium. These steels usually contain no other major alloying element and are all hardenable by heat treatment.

2) The Ferritic group, in which the chromium content may range from 17 to as much as 30%, again with no other major alloying element, but which cannot be hardened by heat treatment.

3) The Austenitic group, which contain about 18% chromium and some 8% nickel. The feature of the steels in this group is that they rapidly harden when cold-worked. A derivative of this group are the semi-austenitic precipitation-hardenable steels. These contain about 17% chromium, 7% nickel and 0.15% carbon, as well as other elements such as molybdenum and aluminium, and derive their name from the fact that they can be heat-treated to high strength by the process of precipitation hardening (1).

Another important type of alloy steel is the high-speed steel used for cutting metals on lathes and other machine tools. A typical high-speed steel may contain about 0.7% carbon, 18% tungsten and 4 to 6% chromium, as well as vanadium and sometimes cobalt. Using such alloys, metal parts can be machined much faster than with tools made from plain carbon steels, which can heat up to such an extent that over-tempering occurs causing the tool to soften.

Certain alloy steels containing about 1% aluminium may secure great surface hardness by a treatment known as 'nitriding'. These metals are heated at about 500^{o}C in ammonia for several hours whence nitrogen atoms diffuse into the surface to form intensely hard nitride precipitates with the aluminium. No subsequent heat-treatment of these nitriding steels is then required.

The remaining types of alloys which are usually encountered

are the ferro-alloys, particularly ferro-manganese and ferro-silicon, and the heat-resistant super-alloys. These metals often contain only a few per cent of iron, however, and are not considered of prime importance with regard to this work.

1.3. Effects of the trace metals

Having outlined the types of metal with which the steel chemist might most commonly be concerned, the next step is to indicate the part played by the trace constituents of such materials. That the need for trace element analysis exists is indicative of the considerable influence exerted by these minor constituents on the characteristics of ferrous metals.

Where the presence of a particular trace element is regarded as beneficial, deliberate additions may be made during the production of the alloy. This may be done to improve, for example, the mechanical properties (such as tensile strength or ductility), corrosion-resistance or the hardenability by quenching. Frequently, however, these advantageous effects are accompanied by other, less desirable results. For example, sulphur is often added to steels to improve their machinability but it simultaneously causes severe embrittlement.

One important reason for the addition of many elements, including some of those dealt with in this work, is their ability to inhibit graphitization in cast iron. Upon cooling a cast piece, considerable internal stresses are set up which may be removed by the process of annealing. This consists of maintaining the metal at a temperature, below its melting point, for some time followed

by slow cooling to room temperature. While achieving the desired end, this treatment also causes the breakdown of the iron carbide, which normally exists in the alloy, into free graphitic carbon and results in a softened material. The presence of even very small amounts of elements such as tellurium, boron etc. helps to stabilize the iron carbide and, therefore, markedly inhibits this graphitization effect.

Thus, it is clear that whether their influences be advantageous or detrimental, it is frequently necessary to be able to control the trace constituents of all types of ferrous metals. This in turn requires accurate chemical analysis in order to establish the nature and amount of additions which are to be made and also to ensure that any pre-determined maximum levels of impurities are not exceeded.

The particular influences exerted by those elements which are specifically dealt with in this work are considered in greater detail in their respective chapters.

1.4. Analytical requirements

In considering which of the available methods is to be used to tackle the problem of ferrous analysis, two major requirements must be met. Firstly, it must be able to satisfy the chemical demands of the system under investigation. This means, in particular, that the chosen technique will be required to provide accurate and reliable determinations of small amounts of the element or elements of interest, typically down to about 0.01% in the specimen sample, despite the presence of large excesses of potentially interfering matrix elements. Thus, a high degree of selectivity and good

sensitivity are essential features.

Chemical considerations are only part of the story, however. Were this not the case, we would need to look no further than the classical chemical methods of trace analysis which have been in use for many years. Unfortunately, such methods are usually laborious and time-consuming and often require the use of highly-skilled operators. This brings us to the second important consideration, which is ultimately concerned with cost.

The demands of the modern laboratory are such that, before a particular analytical technique may find application, its chemical capabilities must be balanced against the overall cost involved in its use. This means that a chemically inferior technique may often be preferred on economic grounds.

There are three contributions to the overall cost of an analysis. Apart from the initial outlay involved in obtaining the appropriate equipment, it is necessary to consider both the cost of the operation and the time taken for its completion. From this viewpoint it is easy to see why the traditional chemical methods of analysis are no longer favoured, with many procedures taking several hours and rarely enabling more than one determination to be made. Modern instrumental techniques help to overcome this problem and, despite the high initial cost, can prove to be less expensive than traditional methods of analysis since they enable many more determinations to be made in a given time. In this respect too, the multi-element capabilities of the analytical technique are of considerable interest as, in many instances, the rapid determination of several elements may be required.

So, to summarise the important features discussed in this section, the ideal analytical technique for ferrous analysis should possess:

1) Good selectivity

not a Sentence

The ability to discriminate between the element of interest and the other elements present, often in great excess. This helps to avoid interference problems which might necessitate laborious chemical separation procedures.

2) Good sensitivity

not a Sentence

The ability to determine accurately very small amounts of the element of interest despite the presence of large excesses of other elements. In using instrumental methods, it is of importance, practically speaking, to have a long linear working range to the calibration curve in order that a wide range of analyses may be made under a given set of conditions. Thus, any attempts to improve the sensitivity of such a method which result in a marked deterioration of the linear range are not to be recommended.

3) Low initial cost

As little basic equipment as possible should be needed; the instrumentation should be simple and inexpensive.

4) Low cost of operation

Speed and simplicity of operation imply low cost, so measurement should be quick and easy to carry out; sample pre-treatment and other time-consuming procedures are to be avoided.

These are, of course, fairly broad headings which encompass a number of more specific points but, having outlined these salient features, the increasing importance of the part played in metallurgical analysis by atomic spectroscopic techniques becomes apparent.

1.5. Choice of technique

While not wishing to claim that they completely satisfy all of the above requirements, the three allied flame techniques of AFS, atomic emission spectroscopy (AES) and atomic absorption spectroscopy (AAS) are clearly much more applicable than other methods of inorganic analysis.

In comparison with most other techniques, AES, AAS and AFS are relatively free from interference problems and require very little sample pre-treatment. In this respect electrochemical methods, particularly, are sometimes at a great disadvantage in requiring quite lengthy separation procedures in order to obtain good selectivity. Such arguments also apply to solution spectrophotometric methods which, although still used in ferrous analysis to a limited extent, find considerably less application now than in the past. Chromatographic methods have also been successfully

applied to the analysis of ferrous metals, but lack the speed and simplicity of operation demanded by the modern analytical laboratory. Furthermore, even the highly automated techniques such as X-ray spectrometry and arc/spark emission spectrometry, which find extensive application in the metallurgical field, as well as the less widely used methods such as mass spectrometry and activation analysis, all suffer from the disadvantages of very high initial cost or the need for highly-skilled operators. Of course, in laboratories where the amount of routine work is sufficiently large to justify the high capital cost involved, such techniques are essential and an appreciation of the part they play in the field of steel analysis can be gained from reviews by Hughes (2), Ramsden (3) and Ohls (4).

1.6. Advantages of AFS

The least well-established of the three allied flame spectroscopic techniques, AFS exhibits certain distinct advantages (and disadvantages) over AES and AAS, being particularly suitable for non-dispersive measurements and simultaneous multi-element analysis. The reasons for this and the particular advantages of such a technique in the field of ferrous analysis are outlined in this section.

Although the instrumentation used for AF measurements (see Section 3.2.1.) is in many ways similar to that used in AES and AAS, the function of some of the basic components may not be the same. In particular, the rôle of the monochromator is considerably less important in AFS than in either AES or AAS.

In AE measurements, for example, a monochromator or an equivalent dispersive device is essential in order to provide the technique with any degree of selectivity, while in AAS a similar device must be used, viewing the source through the atom cell, in order to monitor the absorption of a single line from the emission spectrum produced by the source. In AFS, however, the monochromator does not view the spectral source nor does it greatly affect the selectivity of the technique, which is chiefly governed by the purity (freedom from other elements) of the source. Indeed, the only useful purpose served by the monochromator is to limit the amount of radiation falling on the detector. This may, of course, be a very necessary function if the detector has a wide spectral response and the emission from the atom cell is high. It is evident though, that by minimising such background emission and by using a detector with a limited spectral response, the monochromator may be dispensed with altogether.

There are many advantages to be gained from using this non-dispersive approach and these will be emphasised in this consideration of the more general features which make AFS such a suitable technique for steel analysis.

1) For elements with resonance lines which lie in the ultra-violet region of the spectrum, the limits of detection obtainable by AFS may be considerably better than those of flame-based AES, which is comparatively insensitive in that area. (This is particularly important in steel analysis for the determination of such elements as selenium, arsenic and antimony etc.). In addition, even greater sensitivity may be

obtained with a non-dispersive system, since the absence of a monochromator allows a much greater throughput of energy to the detection system. There is also the possibility of simultaneously collecting a number of lines for elements which exhibit complex fluorescence spectra. An associated feature of this increased sensitivity is the greater linear concentration range given by AFS, compared to AAS. Those ranges provided by AES are usually even greater but are limited to those elements with resonance lines which lie in the visible region of the spectrum.

2) AFS generally requires less complex equipment than AES or AAS. This simplicity of instrumentation is even more marked when one examines a non-dispersive AF spectrometer (see Section 3.2.2.) in which the absence of a monochromator, although partially off-set by the need for a detector of limited spectral response, greatly reduces the overall cost of the system.

3) Since the fluorescence process is dependent upon the absorption of radiation by ground state atoms, the technique of AFS is much less sensitive to temperature fluctuations within the atom cell than is AES. Moreover, comparatively cool flames, which would produce virtually no emission intensity, may be used for the determination of many elements by AFS. This is particularly fortunate if a non-dispersive approach is to be used since, as mentioned previously, it is necessary to reduce the background emission from the atom cell as much as possible. A wide choice of flames is, therefore,

desirable in order to combine the free production of atoms with the least background emission, for the elements of interest.

4) Given that an analysis of the trace metals in steels involves the determination of several different elements, the value of rapid multi-element analysis becomes apparent. It is in this respect that the ease with which AFS lends itself to non-dispersive measurements is of prime importance.

A feature of AFS in general is that the intensity of the measured fluorescence emission is dependent upon the intensity of the spectral source employed. Thus, the simultaneous determination of several elements of widely differing concentrations may be readily achieved, with no instrumental adjustments required, simply by controlling the intensity of the source or sources, although this does necessitate the use of a pre-aligned monochromator for each element to be determined.

The non-dispersive approach obviates the need for such a system, however, making rapid, sequential multi-element analysis easily achieved since, in changing from one element to another, no adjustment of the detection system is necessary. Furthermore, there is no possibility of wavelength drift and the instrument is very easily aligned.

There are, however, a number of disadvantages associated with the technique, although many of them may be overcome fairly easily.

1) As in AAS, a spectral source is required, usually a different one for each element. The requirements of the source

in AFS (see Section 3.2.1.(a)) are not always easy to meet and this is particularly important in non-dispersive work where the selectivity of the technique depends wholly on the spectral purity of the source. Moreover, even with a completely pure source, the chances of spectral overlap interferences (see Section 2.2.3.) are considerably greater in non-dispersive AFS than with a monochromated system.

2) AFS is not suited to the determination of those elements which have their resonance lines in the visible region of the spectrum. Such elements, being fairly easily excited, produce intense emission signals which may overload the detection system and cause a marked increase in the noise level.

Elements which form refractory oxides are also difficult to determine by AFS and high-temperature flames, with their associated high background emission, are often required in order to produce adequate atomisation. Furthermore, the quenching effect of the gaseous species present in such flames may greatly reduce the intensity of the fluorescence signal.

Non-dispersive AFS also suffers from the inability to determine many elements. In using a solar-blind photomultiplier detection system (p.44) with a limited spectral response, the technique is confined to the determination of those elements which produce appreciable fluorescence intensities within that spectral range. Thus, those elements which lie outside that range can only be determined by using a different detection system and this may mean that background emission from the atom cell, for example, may become a problem.

3) The principal difficulty encountered in non-dispersive AFS, in particular, is the problem of dealing with the scattering of radiation from the source by particulate material present in the flame. In the field of ferrous analysis, the high iron concentrations present in the samples under investigation can cause a great deal of such scattering and the methods by which this difficulty may be overcome are considered in depth in this thesis.

1.7. Summary

Non-dispersive AFS is clearly a potentially powerful analytical technique for ferrous analysis, particularly as an inexpensive method for the routine determination of several of the trace elements which commonly occur in steels. The work presented in this thesis is designed to demonstrate the practicability of the technique.

CHAPTER TWO

AFS AND ITS APPLICATION TO METALLURGICAL ANALYSIS

2.1. Introduction

Although this thesis is primarily concerned with the practical application of AFS, it would be wrong to ignore completely the theoretical aspects of the technique. Thus, a brief discussion of the theory of atomic fluorescence measurements is included in this chapter, after which the application of AFS to metallurgical analysis is reviewed.

2.2. Theory of atomic fluorescence measurements

The atomic fluorescence process involves the irradiation of the atomic form of the element under investigation by an external excitation source. Absorption of some of this exciting radiation subsequently leads to deactivation and emission of radiation which is indicative of the nature and amount of the absorbing species.

2.2.1. Types of atomic fluorescence process

The types of atomic fluorescence process are classified according to the electronic transitions involved and the main types may be summarised as follows:

1) Resonance fluorescence

The excitation and deactivation processes take place between the same energy levels, giving rise to fluorescence emission of the same wavelength as the radiation which caused the excitation of the atomic species.

2) Direct-line fluorescence

After excitation of the atomic species from its ground state by the absorption of some of the radiation from the source, deactivation to an intermediate energy level occurs, giving rise to fluorescence emission of a longer wavelength than the exciting radiation. The atom subsequently returns to the ground state, with no further emission of radiation (e.g. by a collisional deactivation process).

3) Stepwise line fluorescence

After excitation of the atomic species, a radiationless transition to an energy level intermediate to the ground state may occur, followed by a radiative deactivation to a still lower level (often the ground state). Such a process results in fluorescence emission of a longer wavelength than that of the exciting radiation.

4) Stepwise excitation fluorescence

This process typically involves the excitation of the atomic species by the absorption of radiation, followed by further excitation to a slightly higher energy level. Subsequent deactivation, either to the ground state or to an intermediate level, gives rise to the emitted fluorescence radiation.

5) Sensitised fluorescence

This process requires the presence of donor atoms which,

after excitation by the absorption of radiation, transfer their energy to atoms of a different species. Thus excited, these atoms may then undergo radiative deactivation. Sensitised fluorescence is of little importance in flame AFS, however, as the concentration of donor atoms in the atom cell is unlikely to be high enough to produce sufficient collisional excitation.

These processes have been discussed in considerably greater detail by Kirkbright and Sargent (5).

2.2.1. Considerations of fluorescence intensity

In this section no attempt will be made to derive rigorously expressions for atomic fluorescence intensity, these calculations having been excellently dealt with by Hooymayers (6), Zeegers and Winefordner (7) and Kirkbright and Sargent (5).

Under ideal conditions, i.e. that

1) the considered fluorescence transition is excited by absorption of energy of one wavelength only,
2) the entire fluorescence cell is within the solid angle viewed by the detector and
3) none of the fluorescence emission is lost by reabsorption within the cell,

we find that, for a continuum source,

$F = aN$ at low concentrations

and that $F = bN^{\frac{1}{2}}$ at high concentrations

where F is the fluorescence intensity,

N is the ground state population

and a, b are constants.

Moreover, for a line source, we find that

$F = cN$ at low concentrations

and that $F = d$ at high concentrations

where c, d are constants.

These relationships are of little practical value, however, and it is necessary to extend the treatment to the non-ideal case. After such considerations, we eventually find that

$$F = \frac{\Omega}{4\pi} V \phi \frac{8\pi}{(\lambda')^2 A N_o} \frac{g_o}{g_1} \int_o^\infty \alpha \, \delta\nu \cdot \int_o^\infty \beta \, \delta\nu'$$

where Ω is the solid angle viewed by the detector,

V is the height of the atom cell,

ϕ is the fluorescence yield,

λ' is the wavelength of the fluorescence line,

A is the transition probability of the fluorescence line,

g_o and g_1 are the respective statistical weights of the lower and upper states,

N_o is the population of the lower state

and $\alpha = I_\nu \exp(-k_\nu \Delta L)[1-\exp(-k_\nu L)]$,

and $\beta = \exp(-k_{\nu'} \Delta W)[1-\exp(-k_{\nu'} W)]$

where I_ν is the incident radiation flux at frequency ν,

k_ν is the absorption coefficient at frequency ν,

$k_{\nu'}$ is the absorption coefficient at frequency ν',

L is the length of the atom cell

and W is the width of the atom cell.

Evaluation of this equation enables theoretical analytical curves to be constructed (6, 7). It may be seen that the intensity of the fluorescence emission depends upon

1) the intensity of the exciting radiation from the spectral source,
2) the fraction of this radiation which is absorbed before it reaches that area of the atom cell viewed by the detector,
3) the fraction of this radiation absorbed by the atomic species under investigation,
4) the fraction of this absorbed radiation which is converted to fluorescence emission,
5) the fraction of this fluorescence emission which is absorbed before it may be detected and
6) the type of fluorescence process involved.

This last point, in particular, slightly complicates the situation encountered in non-dispersive work but, in general, the overall fluorescence intensity produced simultaneously by a number of lines may be considered as the summation of the individual intensities of each line.

2.2.3. Interferences in AFS

Any process which modifies the size of the true fluorescence signal may be described as an interference. Such alterations to the analytical signal may result from any of a number of effects which are conveniently classified as spectral, physical or chemical interferences.

1) Spectral interferences

Such effects may arise either from the scattering of source radiation, by the overlap of the line profiles of two species present in the atom cell or by the detection of background emission.

The scattering of incident radiation, typically by particulate material in the flame, is quite important in non-dispersive AFS. Even with a dispersive system, resonance fluorescence measurements may be greatly enhanced as a result of the scattering of radiation from the source. In this case, however, measurement of direct-line or stepwise fluorescence eliminates such difficulties. The same is not possible with a non-dispersive system, unfortunately, and the effects of scattered radiation have to be corrected for, rather than eliminated.

The occurrence of spectral line overlap interferences is well known in AFS. This type of interference can be encountered if there is present in the atom cell a concomitant species with a resonance line of a wavelength almost coincident with that of the element under investigation. As an extension of this effect, if a continuum source or an incorrectly operated line source is used in AFS, it is possible to stimulate fluorescence emission from two elements simultaneously at wavelengths that are sufficiently close together. In particular, arsenic emission at 228.812 nm has been used to stimulate cadmium resonance fluorescence at 228.802 nm (8) while the AFS determination of bismuth may be conveniently carried out using an iodine excitation source (9, 10).

The interference problems produced by the background emission radiation from the atom cell are frequently overcome by the use of an AC source and detection system. Generally, the emission from flames may be of sufficient intensity to overload the photomultiplier severely and, although this signal is not amplified by an AC detection system, a considerable increase in noise level may result. Efforts should be made to minimise background emission before detection, however, and the methods used to do this in this work will be described later.

2) Physical interferences

Any alteration of the concentration of analyte atoms present in the atom cell which arises from a modification of the physical processes involved in nebulisation and atomisation may be termed a physical interference.

Such types of interference may often be encountered when using flame cells and are usually the result of increased solution viscosity, due to the presence of large amounts of matrix material, such that the rate of aspiration of the sample may be decreased. The physical properties of the sample solution, i.e. the surface tension, vapour pressure, temperature etc., may also affect its aspiration rate as well as altering the rate of the atomisation process. There is also the possibility of some of the analyte atoms becoming occluded within the solid particulate material formed during evaporation of the sample solution.

Where interference problems in AFS are known to result from

the physical processes described above, they may be overcome by preparing standard solutions with physical properties similar to those of the sample solutions.

3) Chemical interferences

This type of interference may be encountered when the concentration of the analyte atoms in the cell is altered as a result of reactions with concomitant materials present in the sample solution. Such reactions may occur in either the solid or vapour phase but are usually quite easily overcome, often by the addition of various agents to the sample solution or the judicious choice of flame stoicheiometry etc.

To complete this section on interferences in AFS, a brief description of fluorescence quenching is included at this point. While not strictly an interference, the process of quenching may certainly reduce the intensity of the fluorescence emission as a result of collisional deactivation of excited analyte atoms by foreign atoms or molecules present in the atom cell.

The quenching effect of molecules is generally greater than that of atoms and this is usually attributed to the large number of vibrational energy levels present within molecules which can facilitate the transfer of energy from the excited analyte atoms. For this reason, argon has found wide application as a flame diluent and separator, although nitrogen may be used for the determination of many elements with only a small loss of analytical sensitivity.

Kirkbright and Sargent (5) have discussed the mechanism of quenching processes in some detail and have also included a very informative chapter on the interferences briefly described above.

2.3. The application of AFS to metallurgical analysis

To date the application of AFS to metallurgical analysis has been reported for the determination of 18 elements in a wide variety of matrices. These applications are described in detail in this section with particular emphasis on those determinations in which a non-dispersive approach is used (10, 24, 28, 29).

Antimony:

Norris and West (11) have reported the determination of antimony in copper-based alloys using an electrodeless discharge lamp (EDL) and an argon-hydrogen diffusion flame. Samples were dissolved in aqua regia and diluted with water after which a sodium nitrite solution was added, followed by extraction with methyl iso-butyl ketone (MIBK). The reported limit of detection for antimony was 0.02 µg/g.

Arsenic:

The determination of arsenic in steels has been described in a paper by Michel, Ebdon and Hubbard (12). An EDL source and a nitrogen-flushed monochromator were used to obtain a detection limit for arsenic of 0.01 µg/ml at 189.0 nm, interference problems not being encountered in the air-acetylene flame.

Arsenic in nickel-based alloys has been determined by Dagnall, Taylor and West (13), down to 1 ppm in the alloy, with a nitrogen-hydrogen diffusion flame. Interferences were eliminated by solvent extraction.

Bismuth:

A method for the determination of bismuth in steels based on the extraction of the bismuth-APDC (ammonium pyrrolidine dithiocarbamate) complex into MIBK has been described (14). The bismuth EDL employed gave a detection limit of 0.012 µg/ml at 306.8 nm in an argon-hydrogen-oxygen flame and no interferences were observed when bismuth was determined in high-alloy steel.

Hobbs and co-workers have utilised the spectral line overlap of bismuth and iodine to determine bismuth in aluminium alloys (15), the 206.16 nm line from a modulated iodine EDL being used to stimulate bismuth direct-line fluorescence at 302.5 nm. Nitrogen-separation enabled measurement at this wavelength to be made without interference from the hydroxyl radical emission normally encountered in the air-acetylene flame.

An air-propane flame was used by Dagnall, Taylor and West (13) to determine bismuth down to 1 ppm in nickel-based alloys, although solvent extraction was found to be necessary to overcome interference problems from the matrix.

A non-dispersive approach to the determination of bismuth in various iron-based and nickel/cobalt alloys has also been reported (10). An absolute limit of detection for bismuth of 4×10^{-11} g was obtained using an iodine EDL and a resistively heated tantalum loop atomiser, the linear dynamic range extending over four orders of magnitude.

Cadmium:

Malmstadt and Cordos (16) have described an automated atomic fluorescence spectrometer which can determine up to eight elements, including cadmium, in steels, bronzes and zinc alloys on a rapid, sequential basis. Standard hollow-cathode lamps (HCLs) were used and interchange from one element to another required about three seconds.

In addition, Murugaiyan and co-workers (17) have determined cadmium at 228.8 nm in high-purity zinc, copper and indium using an air-acetylene flame.

Calcium:

The determination of calcium in metal alloys using an argon-hydrogen-oxygen flame was included in the work of Malmstadt and Cordos (16) described previously.

Chromium:

A number of workers have reported the application of AFS to the determination of chromium in steels. In particular, Norris and

West (18) were able to measure contents of up to 25% of chromium using a dual-element EDL and a separated air-acetylene flame, although at low concentrations extraction of iron with amyl acetate was found to be necessary.

In a paper describing the cathodic sputtering technique for the direct analysis of solid samples of metals and alloys by AFS (19), Walsh included the determination of chromium in low-alloy steels and reported a limit of detection of 20 µg/g.

The application of cathodic sputtering to the analysis of flat, metallic samples was also reported by Gough, Hannaford and Walsh (20), linear calibration curves being obtained for the determination of five elements, including chromium, in various iron-based alloys.

In addition, Malmstadt and Cordos (16) included the determination of chromium in metal alloys in their paper on the application of an automated AF spectrometer to metallurgical analysis.

Cobalt:

A dual-element EDL and an argon-separated air-acetylene flame were used by Norris and West (21) for the determination of cobalt in steels. Dilute aqua regia solutions of steel were aspirated and the fluorescence emission measured at 240.7 nm. After correction for thermal emission by cobalt, these signals were matched against those obtained from pure cobalt solutions and the method was reported to be accurate and precise.

Copper:

A six-channel prototype AF spectrophotometer was used by Dagnall, Kirkbright, West and Wood (22) for the simultaneous determination of up to six elements, including copper, in a number of aluminium alloys. The fluorescence measurements for all six elements could be read in a cycle of only 16 seconds duration and the reported limit of detection for copper was 0.03 µg/ml at 324.8 nm. Pulse modulated HCLs and a nitrogen-separated air-acetylene flame were used in this work.

The determination of copper in aluminium alloys has also been reported in a very interesting paper by Butler, Laqua, Hagenah and Kroger (23). These workers used a Grimm glow discharge lamp (GDL) as excitation source with fluorescence detection using single element, demountable resonance detectors and reported a detection limit of 65 µg/g for copper.

The application of cathode sputtering to the determination of copper was reported in two papers by Walsh (19, 20), who quoted a detection limit of 20 µg/g in low-alloy steels. This technique enables direct analysis of solid samples to be made and simultaneous, multi-element analysis is possible, with very little interference problems.

Copper in metal alloys has also been reported by Malmstadt and Cordos (16).

Iron:

Apart from Malmstadt and Cordos (16), only Dagnall, Kirkbright, West and Wood (22) have reported a metallurgical application of AFS to the determination of iron, specifically in aluminium alloys, obtaining a detection limit of 0.1 µg/ml at 248.3 nm.

Lead:

A non-dispersive approach to the determination of lead in various nickel/cobalt alloys has been reported by Mounce (24) using a tantalum loop atomiser, although extensive sample pre-treatment was found to be necessary in order to achieve the desired sensitivity.

Similar findings were reported by Dagnall, Taylor and West (13) in a paper dealing with the determination of a number of elements, including lead, in nickel-based alloys. As no certificated standards were available, simulated alloy solutions were used, lead being extracted from these solutions into MIBK, with measurement of the direct-line fluorescence signal at 405.8 nm (after excitation at 283.3 nm). Under these conditions, the limit of detection in an air-propane flame was found to be 0.015 ppm. The validity of this method of sample preparation was checked by applying it to the determination of lead in various British Certificate Steels (BCS 326 $\longrightarrow$ 329).

Magnesium:

Magnesium has been included in the multi-element schemes of Malmstadt and Cordos (16) and Dagnall, Kirkbright, West and Wood (22).

The latter paper quotes a limit of detection of 0.008 µg/ml at 285.2 nm for magnesium and claims excellent agreement with various BCS certificated aluminium alloy samples.

Manganese:

A dual-element EDL containing chromium and manganese was used by Norris and West (18) to determine contents of up to 0.85% manganese in steels. The fluorescence measurements were made at 279.8 nm in a separated air-acetylene flame and, although sample pre-treatment was not generally found to be necessary, the extraction of iron with amyl acetate was required when the total content of chromium and manganese in the steel was less than 0.5%.

Two papers deal with the application of cathode sputtering to the determination of manganese in iron-based alloys (19, 20). The first reports a detection limit of 70 µg/g in various low-alloy steels, while the second (20) deals with the analysis of a number of certificated steels (BCS 401 $\longrightarrow$ 410). Linear calibration curves were obtained and the reproducibility of the technique was $\pm$ 1%.

In addition, Dagnall, Kirkbright, West and Wood (22) have reported the determination of manganese in aluminium alloys, using a nitrogen-separated air-acetylene flame to obtain a detection limit of 0.06 µg/ml at 279.5 nm. Malmstadt and Cordos (16) too, have included manganese in their multi-element work.

Nickel:

An analytical procedure for the determination of nickel in steels has been described by Norris and West (21). A dual-element EDL containing cobalt and nickel was used to excite the fluorescence which, in the case of nickel, was measured at 232.0 nm. Direct aspiration of a dilute aqua regia solution of the steel samples into an argon-separated air-acetylene flame was found to give no significant interference problems.

Direct analysis of solid steel samples has been reported by Walsh (19, 20) with the limit of detection for nickel being 20 µg/g using the technique of cathode sputtering, while nickel in aluminium alloys was reported by Dagnall, Kirkbright, West and Wood (22). Measurements at 232.0 nm gave a detection limit of 0.07 µg/ml.

Selenium:

The only reported application of AFS to the determination of selenium in metals has been that of Dagnall, Taylor and West (13) who outlined a solvent extraction method for the determination down to 1 ppm in nickel-based alloys. Extraction of selenium into MIBK was followed by atomic fluorescence measurement at 196.1 nm in an air-propane flame, giving a limit of detection of 0.025 ppm. Only molybdenum was found to interfere significantly and had to be removed by back-extraction.

Silicon:

The cathodic sputtering technique has been applied to the

determination of silicon in various iron-based alloys and low-alloy steels by Walsh (19, 20), typically at levels of about 400 µg/g. Kirkbright, Rao and West (25) have, however, reported a more conventional, and more sensitive, method for the determination of silicon in low-alloy steels in which a separated nitrous oxide-acetylene flame was used and atomic fluorescence measurements made at 351.6 nm. The reported detection limit of 0.7 ppm compares favourably with the atomic absorption detection limit of 4 ppm at the same wavelength.

Tellurium:

A solvent extraction procedure for the determination of tellurium in simulated nickel-based alloy solutions has been described (13). Extraction into MIBK followed by measurement at 214.3 nm in an air-propane flame gave a limit of detection for tellurium of 0.007 ppm with no significant interference problems.

Tin:

Ebdon, Hubbard and Michel (26) have reported the determination of tin in steels, with detection limits of 0.05 µg/g using an argon-separated air-acetylene flame and 0.01 µg/g with an argon-oxygen-hydrogen flame, at 303.4 nm. The most serious interference effects were eliminated by adding ferric chloride to the standard calibration solutions and removal of silicon was found to be necessary.

Zinc:

That zinc is one of the more easily determined elements by AFS may be seen from the large number of papers which deal with this element. Murugaiyan and co-workers (27) have recently described the determination of zinc in high purity copper, indium and cadmium at the 1 µg/g level using an air-acetylene flame. Measurements were made at 213.9 nm although, for the determination of zinc in cadmium, interference problems were encountered in the form of ionic fluorescence of cadmium at 214.4 nm caused by the presence of cadmium impurities in the zinc EDL. In order to overcome this, it was necessary to use a cadmium-free lamp or to suppress ionisation by adding potassium to the test solutions.

In addition, Malmstadt and Cordos (16) have determined zinc in various metal alloys and Dagnall, Kirkbright, West and Wood (22) have reported a detection limit of 0.008 µg/ml for zinc in aluminium alloys using the six-channel Technicon AF spectrophotometer.

A non-dispersive approach to the determination of zinc has also been adopted. Norris and West (28) have described the use of a non-dispersive AF spectrometer for the determination of zinc in soils and non-ferrous metal alloys and Warr (29) has described the determination of zinc in copper down to 0.1 µg/g using an air-acetylene flame, although his system is best described as "low-dispersive".

CHAPTER THREE

ATOMIC FLUORESCENCE INSTRUMENTATION

3.1. Introduction

Although some instrument manufacturers produce atomic absorption spectrometers which have provision for the attachment of atomic fluorescence accessories, there is no purpose-built commercially available AF instrument at present. This seems to be due to the prevalent feeling among manufacturers that AFS fails to show any significant practical advantages over AAS, except in the area of simultaneous multi-element analysis (where the expense involved in production, however, may be considerable).

Some years ago a six-channel non-dispersive AF spectrometer (Technicon Corporation, Model AFS-6) based upon the design of Mitchell and Johansson (30) became available (31) but, despite some encouraging applications (22, 32), the high cost of the instrument lead to its discontinuation.

Thus, most AFS work is usually carried out on modified AA spectrometers or laboratory-constructed AF instrumentation. Nevertheless, this approach frequently gives rise to very versatile and quite sophisticated spectrometers (16, 33-43) with the tendency at present being towards highly automated, often computer-controlled, multi-element systems.

In this chapter, the basic features of AF spectrometers are discussed, after which the instrumentation used in this work is described in detail.

3.2. Complete systems

3.2.1. Conventional AF system

Figure 3.1 shows a schematic representation of a conventional dispersive AF system.

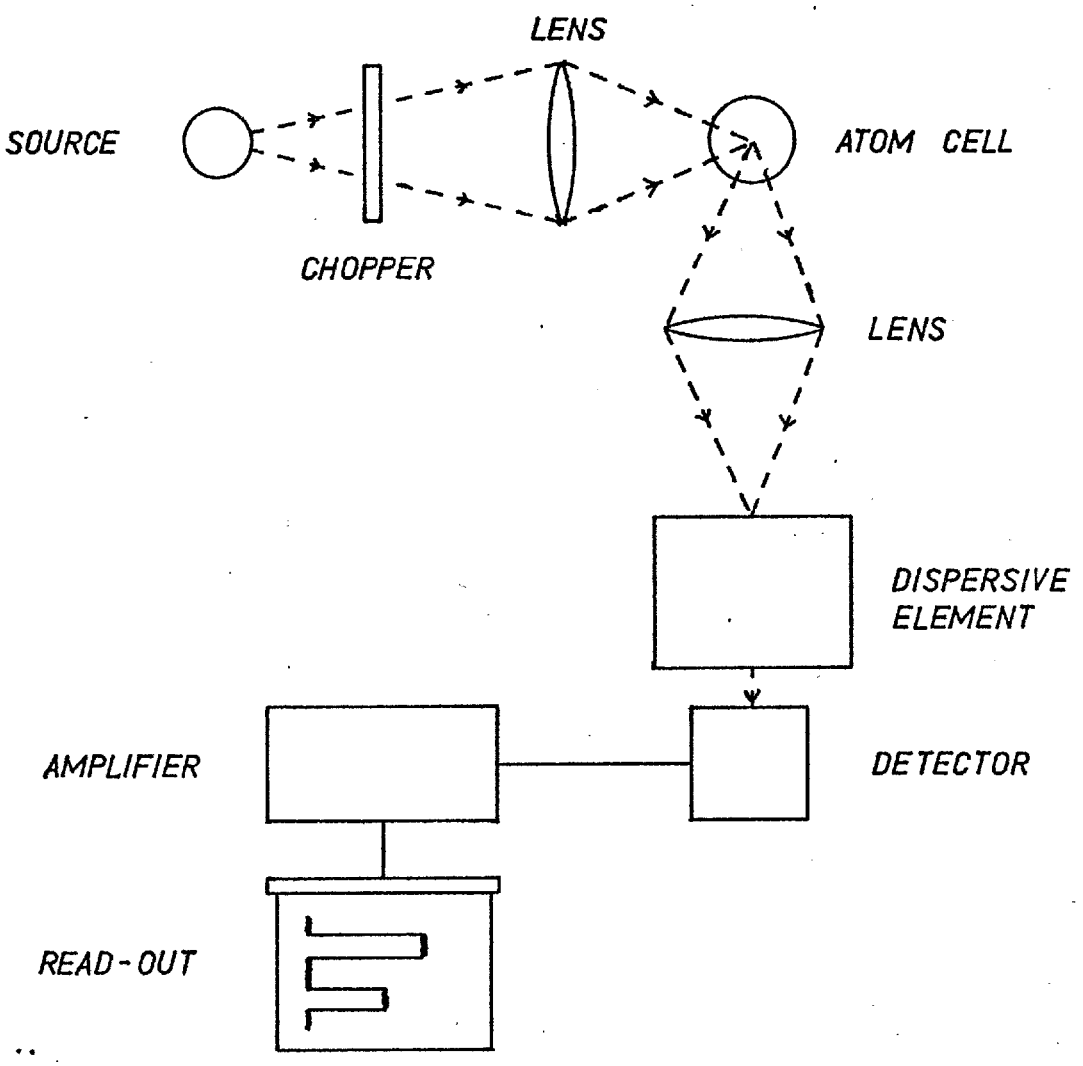
3.2.1.(a) The spectral source

Although many types of excitation source may be used in AFS, the most commonly used are the metal vapour discharge lamp (VDL), the hollow-cathode lamp (HCL) and the microwave-excited electrodeless discharge lamp (EDL) since such sources possess, to varying degrees, the essential features of high intensity and stability required by the technique.

The VDL now finds much less application than in the past since, although this type of source gives excellent intensity, it suffers severely from the effects of line-broadening and self-absorption (unless operated at low powers, whence the lamp intensity is considerably reduced). Moreoever, as the range of elements for which these sources may be used is quite small, they lack the versatility of the other types of source presently available.

In contrast, hollow-cathode lamps are available for a wide range of elements but give insufficient intensity for most AF applications. However, intensity enhancement can be achieved either by operating the lamp for short periods of time at currents well above the manufacturer's recommended maximum or by using an additional discharge from a second cathode to excite the sputtered

Figure 3.1 CONVENTIONAL AF SYSTEM



atomic vapour produced by the first (44). High intensity lamps of this type reported by Lowe (45) have found wide application in AFS, especially in the non-dispersive work of Larkins (46, 47).

The demountable HCL, in which cathodes of different metals may be employed, has been described by Dinnin and Helz (48) and used for the AF determination of a number of elements (49). In addition, Omenetto and Rossi have described the water-cooled HCL (50) and its application to AFS, quoting limits of detection for twelve elements. In general, however, the demountable HCL offers no great advantage over conventional lamps, unless the determination of several elements is required, and is not widely used for routine analysis.

Perhaps the most popular type of narrow-line source, especially since the advent of suitable temperature-controlling devices, has been the EDL. The application of these sources to AFS was originally somewhat limited owing to the instability of their output compared to that of conventional HCLs, but after Winefordner and co-workers (51) demonstrated that the problems of EDL operation could be overcome by simple temperature-control, their popularity increased considerably. Fixed-temperature operation also facilitates the use of multi-element lamps for the simultaneous determination of a range of elements by AFS.

EDLs are now used extensively in AFS for the determination of many elements and are generally regarded as extremely useful sources. Bartley (52) has compiled a comprehensive 'list of previously reported EDLs' which is of great value to those workers

wishing to construct their own lamps (as is the review of Haarsma and co-workers (53) on the preparation and operation of EDLs).

The advent of the tunable organic dye laser has been of considerable importance to many AF workers since the narrow line widths and high intensity of emission associated with this type of source enable excellent limits of detection to be obtained for many elements (54-60). Indeed, a theoretical discussion by Piepmeier (61) on the use of lasers to saturate the excited state of an element indicates that, under such conditions the magnitude of the fluorescence signal becomes virtually independent on the intensity of the source. The exceptionally high cost of laser-type sources (together with the unsuitability of the cheaper commercial units, which operate mainly in the visible region of the spectrum) has limited the extent to which they have found routine application in AFS, however. Nevertheless, it seems certain that if a reasonably priced laser source capable of operation in the ultra-violet region is produced, it would be used extensively for a variety of applications.

Some other types of line source have also been used for AFS but with no significant advantages in performance over the more commonly used types of source already discussed. In general, these sources give poor intensity or suffer severely from self-reversal.

Continuum sources are quite widely used by many AF workers since they enable the fluorescence of a wide range of elements to be excited using just one source. The most commonly encountered source of this type is the high pressure xenon arc lamp, although

recent developments in this area have included the investigation of the use of the exploding wire as an intense source of radiation (62). Scattering of radiation can be a serious problem in AFS when using a continuum source, however.

3.2.1.(b) The atom cell

Despite the increasing interest in non-flame cells, the flame is still probably the most widely used means of producing an atomic population in AFS. This is due to the extreme flexibility and versatility of operation when using this type of atom cell for practical analysis, as many practical problems can be overcome by altering the type or composition of the flame. Several types of flame have been employed in AFS but the most commonly used are the hydrogen flame, the air-acetylene flame and the nitrous oxide-acetylene flame. Each of these possesses certain distinct features which govern its suitability for any particular application.

Hydrogen flames (usually air-hydrogen or argon-oxygen-hydrogen) exhibit exceptionally low background emission which is of importance in obtaining good sensitivity and precision in AFS. Moreover, these flames do not cause any great degree of fluorescence quenching and can, therefore, give good limits of detection for many elements. However, the practical applications of hydrogen flames are limited to some extent because of their comparatively low temperatures. This often means that some elements may not be satisfactorily determined as a result of poor atomisation or susceptibility to matrix interference effects.

In contrast, the air-acetylene flame has found considerable practical application in AFS as its higher temperature helps to overcome the matrix interference problems often encountered. Thus, even though the air-acetylene flame exhibits a higher level of background and contains a greater concentration of fluorescence quenching species than the hydrogen flames, it has proved to be a popular choice for many applications.

It many instances, however, even the air-acetylene flame may fail to give efficient atomisation of the sample or fail to avoid the interference effects of the matrix material. Under these circumstances, the use of the extremely hot, but considerably less stable nitrous oxide-acetylene flame may help to overcome these difficulties. This flame is particularly effective at breaking down the comparatively stable refractory oxides of elements such as aluminium and beryllium and can, therefore, provide good limits of detection in situations where other types of flame prove to be inadequate (63-66). The major limitations on the use of the nitrous oxide-acetylene flame come from the very high level of background emission (even greater than that of the air-acetylene flame) and the high concentration of fluorescence quenching species present. However, Winefordner and co-workers (54, 55, 67) have shown that, by using a tunable laser as the spectral source and with an efficient system of detection, excellent sensitivity may be obtained for several rare-earth and refractory-oxide type elements because of the high degree of atomisation produced by this flame.

Distinct from the pre-mixed types of flame which have been discussed up to this point are the laminar diffusion flames and the total-consumption type flames. These are mentioned only briefly here as their application in AFS is somewhat limited (particularly the diffusion flames which often give poor atomisation and suffer greatly from chemical interference effects).

Sample introduction into a flame atom cell is best effected in liquid form and, to this end a nebulisation device which can present the sample solution to the flame in the form of a fine mist or spray is generally used. A variety of such devices may be encountered, but the most common are pneumatic nebulisers which are operated by a high velocity jet of the flame support gas. In addition, ultrasonic nebulisation, in which the liquid sample is broken up by vibrating crystal transducers, may be used. Other types of nebulisation device include centrifugal nebulisers, which employ a rapidly spinning disc to break up the liquid, and electrostatic nebulisers, which operate by producing a spark at the surface of the liquid.

Despite the general usefulness and versatility of flames as atom cells, situations often arise in which their performance may prove to be unsatisfactory. In such cases, perhaps where only a very small volume of sample is available, the use of a non-flame atom cell may be preferred. These devices are usually resistively heated and enable precise control to be exerted over the sample atomisation procedure. This in turn results in the reliable and efficient production of atoms

within the cell and generally gives rise to better limits of detection for many elements than could be obtained using a flame cell. A review of furnace and filament type atom cells has been published by Kirkbright (68) and features some considerations of their application to AFS.

In addition, some metal filament devices have been used in AFS for the production of atomic vapour from small amounts of sample (24, 69). These take the form of a platinum or platinum-rhodium wire loop onto which is placed a drop of the sample solution which is then vaporised by resistive heating of the atomiser. Mounce (24), in particular, has used such a device for the determination of a number of elements in various metal alloys, although considerable sample pre-treatment was found to be necessary before measurement could be made.

Perhaps the most promising method of sample presentation in AFS appears to be the technique of hydride generation (70). Excellent limits of detection may be obtained for several elements (71, 72) using this approach which has already found some practical AAS application in metallurgical analysis (73, 74).

Another particularly useful method of atomisation for the analysis of metals by AFS is the cathode sputtering technique. With this method good limits of detection have been obtained for the determination of nickel, chromium and copper in solid samples of some iron-based alloys (20), while Walsh (19) has reported the determination of a similar range of elements in low-alloy steels. The major advantage to be

derived from this method of atomisation is that no chemical pre-treatment of the sample is necessary, although suitable solid standards are required.

The remaining types of atom cell which have been used for AFS include the radio-frequency induction heated carbon bed (75) which proved to be unsuitable for the determination of cadmium and mercury in air only because of the fluorescence quenching effect of carbon monoxide and nitrogen in the atomised sample, the tantalum sampling boat (76) and a radio-frequency pulse system which generates an atomised sample vapour (77). Finally, a number of flameless cells for the cold-vapour determination of mercury by AFS have been reported (78-84). Such devices are, in fact, commercially available as accessory kits for many atomic absorption instruments.

3.2.1.(c) The optics and dispersive element

The purpose of the optical components in an AF spectrometer is to focus the radiation from the spectral source into the atom cell and to collect as much fluorescence radiation as possible. To this end, a variety of arrangements have been devised which employ various combinations of mirrors and silica lenses (for high transmission in the ultra-violet region of the spectrum) as well as the system of Shull and Winefordner (85) which consists of a polished aluminium ellipse with the spectral source and atom cell each situated at a principal focus. This arrangement gives a considerable increase in sensitivity for many elements as a result of the highly efficient irradiation of the sample in the atom cell.

Wavelength selection in dispersive AF systems is usually effected by prism or grating monochromators although for some applications the use of simple interference filters may be preferred. These tend to have a higher transmission than that of a typical monochromator which is a considerable advantage in AFS but, as good quality interference filters are relatively expensive, their use is best confined to the routine determination of, perhaps, one or two elements.

Some of the difficulties traditionally associated with conventional monochromators (such as wavelength drift or poor transmission) can be overcome by the use of resonance monochromation as described by Russell and Walsh (86). With this type of wavelength selection, fluorescence radiation from the atom cell is passed through an evacuated bulb containing atoms of the analyte element. This stimulates characteristic resonance fluorescence, the intensity of which is proportional to the intensity of fluorescence radiation from the atom cell, which may be detected and recorded in the conventional way. By isolating the wavelength of interest in this manner a relatively high level of transmission combined with a narrow bandpass may be obtained. The practical applications of such monochromators are somewhat restricted, however, owing to their limited life and instability of operation compared with ordinary dispersive devices. Some decrease in sensitivity may also be encountered when using this type of system, particularly for those elements which exhibit fairly complex fluorescence spectra, making it generally unsuitable for most fluorescence applications.

3.2.1.(d) The detection and signal processing system

Fluorescence radiation is detected almost exclusively by photoelectric devices which convert the light energy into an electrical signal suitable for amplification and measurement. These detectors range from the simple photocell to the extremely sensitive photomultiplier tubes which incorporate their own amplification system. The response characteristics of these tubes depend primarily on the nature of the material used as the photocathode which means that particular photomultipliers may be chosen for certain specific applications. This is of considerable value when using a non-dispersive approach as a detector of limited spectral response may be employed to minimise the effects of background radiation from the atom cell. The use of such detectors is considered in more detail in the next section.

Most photomultipliers may be used as part of a photon counting system in which the electrical signal is handled by a digital processing device. This sort of approach has many advantages over other methods of signal processing, especially in improving sensitivity to low light levels, increasing the signal-to-noise ratio and facilitating the integration of signals (87-89). Indeed, Arnold and Smythe (90) have described a digital AF spectrometer designed for the determination of selenium down to levels of 0.1 µg/ml. Most applications of flame AFS involve the use of an AC amplifier with a modulated spectral source, however, while the non-flame approach often requires high-frequency AC detection or, more commonly, DC

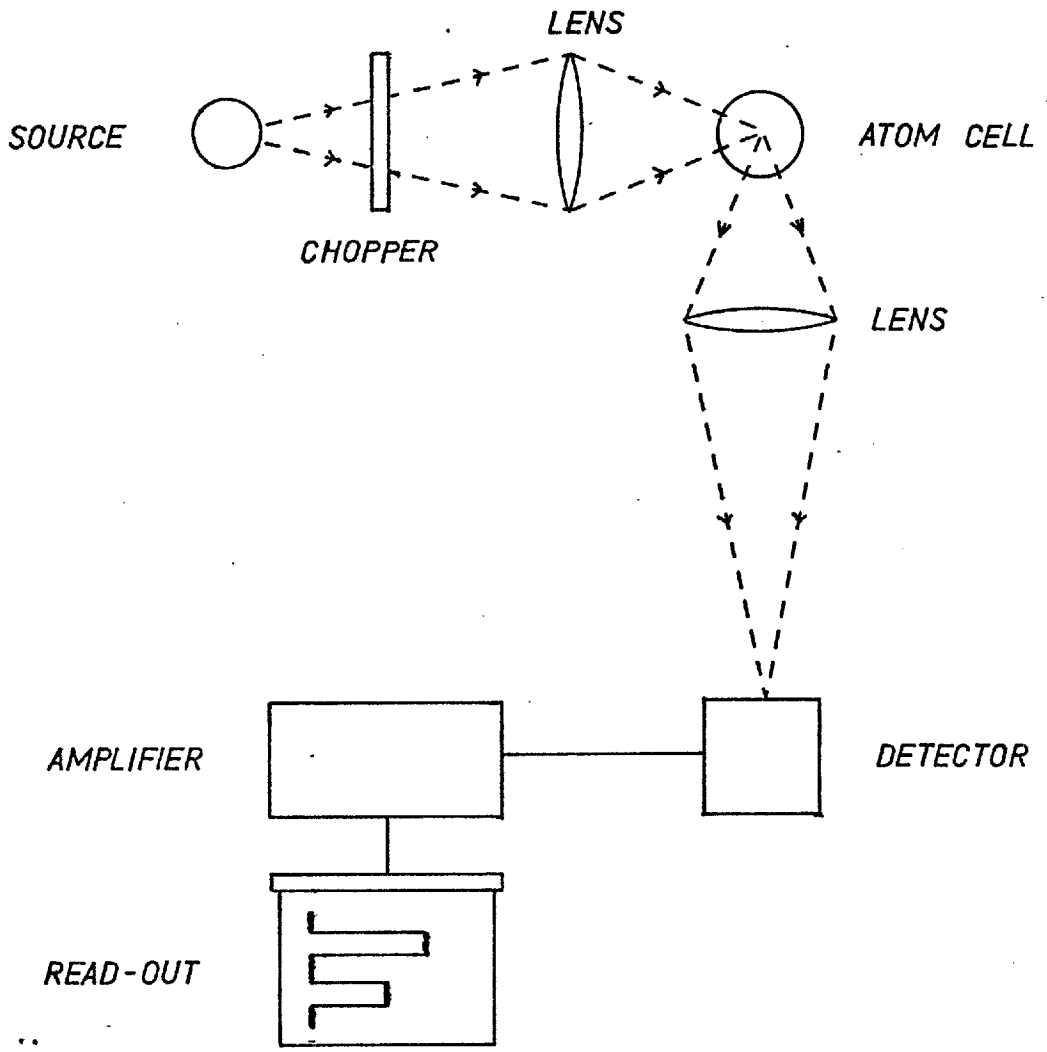
detection. In general, most types of recording device may be employed for signal presentation, although a fast-response unit (such as an oscilloscope) is usually necessary to monitor the transient atomic fluorescence signals generated by many non-flame atom cells.

3.2.2. Non-dispersive AF system

It can be seen from the schematic representation of a non-dispersive AF spectrometer shown in Figure 3.2 that the essential components are of the same type as those of the conventional dispersive AF system. It is generally true that the same individual units may be employed in both types of system, although the performance of the non-dispersive instrument may often be improved by using particular units more suited to such an approach. Since non-dispersive AFS features no form of wavelength selection a great deal of unwanted background radiation, particularly from the atom cell, may reach the detector and affect the overall performance of the system. The instrumentation used for non-dispersive AFS is usually chosen, therefore, with the intention of minimising or avoiding the effects of background radiation.

The most common method of achieving this is to use a detector of limited spectral response (i.e. one which is insensitive to the unwanted radiation but retains its sensitivity towards the fluorescence radiation). For most flame AFS applications the solar-blind photomultiplier has proved to be extremely useful since it does not respond significantly to radiation of wavelength greater than about 300 nm or less than 180 nm. (Typical response

Figure 3.2 NON-DISPERSIVE AF SYSTEM



characteristics are shown in Figure 3.11). Thus, the intense hydroxyl band emission, for example, which is produced by many flame atom cells falls outside the range of the detection system and the level of background radiation is accordingly reduced. Of course, the use of such a system may make the determination of those elements whose main resonance lines lie in the visible region of the spectrum more difficult (e.g. copper, silver or chromium) but, in general, most elements of interest can be determined. At worst, the limited spectral response may reduce the sensitivity of the instrument for the determination of some elements (e.g. lead, where the extremely sensitive 405.8 nm resonance line is undetected). Aidarov and co-workers (91) have described the use of a solar-blind photoresistor in the non-dispersive determination of copper and silver by flame AFS, moreover, which serves to underline that the capabilities of the technique are not unduly affected by choosing such types of detector.

Background radiation from flame atom cells may also be reduced by flame separation. This involves passing a stream of inert gas (usually nitrogen or argon) around the outside of flame such that the outer, secondary reaction zone is physically separated from the inner, primary reaction zone. An extended interconal region is then formed between these two zones and is accompanied by an overall decrease in the level of background emission. Applications of the separated nitrous oxide-acetylene and air-acetylene flames are widespread and typically result in ten-fold improvements in sensitivity.

Having minimised the level of background emission by the methods described above, the effects of this unwanted radiation can be reduced still further by suitable electronic processing. A most effective way of doing this is to use a modulated spectral source in conjunction with a phase-sensitive detection system. With this type of system only those signals of the correct frequency and in phase with a synchronously-generated reference waveform are accepted, while those components of the observed signal which are produced by the background radiation, being of a random nature, are rejected. The overall effect is to give a significantly improved signal-to-noise ratio. A more detailed consideration of the principles of phase-sensitive detection may be found in a paper by Blair and Sydenham (92).

Two papers have recently appeared (93, 94) which emphasise the importance of reducing the level of background radiation in non-dispersive AFS. These conclude that non-dispersive systems do not generally show any significant improvement in sensitivity in comparison with dispersive systems, except where the latter cannot be adjusted for optimum throughput of energy or where the background signal is very small.

A number of non-dispersive AF instruments have been described which incorporate some of the features described in this section (95-98) while several other spectrometers of this type are discussed, when appropriate, throughout this thesis. Moreover, the application of non-dispersive AF systems for the direct analysis of metals and alloys has been reviewed by Dagnall (99).

3.2.3. Simultaneous multi-element AF system

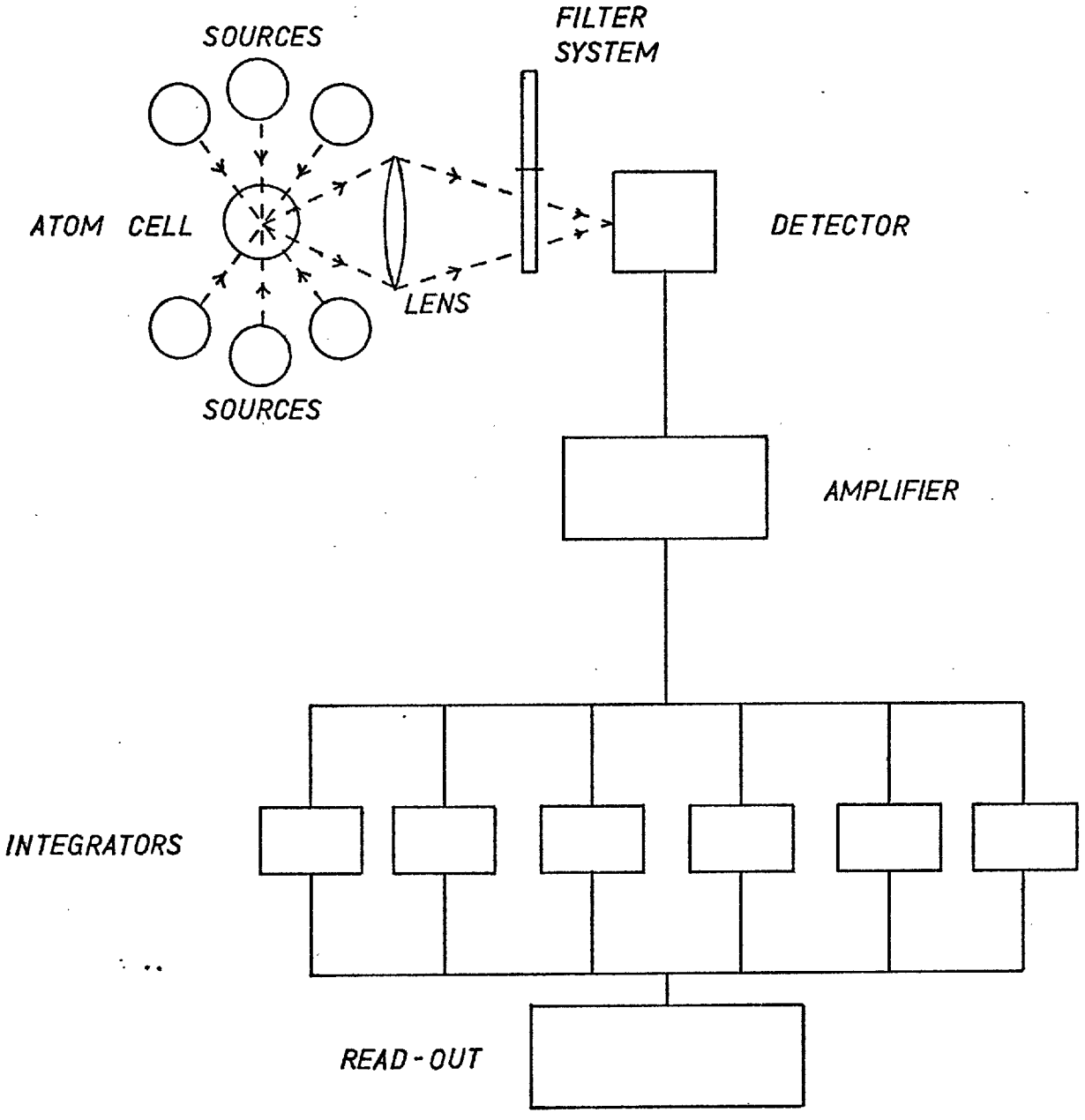
Figure 3.3 represents the culmination of the development of the simple non-dispersive AF spectrometer. This type of arrangement allows the full potential of the technique to be realised simply by using some of the individual components previously described in this chapter.

The operating procedure of such an instrument might typically involve bringing the first filter into position whence the appropriate source is pulsed to produce fluorescence emission from the first element. This signal is then stored in the first integrator and the next filter brought into position, whence the cycle is repeated for a pre-determined number of times and the overall signals for each element read out.

Clearly, although the basic instrumentation required for such a system is essentially the same as that used in the more simple, single-channel AF spectrometers, the control circuitry needs to be very sophisticated to ensure correct operation. Furthermore, the application of Fourier transform techniques, for example, as a method of noise reduction in multi-element AFS (100) has resulted in the development of a very complicated non-dispersive flame AF spectrometer which utilises several spectral sources, each modulated at a different frequency (101).

Thus, the practical multi-element capabilities of the technique of non-dispersive AFS are easily demonstrated and, although for many applications the simple, single-channel instrument may be preferred, it is reassuring to know that a sophisticated and

Figure 3.3 SIMULTANEOUS MULTI-ELEMENT AF SYSTEM



versatile simultaneous multi-element system may be developed if required.

3.3. Non-dispersive AF system used in this study

A schematic representation of the instrument used in this study is shown in Figure 3.4. Although based on the simple, single-channel system depicted in Figure 3.2, this instrument possesses a number of additional features designed to minimise the effects of unwanted background radiation. These include a phase-sensitive AC detection system, a solar-blind photomultiplier and an inert gas-separated flame atom cell.

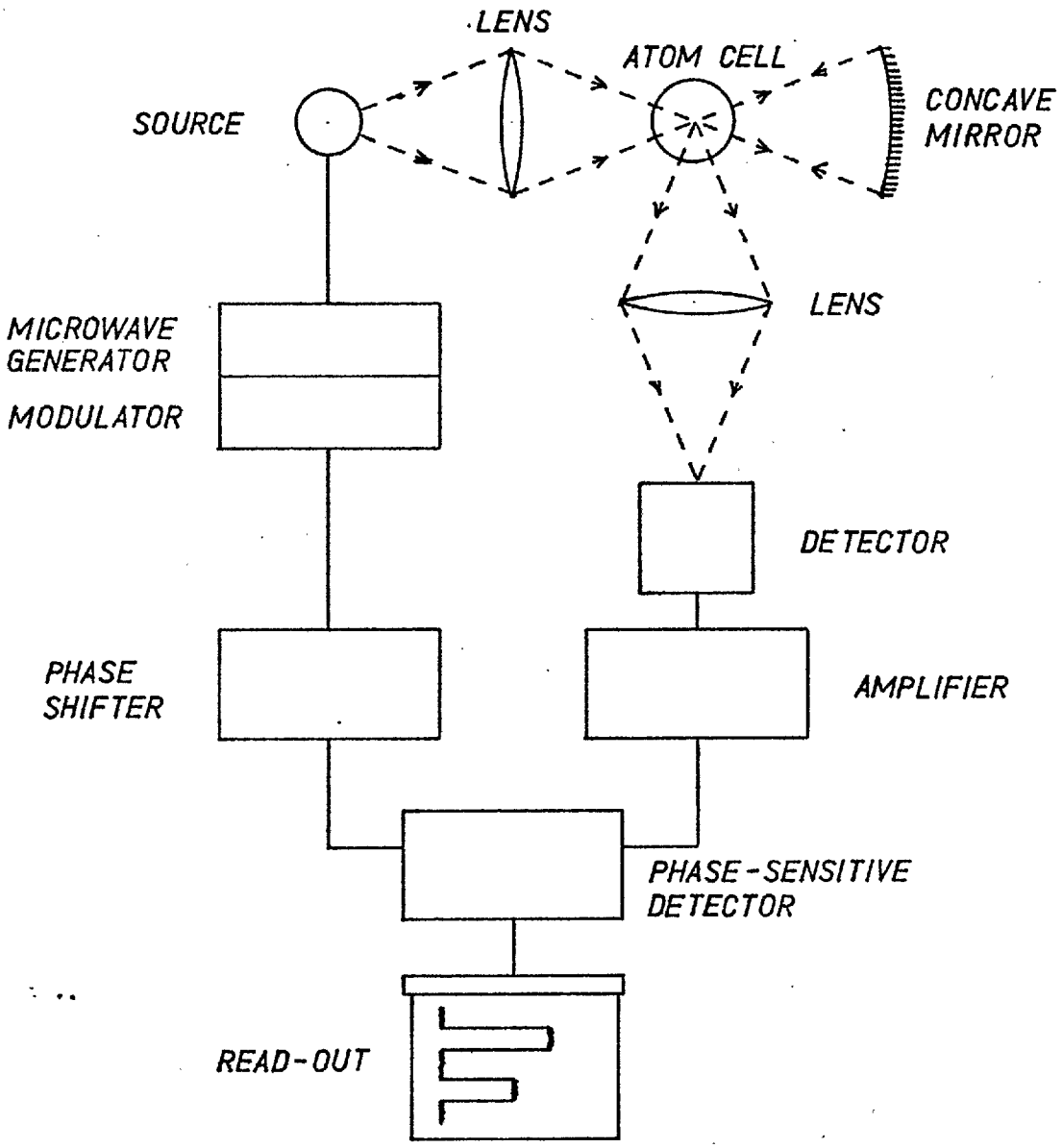
The following sections contain a detailed discussion of these and the other instrumental units used in this work.

3.3.1. The spectral source

3.3.1.(a) Preparation of EDLs

Temperature-controlled, microwave-excited EDLs were used exclusively throughout this study and were prepared in the laboratory in accordance with the general method described by Bartley (52) and King (102). Briefly, this consists of constructing lamp blanks from an appropriate length of silica tubing (usually 7 or 8 mm internal diameter) which has been cleaned in concentrated nitric acid, successively rinsed with water and acetone and then dried. These blanks are heated under vacuum to remove any devitrified silica from the bulb

Figure 3.4 NON-DISPERSIVE AF SYSTEM USED IN THIS STUDY



and flushed several times with argon, after which the lamp fill material is introduced, the pressure reduced to a few torr and the bulb rapidly sealed.

The nature and manner of introduction of the lamp fill material have a considerable effect on the performance of an EDL. It is of particular importance, for example, that extremely pure material be used, since the presence of impurities, especially oxides, is a common cause of lamp failure. Moreoever, with lamps containing metal and halogen (usually iodine) it is necessary to ensure that there exists an excess of metal over the halogen as failure to do so may result in a lamp with a shortened or constricted discharge or, at worst, one which fails to light at all.

More detailed information on the preparation of the individual EDLs used in this work may be found in their appropriate chapters.

3.3.1.(b) Operation of EDLs

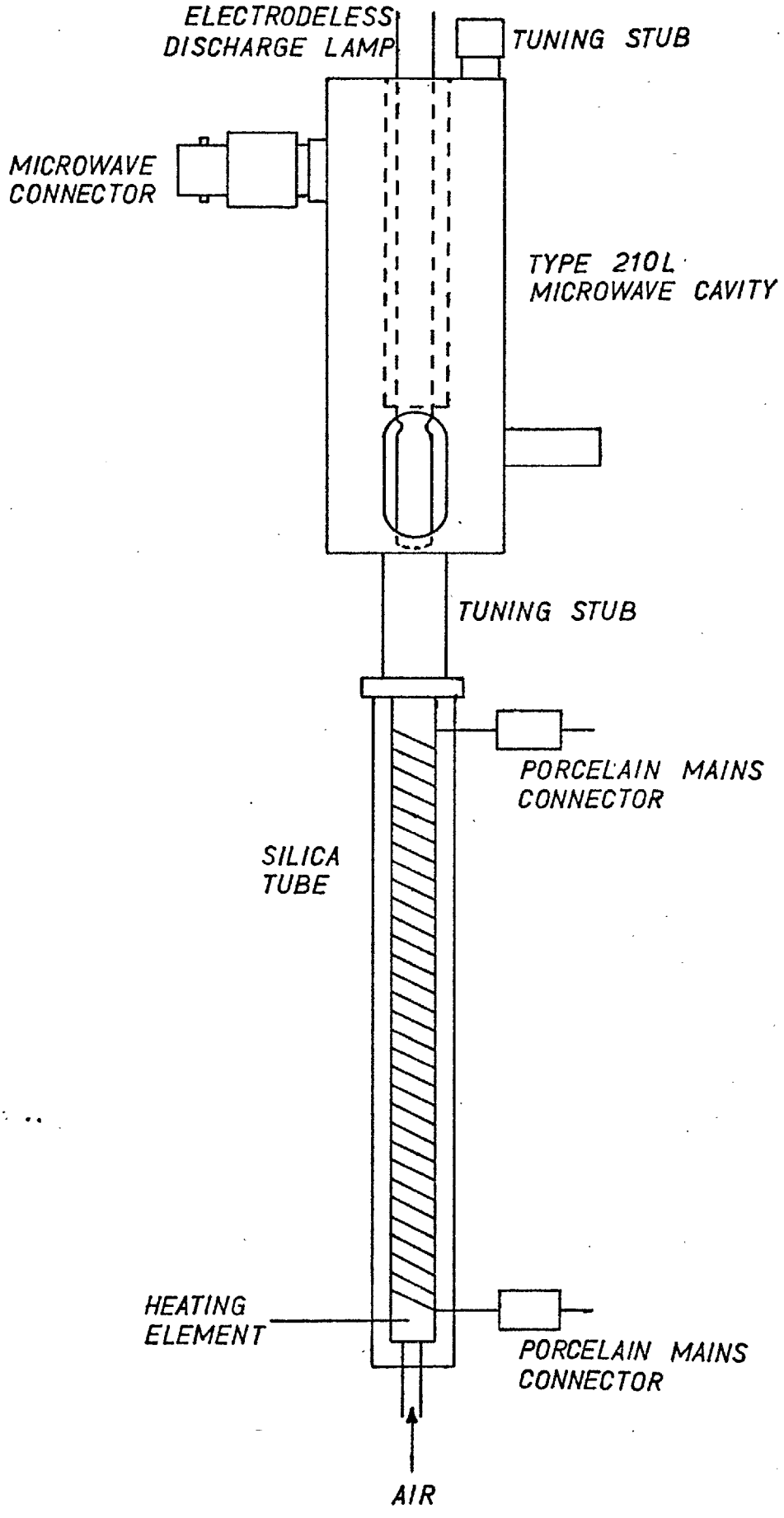
All the lamps used in this study were operated in a 210L (three-quarter wave) resonant cavity and powered by a Microtron 200 Mark I 200W microwave generator (Electro-Medical Supplies Ltd., London). This unit features a stabilised power supply and operates at a frequency of 2450 MHz. A Microtron Mark 2 modulator unit was used in conjunction with the microwave generator and enabledeach source to be operated in an AC (sinusoidal) mode at a frequency of 285 Hz. This unit also provided a synchronous square-wave output which, after the required modification as outlined in Section 3.3.4.,

acted as the reference waveform for the electronic detection system used in this work.

Precise temperature-control of EDLs can result in a considerable increase in emission intensity compared to the output at normal temperatures (51, 103-105). Furthermore, the operation of an EDL at its optimum temperature reduces the dependence of its emission intensity on the applied microwave power so that an increase in the stability of output may result since the effect of fluctuations in applied power are minimised. In this study, temperature-control of each EDL was effected by passing a heated air-stream around the lamp bulb. This was achieved by using a number of devices based on the design of Bartley (52). In principle, this involves the use of a resistively heated element over or through which is passed a supply of air. On heating, this air-stream is introduced into the microwave cavity (see Figure 3.5) and provides a stable thermal environment in which the EDL can operate.

The temperature-control device used at the outset of the work described in this thesis consisted of a 20 cm hollow electric fire element (Wellco Electric Ltd., Hitchin, Herts) rated at 1 kW and mounted in a laboratory-constructed asbestos box. Air from a compressor (GEC Machines Ltd., Newcastle, Staffs) was passed through a flow meter, through the heating element and into the microwave cavity via a piece of silica tubing inserted into the large tuning stub. The heating element was powered from a Regulac variable transformer (Type RK8-M, Claude Lyons Ltd., Hoddesdon, Herts) which was

Figure 3.5 MICROWAVE CAVITY AND HEATER ASSEMBLY



capable of delivering up to 275 Volts at 8 Amps. By suitable control of the applied voltage and air flow-rate, any temperature between ambient and 500°C could be obtained. (All EDL temperatures referred to in this work relate to the temperature of the air-stream in which the lamp is positioned. This was measured by placing a 0-550°C mercury thermometer inside the microwave cavity such that the bulb occupies the position normally taken by the bulb of the lamp).

An attempt was made to improve upon the temperature-control device described above and some success was achieved with a similar, but slightly more convenient unit which consisted of a length of Nichrome V wire (British Driver-Harris Ltd., Stockport, Cheshire) wound onto a silica former. This assembly was placed inside a piece of silica tube, through which the air from the compressor was passed, and the complete unit inserted into the large tuning stub of the microwave cavity. This gave an extremely compact and powerful temperature-control device which typically produced a given air-stream temperature at a lower applied voltage than the device described previously. However, the smaller unit appeared to undergo a greater degree of deterioration after prolonged running at high temperatures so that, despite its satisfactory performance, it was felt to be unsuitable for extensive routine use.

The final choice of heating device, which was used during the major part of the work described in this thesis, was essentially a combination of the two previously described units. This consisted of the 20 cm electric fire element mounted inside

a 2.5 cm diameter silica tube positioned vertically, such that the end of the heating element could be inserted into the large tuning stub of the microwave cavity. This arrangement is depicted in Figure 3.5. Calibration of this heating device was effected by positioning a 0-550^{o}C mercury thermometer in the microwave cavity (with the microwave power switched off) since continuous monitoring of the air-stream temperature was felt to be unnecessary. The performance of the device was checked by periodic re-calibration, however, and showed little change over a long period of almost continuous operation. The variations in air-stream temperature with applied voltage and with air flow-rate are shown in Figure 3.6 and Figure 3.7 respectively.

With all these types of temperature-control device, it is important to ensure that, however the heating element is mounted or positioned, any excess heat which might be generated be allowed to dissipate fairly rapidly as failure to do so could result in the collapse of the former on which the heating wire is wound. This means that the heating element should not be mounted in a heavily-lagged container or box as excessive thermal insulation could prove to be dangerous.

3.3.2. The atom cell

With the exception of the determination of tin, in which a nitrogen-separated air-hydrogen flame was used, the separated air-acetylene flame was used throughout this study. Both types of flame were supported on the same burner, which is depicted

Figure 3.6 CHARACTERISTICS OF EDL HEATER

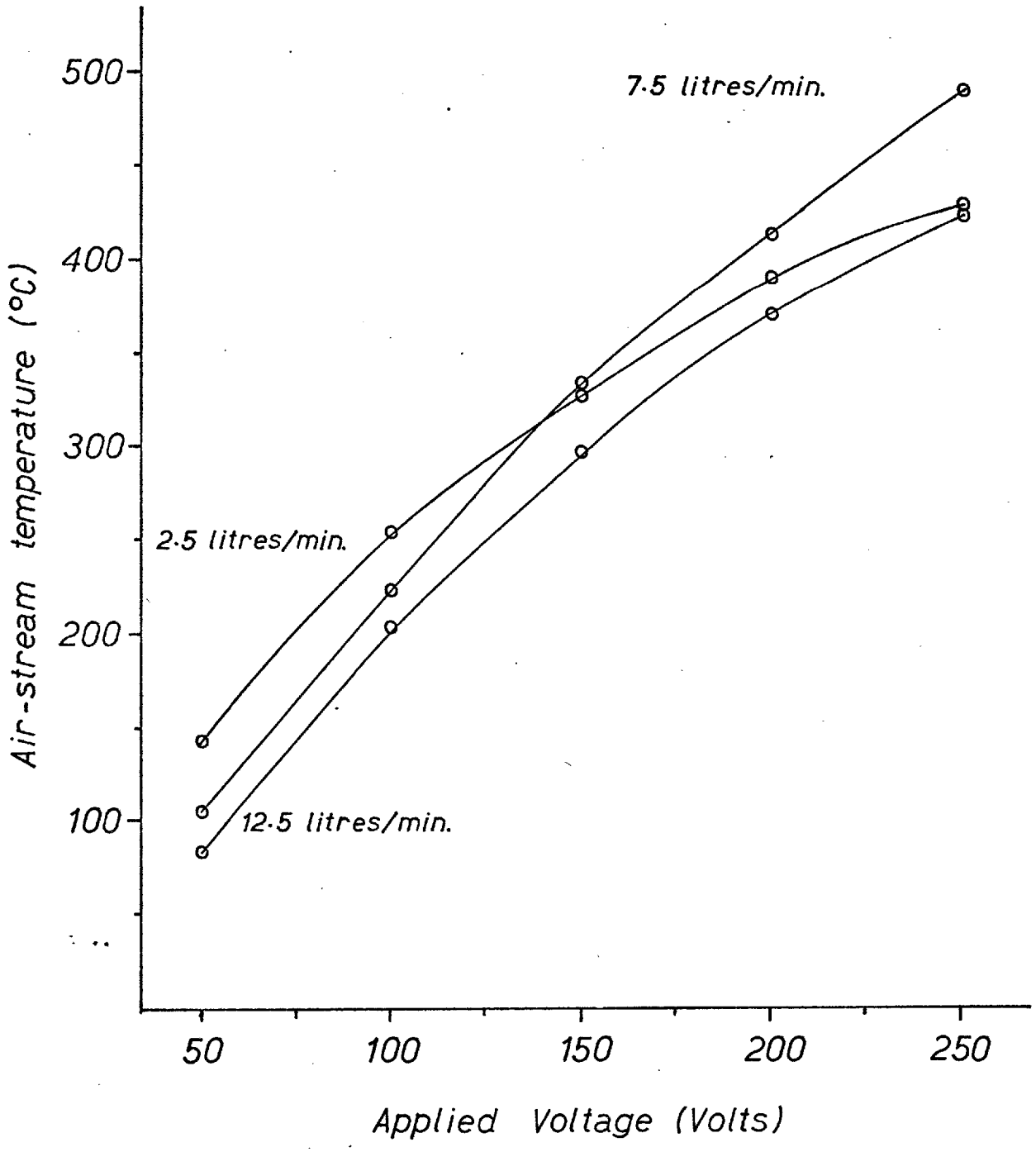
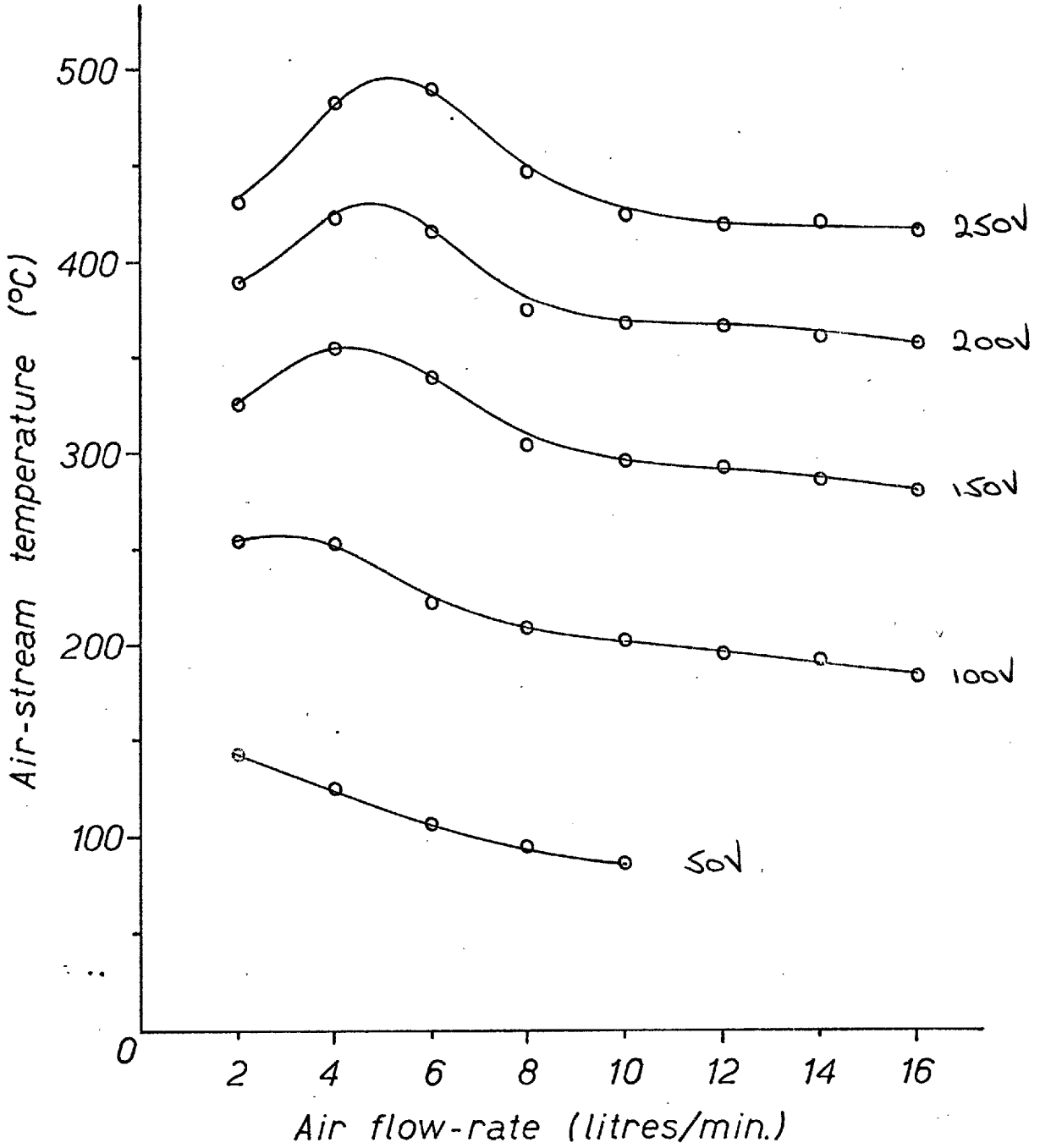


Figure 3.7 CHARACTERISTICS OF EDL HEATER

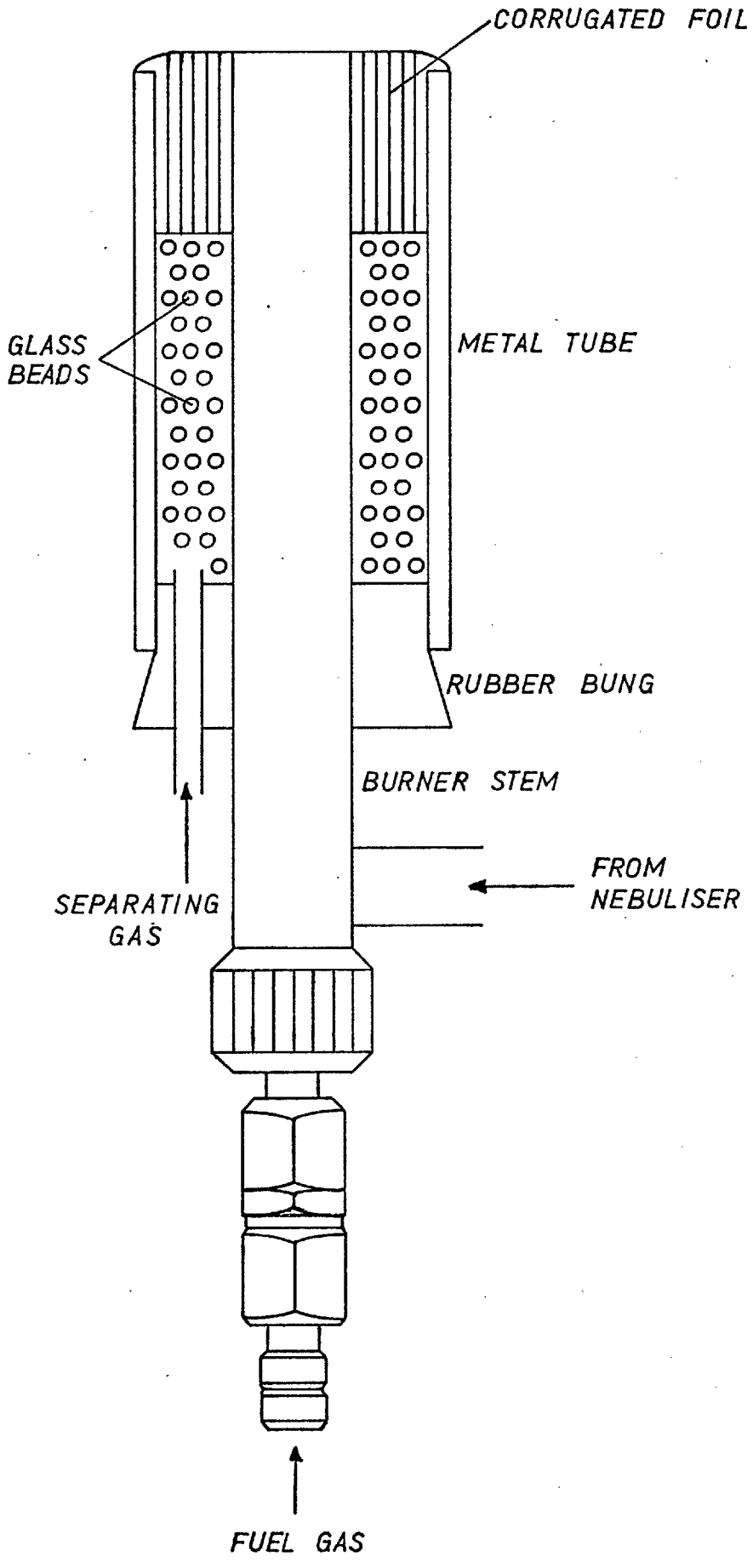


in Figure 3.8 and described by Norris (106). This consists essentially of a standard circular burner stem around which is constructed a laminar-flow chamber to provide efficient flame separation. The inert separating-gas is passed into this chamber where its passage through the tightly-packed glass beads (3 mm diameter) gives it some turbulent behaviour. This in turn ensures reasonably uniform separation of the flame as the inert gas escapes through the corrugated foil around the top of the burner stem.

The actual flow-rate and nature of the separating-gas were not found to be critical in this work. Provided that sufficient gas was supplied to separate adequately the secondary reaction zone of the flame from the inner zone (i.e. such that the lowest part of the secondary zone was lifted above the optical path), variations in flow-rate had little effect on the observed atomic fluorescence signals. For this reason the separating-gas flow-rate was not continuously monitored although periodic measurement revealed that about 15 litres/min of gas were typically required to separate the flame adequately.

At the outset of this work, argon was chosen as the separating-gas. It was very quickly realised, however, that the routine use of this gas would add greatly to the overall cost of operation, so it was decided that the use of nitrogen as the separating-gas would be investigated. In general, it was found that this gas gave a slight decrease in sensitivity for those elements considered in this work (presumably as a

Figure 3.8 BURNER ASSEMBLY



result of a greater degree of fluorescence quenching by nitrogen molecules compared to that of argon) but that this slight decrease (usually of the order of 20%) was greatly outweighed by the considerable saving involved in using nitrogen - at the time of writing, the cost of argon was about six times that of nitrogen. Thus, nitrogen-separated flames were used throughout this study and gave sufficient sensitivity for all practical applications of the technique.

The effectiveness of flame sheathing was also briefly considered at the outset of this work. A 10 cm length of glass tube (5 cm diameter) was fitted over the burner assembly in the hope that less separating-gas would be needed after excluding air from the region around the flame. This tube featured two plane silica windows positioned about 4 cm above the top of the burner to allow radiation to pass in and out of the atom cell with the minimum loss in intensity due to absorption. During operation, however, this device had a tendency to resonate quite violently and cause some turbulence within the flame. Furthermore, no significant reduction in the amount of separating-gas required was observed and it was concluded that little advantage could be gained from sheathing the flame.

The flow-rate of the fuel-gas (acetylene or hydrogen) was monitored and controlled by passing the gas directly from the cylinder through a Meterate flowmeter tube - size F (Glass Precision Eng.Ltd., Hemel Hempstead, Herts). The air supply was produced by a compressor (GEC Machines Ltd., Newcastle, Staffs) and maintained at a pressure of 30 psi (0.2 MN/m^2) using

a Hymatic pressure-control unit (Hymatic Eng.Co.Ltd., Redditch, Worcs).

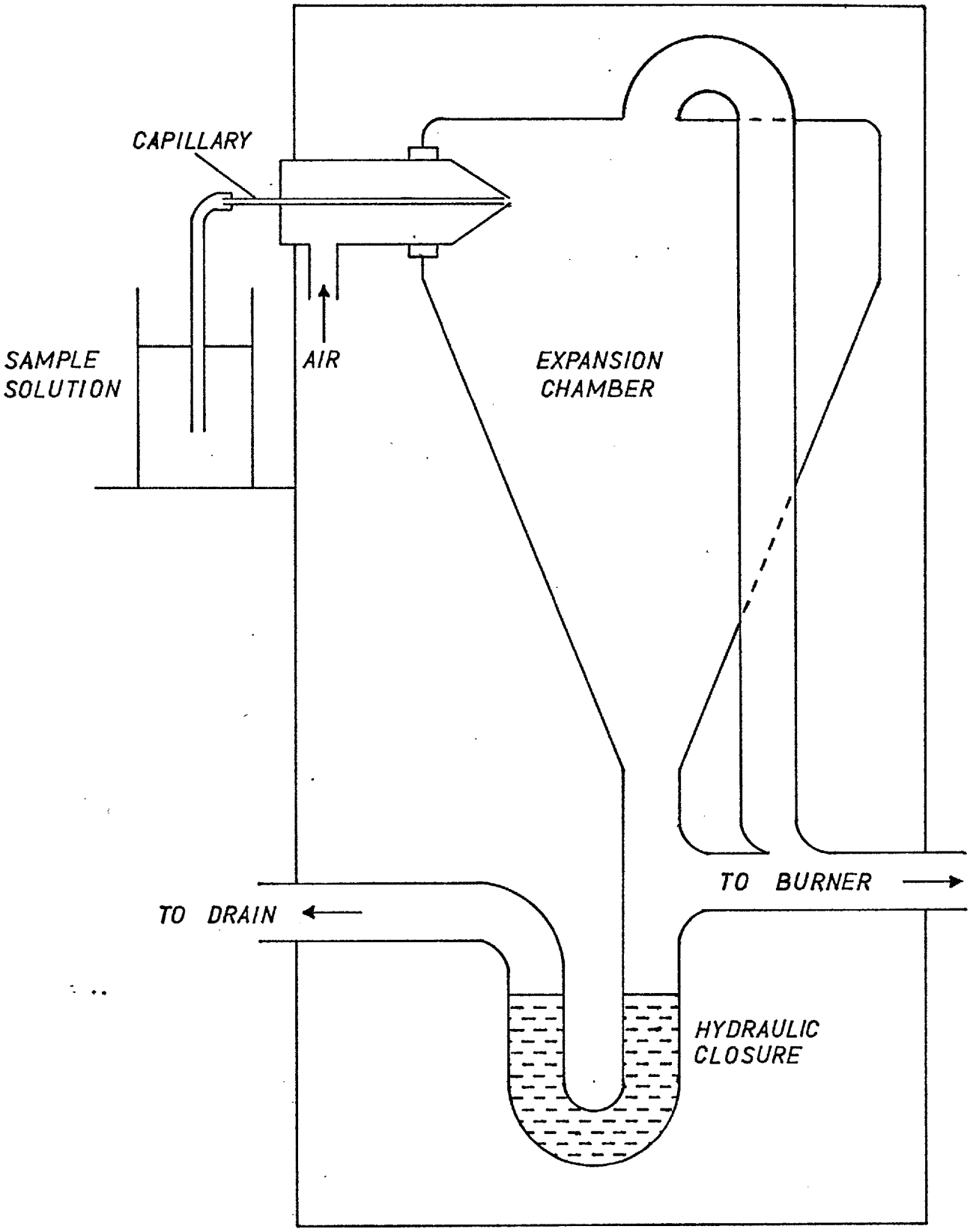
The entire burner assembly was mounted on a laboratory-constructed height-control device which allowed the burner to be moved vertically through a height of about 5 cm simply by turning a small knob (1 turn being equivalent to a 1 mm change in height). This device facilitated the optimisation of viewing position in the flame.

Sample introduction was effected in this work by using an unmodified Pye Unicam SP1900 concentric type pneumatic nebuliser (Pye Unicam Ltd., Cambridge, England) which is shown schematically in Figure 3.9. This unit was operated by the air supply from the compressor and had an optimum uptake rate of about 2 ml/min. The efficiency of atomisation was typically found to be about 15% (calculated as the fraction of aspirated sample solution which fails to appear at the drain outlet of the nebuliser).

3.3.3. The optical system

The optical arrangement used for the greater part of this study is shown in Figure 3.10. At the outset of this work, no optical system whatsoever was employed and satisfactory limits of detection for selenium (see Chapter 4) and tellurium (Chapter 5) were obtained with the spectral source and photomultiplier arranged as close to the atom cell as possible to facilitate the irradiation of the sample and collection of the fluorescence radiation. During the determination of lead, however, it was felt that some improvement in sensitivity was required and the

Figure 3.9 CONCENTRIC-TYPE PNEUMATIC NEBULISER



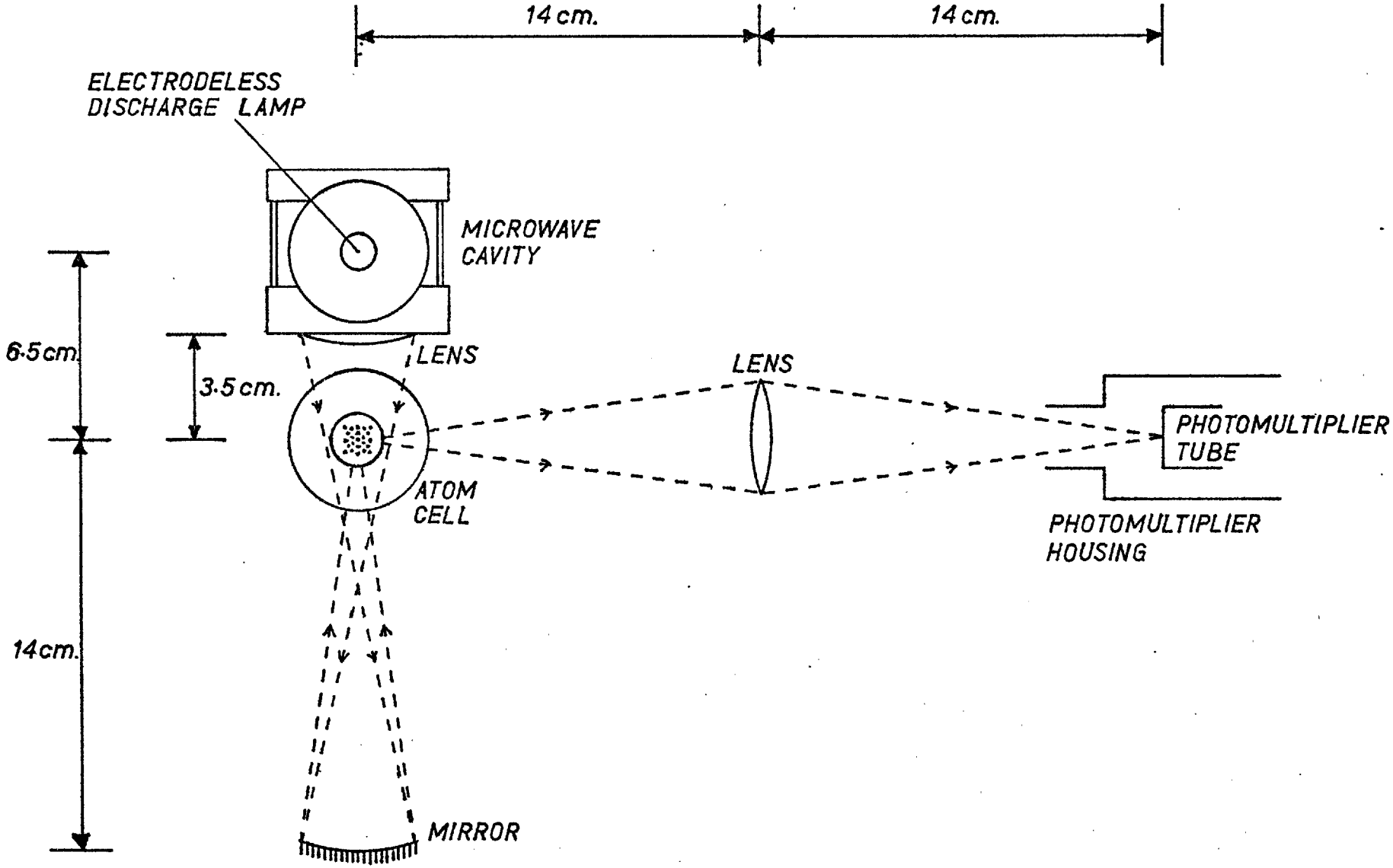


Figure 3.10 OPTICAL ARRANGEMENT

optical system shown in Figure 3.10 was devised.

Radiation from the spectral source was passed through a 2.5 cm diameter, 4.0 cm focal length bi-convex silica lens (Ealing Optical Works, Ealing, London) which was fixed to the front of the microwave cavity using a laboratory-constructed, aluminium-alloy collar. On passing through the flame atom cell, this radiation was collected by a 5.0 cm diameter, 7.5 cm focal length concave mirror (Ealing Optical Works, Ealing, London) and re-focussed at the centre of the flame. In this way, the amount of radiation passing through the atom cell was approximately doubled, with a corresponding increase in sensitivity.

The fluorescence radiation was collected by a 3.5 cm diameter, 7.5 cm focal length bi-convex silica lens (Ealing Optical Works, Ealing, London) and focussed onto the photomultiplier window.

It must be stressed that this optical arrangement was considered far from ideal. The mirror and lenses employed were chosen simply on the grounds of being the best available in the laboratory and there can be little doubt that the whole optical system could be substantially improved by using more suitable components. Despite this, however, the sensitivity of the system was almost doubled using the optical arrangement as described and, since this improvement was felt to be sufficient for most practical applications of the technique, this optical system was retained throughout the remaining part of this work.

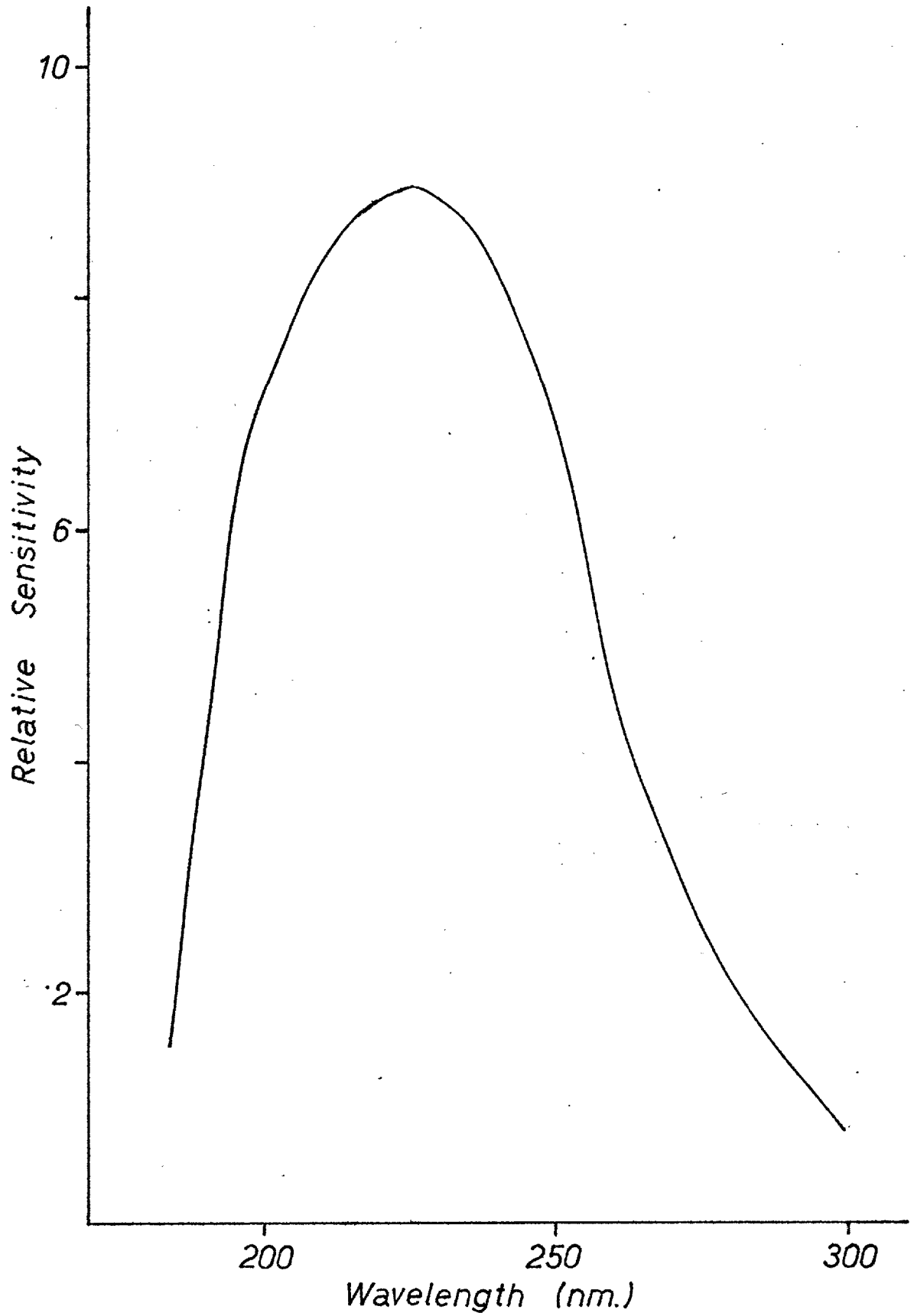
3.3.4. Detection and signal processing system

Although the instrument which has been described in this chapter is overall fairly simple in nature, the electronic detection and signal processing system is quite sophisticated. Broadly speaking, this system operates as follows:

Electronic modulation of the spectral source results in a modulated fluorescence signal of the same frequency (285 Hz) and phase (since the fluorescence process may be regarded as virtually instantaneous). This signal, plus some unwanted background radiation and random noise fluctuations, is detected by the photomultiplier and converted into an equivalent electrical signal which is then amplified and fed into the phase-sensitive detector. A reference waveform, from the modulator unit which produces the modulation of the spectral source, is passed through the phase shifter and into the phase-sensitive detector where the two waveforms are compared for frequency and phase. Any component of the signal waveform which is of the same frequency and phase as the reference waveform is converted into a DC signal which may be displayed on a suitable read-out device.

The detector used throughout this study was an eleven stage, end window R431 solar-blind photomultiplier tube (Hamamatsu T.V. Co.Ltd., Japan). The Cs-Te coated cathode of this photomultiplier limits its response to radiation of wavelength from about 180 to 300 nm (see Figure 3.11) which makes it particularly suitable for the AF determination of many elements of metallurgical interest.

Figure 3.11 RESPONSE CHARACTERISTICS OF A Cs-Te SOLAR-BLIND PHOTOMULTIPLIER (R 431)



This tube was powered by a model 475R Brandenburg photomultiplier power supply (Brandenburg Ltd., Thornton Heath, Surrey) which had a maximum output of 2100 Volts, although the photomultiplier was typically operated in the range 900 to 1200 Volts. Changes in voltage over this range showed no significant change in fluorescence signal-to-noise ratio, although the magnitude of the actual fluorescence signal increased with increasing voltage.

A Brookdeal model 450S low-noise amplifier (Brookdeal Electronics Ltd., Bracknell, Berks) was used to amplify the signal from the photomultiplier. Although this device is not frequency-tunable, the bandwidth may be limited by selecting the appropriate low and high pass filter frequencies. This amplifier, with a maximum gain of + 100 db, exhibits exceptionally good linearity, gain stability and immunity to extraneous signals, while good noise performance is maintained over the whole gain range. More detailed information on the specification and use of this unit may be found in the appropriate instruction manual (107).

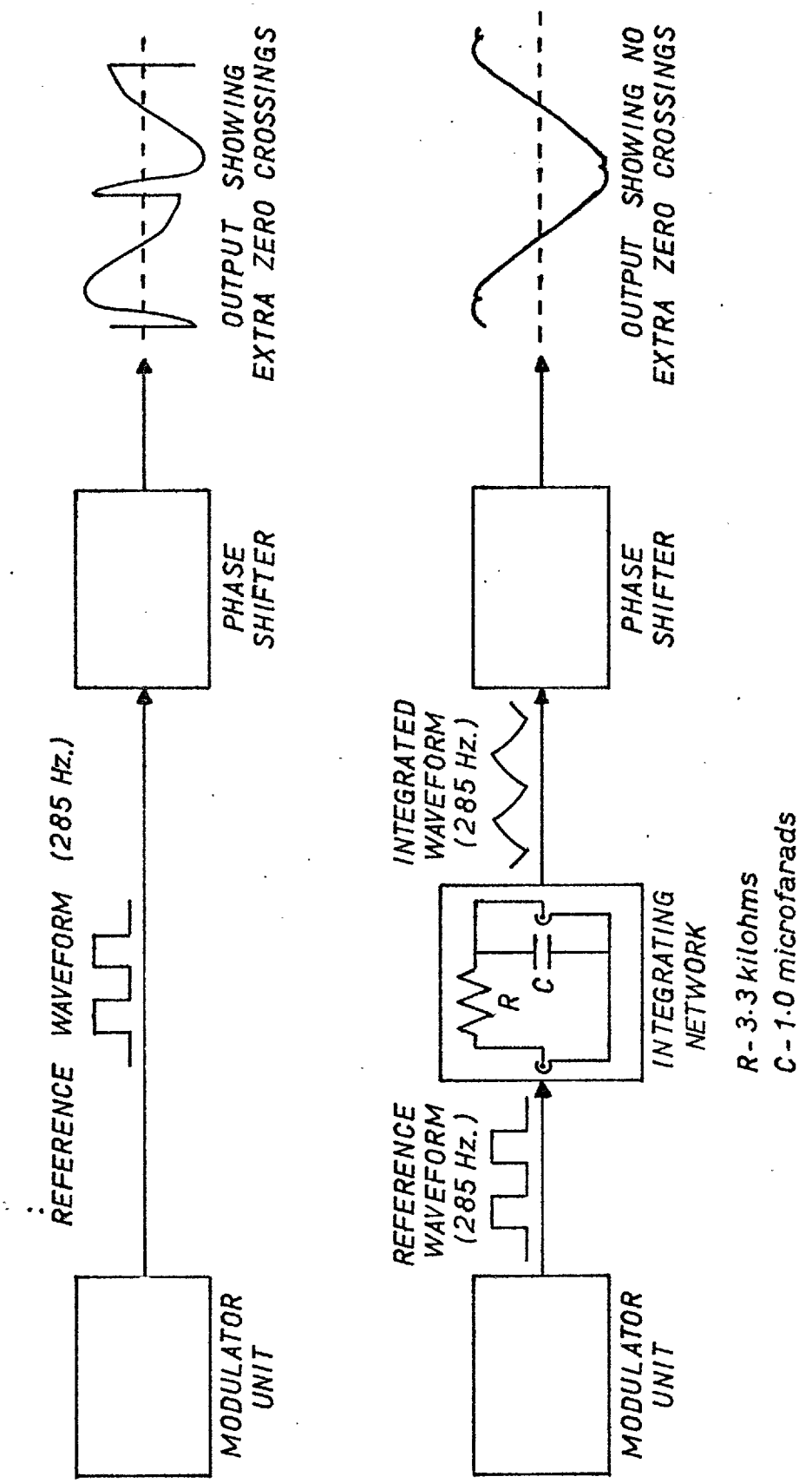
A Brookdeal model 411 phase-sensitive detector (Brookdeal Electronics Ltd., Bracknell, Berks) was used to select that component of the signal from the amplifier of the correct frequency and in phase with the reference waveform. This action is effected by using a two-way switch system which gives full-wave rectification into a DC read-out device and, along with an outline of the principles of phase-sensitive detection, is described in detail in the appropriate handbook (108).

To ensure that the reference waveform, which determines the frequency and phase of the switching operation within the phase-sensitive detector, is exactly in phase with the signal waveform, it is necessary to use a phase shifter unit. This enables the two waveforms to be matched exactly, simply by shifting the phase of the reference waveform. Clearly, once the two waveforms have been matched in this way, no further adjustment of the phase shifter is necessary.

The phase shifter used in this work was a Brookdeal model 421 (Brookdeal Electronics Ltd., Bracknell, Berks) which, although designed as a general purpose sinewave phase shifter, was capable of dealing with non-sinusoidal waveforms. In fact, the synchronous output produced by the modulator unit of the microwave generator used in this work takes the form of a square wave and difficulties can arise when trying to phase shift such a waveform. Briefly, if the original waveform contains large harmonics, the phase shifter may introduce extra zero crossings (see Figure 3.12) which cause the phase-sensitive detector to switch wrongly. Furthermore, the phase shifter may so rearrange the waveform that the output signal slope becomes low at the zero crossing points and the phase-sensitive detector fails to switch sufficiently quickly, or at the correct time, causing large errors in measurement.

In order to avoid these difficulties, a simple integrating network was placed between the reference waveform generator and the phase shifter unit thereby integrating out any spikes in the reference waveform. This network and the problems involved in

Figure 3.12 INTEGRATING NETWORK AND REFERENCE WAVEFORM PHASE SHIFT

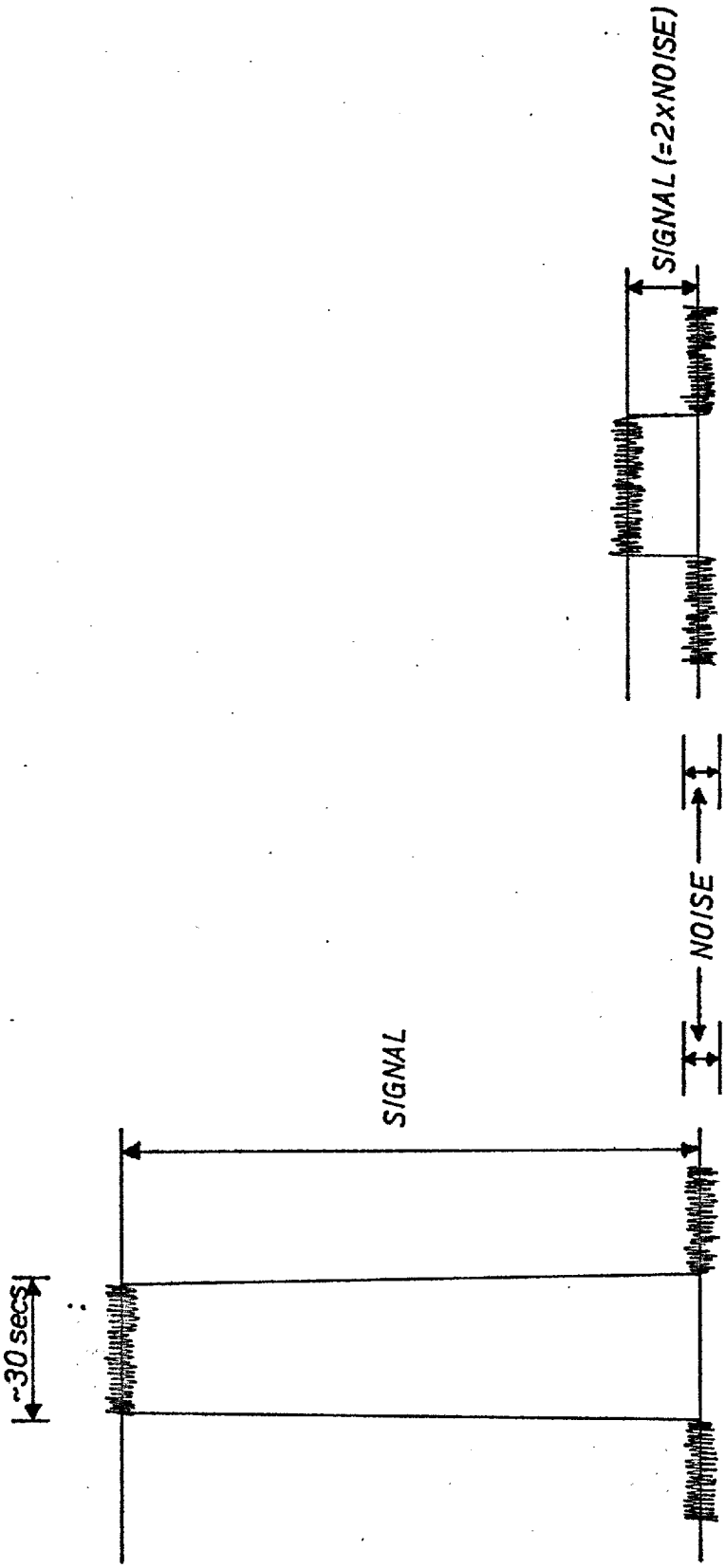


the phase shifting of square waves are outlined in Figure 3.12 although a fuller description may be obtained elsewhere (109).

The DC output from the phase-sensitive detector was displayed on a Servoscribe type RE 541.20 potentiometric flatbed recorder (Smiths Industries Ltd., Cricklewood, London). The multi-range facility of this unit enabled signal voltages of up to 20 Volts to be measured. Thus the amplifier gain and the operating voltage of the photomultiplier were usually adjusted so that this level of output would be obtained when aspirating a 1000 µg/ml solution of each element considered in this work (as this was felt to be the highest concentration of sample solution which would be encountered under normal practical circumstances).

Figure 3.13 shows the way in which the terms 'signal' and 'noise' are defined in this study. All limits of detection quoted in this work are defined, unless otherwise stated, as that concentration which produces a signal equal to twice the magnitude of the accompanying noise. Again this is depicted in Figure 3.13 and shows that measurement on a sample solution of a concentration equal to the limit of detection may be easily performed. This is in direct contrast to many published reports which quote detection limits calculated on a statistical basis rather than by actual measurement.

Figure 3.13 EXAMPLES OF RECORDER TRACES



TYPICAL TRACE DEFINING THE TERMS "SIGNAL" AND "NOISE".

TRACE SHOWING THE SIGNAL PRODUCED BY A SAMPLE SOLUTION OF A CONCENTRATION EQUAL TO THE LIMIT OF DETECTION (SIGNAL/NOISE = 2).

CHAPTER FOUR

THE DETERMINATION OF SELENIUM BY NON-DISPERSIVE AFS

4.1. Introduction

The determination of selenium by non-dispersive AFS was first reported by Larkins (46) who used a HCL and a separated air-acetylene flame to obtain an aqueous detection limit of 6 µg/ml. Previous workers (90, 110-112) had determined selenium at 196.0 or 204.0 nm and reported detection limits ranging from 0.1 to 0.4 µg/ml.

Multi- element EDLs have been used for the AFS determination of selenium. In particular, Cresser and West (113) used a dual-element EDL containing arsenic and selenium to obtain a detection limit of 0.6 µg/ml while Marshall and West (114) quoted 10 µg/ml using a multi-element source containing bismuth, selenium, mercury and tellurium.

Of the more recent determinations (72, 115, 116), the method of hydride generation (72) gives the best sensitivity, a detection limit of 0.00006 µg/ml at 196.1 nm being reported.

In addition, Thompson and Wildy (117), in demonstrating the advantages of using an electronically modulated spectral source, have included the determination of selenium, as have Browner and Manning (118) in their consideration of the use of separated and unseparated air-acetylene flames in AFS.

4.2. Selenium in ferrous alloys

Although a fairly rare constituent, selenium does have a detrimental effect on the mechanical properties of several ferrous

alloys, but is often added to nitriding and stainless steels, typically at a level of about 0.25%, to improve machining properties (119). In this respect, selenium is not only more effective than sulphur but also impairs the corrosion-resistance to a lesser extent.

Despite the fact that there have been several papers published on the determination of selenium in ferrous alloys by AAS (73, 120-124), only Dagnall, Taylor and West (13) have reported such an application by AFS, determining selenium down to 1 ppm in nickel-based alloys.

This chapter describes the first application of non-dispersive AFS to the determination of selenium in ferrous metals.

4.3. Experimental

4.3.1. Reagents

A 1000 ppm stock solution of selenium was prepared by dissolving 0.250 g of selenium in 5 ml of a 1:1 mixture of concentrated nitric and hydrochloric acids and diluting to about 100 ml with glass-distilled, de-ionised water. Concentrated ammonia solution was then added to a slight excess and the whole diluted to 250 ml. Standard solutions were prepared by the appropriate dilution of this stock solution and were usually prepared freshly each day. Analytical grade reagents were used wherever possible in this work.

4.3.2. The principal selenium fluorescence lines

Figure 4.1 shows the emission spectrum produced by the heated selenium EDL used throughout this study. This was obtained by focussing the radiation from the lamp onto the slit of a Varian-Techtron AA4 monochromator scanning at a rate of 5 nm/min and having a slit width of 200 microns. The R431 photomultiplier described in Section 3.3.4. operating at 1100 Volts was used to convert the radiation passing through the monochromator into an electrical signal which was fed directly to a potentiometric chart recorder set at 200 mV full-scale deflection

The $^3P_2$ ground state of selenium is part of a triplet ($^3P_2$, $^3P_1$ and $^3P_0$) in which the separation of the states is small. Thus, there are three main contributions to the overall fluorescence intensity resulting from absorption of radiation to the $^3S_1^o$ excited state followed by deactivation to each of these three states. The relative intensities of the lines emitted by the spectral source give no real indication as to which are the most intense fluorescence lines, however, as it is also necessary to consider the extent to which the absorption of each line by selenium atoms occurs. In practice, it has been found (125) that the 196.1 nm line ($^3P_2$ to $^3S_1^o$ transition) absorbs about five times as strongly as the 204.0 nm line originating from the next state ($^3P_1$). This indicates that the major contributions to the measured fluorescence intensity come from resonance fluorescence at 196.1 nm and direct-line fluorescence at 204.0 nm and 206.3 nm (excitation at 196.1 nm

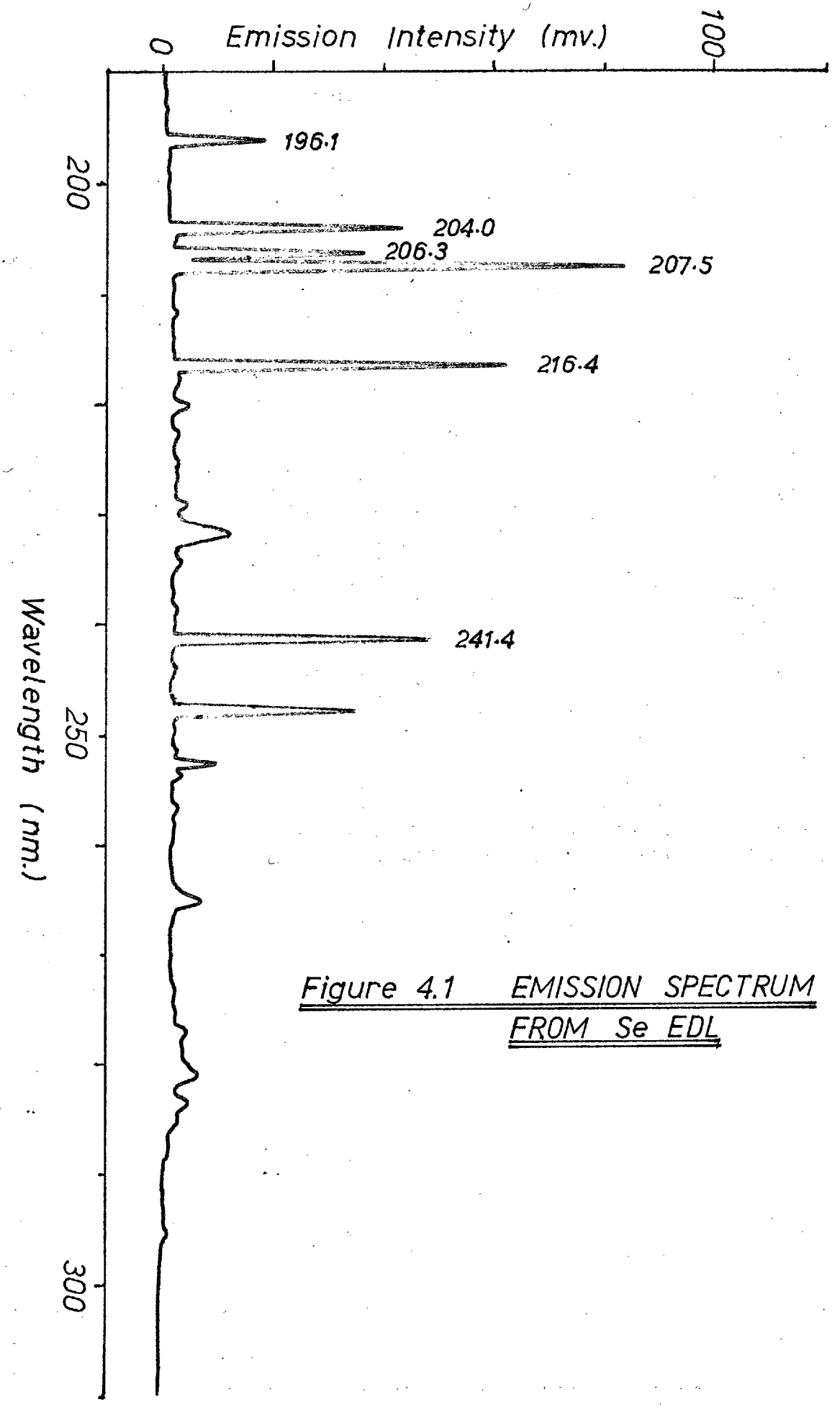


Figure 4.1 EMISSION SPECTRUM FROM Se EDL

followed by deactivation to the $^3P_1$ and $^3P_0$ states respectively). It is possible that some atoms could be thermally excited to these states and that resonance fluorescence at 204.0 nm and 206.3 nm could occur but these processes seem less probable than the direct-line pattern described above.

No atomic fluorescence signals for the 207.5 nm and 216.4 nm intercombination lines ($^3P_2$ to $^5S_2^o$ and $^3P_1$ to $^5S_2^o$ transitions respectively) were observed by Thompson (125) so that, despite the intensities of these lines as shown in Figure 4.1, they were not felt to be of importance in contributing to the overall fluorescence signal.

4.3.3. Experimental procedure

All measurements were made by aspirating the sample solution for at least 30 seconds with distilled water as the reference solution. Thus, once a steady base-line had been obtained when aspirating distilled water into the flame, the sample solution was nebulised after which the distilled water was re-introduced. When aspirating aqueous solutions of selenium (and, indeed, of the other elements determined in this work) a check was made for scatter and atomic emission signals. Scatter was checked by aspirating a selenium solution and irradiating with a cadmium lamp, and atomic emission was checked by aspirating the solution with no irradiation. No signals were observed during these exercises indicating that any signals obtained under normal circumstances were due to atomic fluorescence.

4.3.4. Preparation and characteristics of the selenium EDL

The preparation of the selenium EDL used throughout this study has been described elsewhere (52). The instrumentation used for the determination of selenium was described in Section 3.3. although no optical components were employed at this stage (except during the analysis of the steel samples) as adequate irradiation of the flame and collection of the fluorescence signal were accomplished by placing the source and the photomultiplier as close to the burner as possible. With this arrangement it is important to ensure that the photomultiplier does not become overloaded by radiation received directly from the spectral source. This can be done by placing a baffle or screen between the source and photomultiplier or by stopping down the photomultiplier.

With this instrumentation and by aspirating a 10 ppm selenium solution, the fluorescence characteristics of the source as shown in Figures 4.2 and 4.3 were established. The optimum operating conditions for this lamp were found to be at an air-stream temperature of 119^{o}C (with an air flow-rate of 7.5 litres/min) and 70 Watts applied microwave power.

Reasonably careful control of these operating conditions was found to be necessary as this lamp (and, indeed, other lamps containing non-metallic elements) showed some unusual behaviour. In particular, the variation of emission intensity with air-stream temperature seemed somewhat irregular and was accompanied by some dramatic colour changes within the lamp.

Figure 4.2 CHARACTERISTICS OF Se EDL

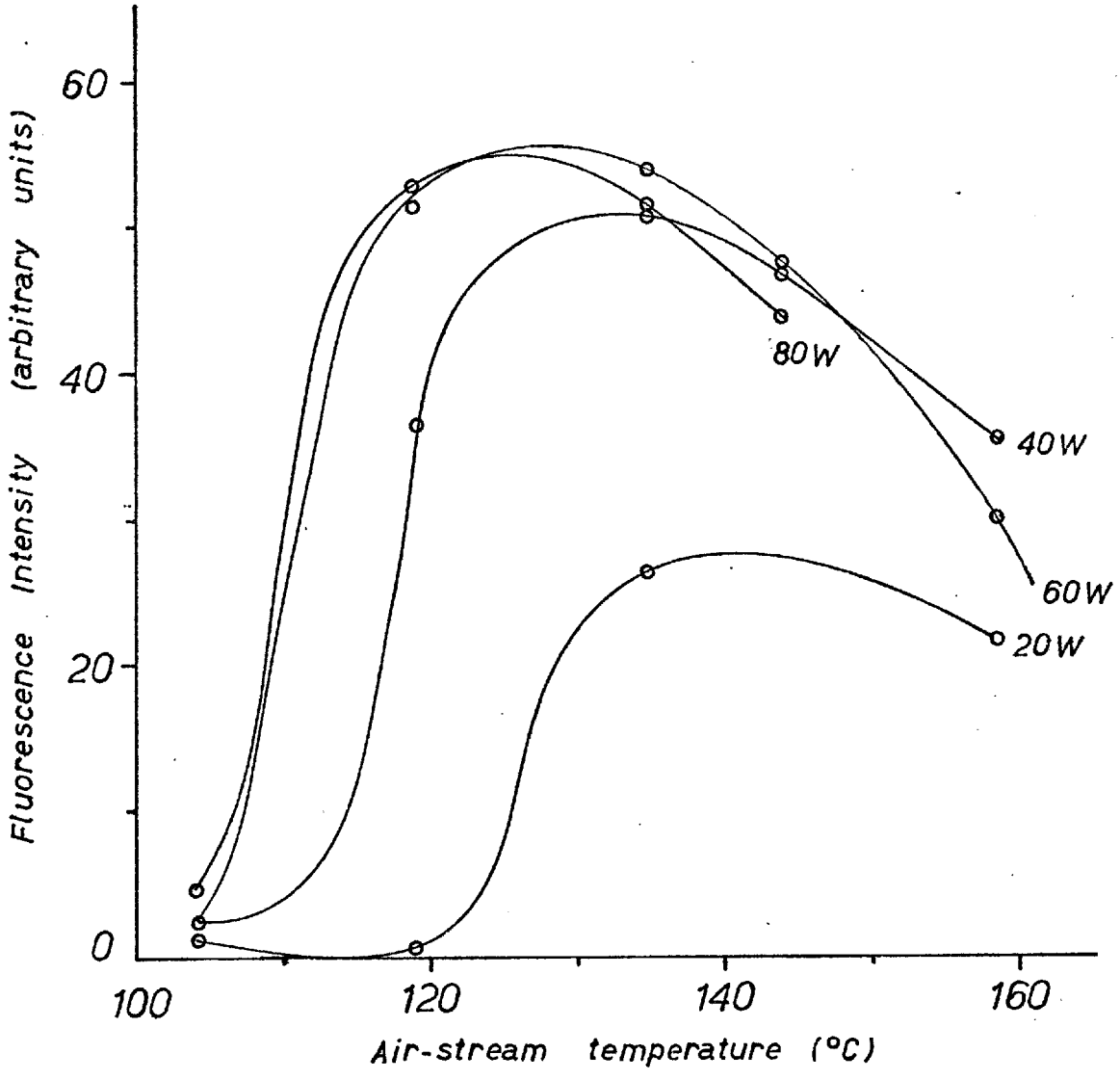
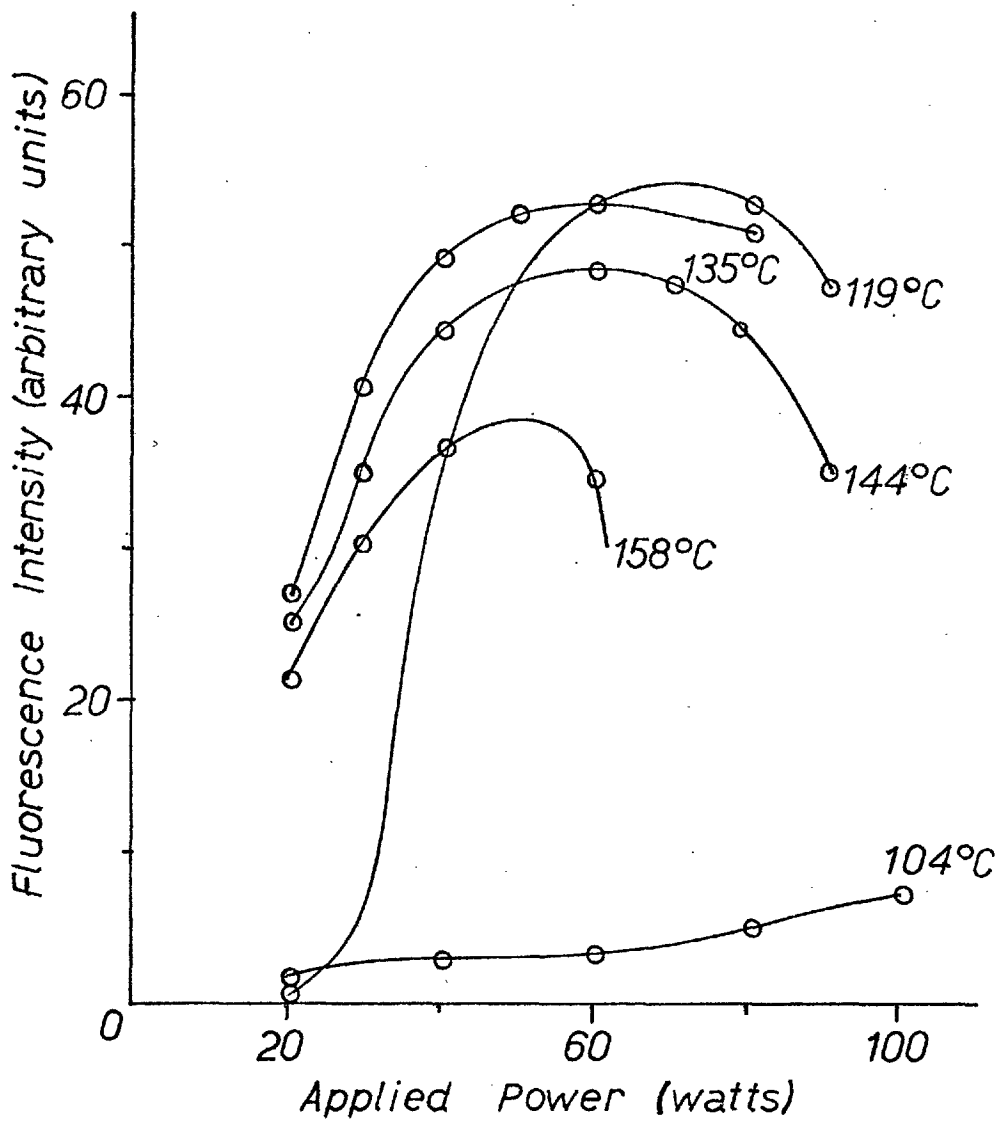


Figure 4.3 CHARACTERISTICS OF Se EDL



Bartley (52) has discussed in detail these changes of colour which occur at various operating temperatures and has indicated that the presence and breakdown of molecular species in the lamp might account for this odd behaviour.

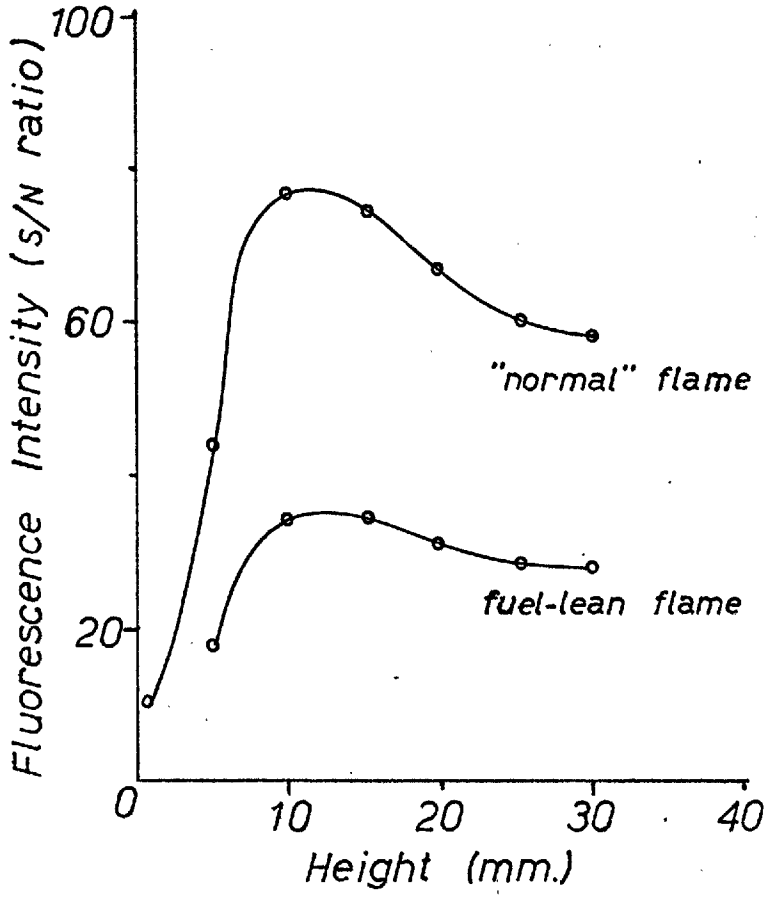
4.3.5. Optimisation of flame height and flame composition

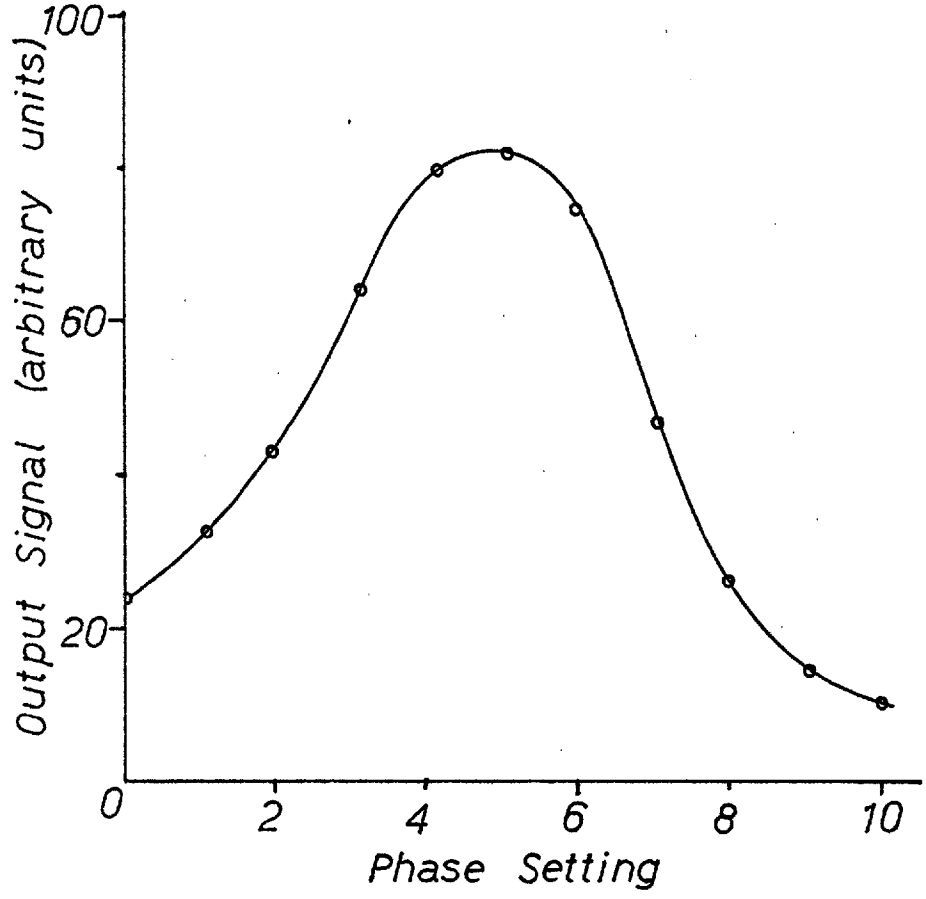
A nitrogen-separated air-acetylene flame was used in this determination. The use of argon as the separating-gas was considered but the marginal increase in sensitivity which was observed was felt to be insufficient to justify the considerably higher expense involved.

Figure 4.4 shows the variation of the atomic fluorescence signal-to-noise ratio with various flame conditions. The "normal" flame, which is characterised by having a slightly yellow inner cone, was used throughout this determination, although the fuel-rich flame could have been used with no loss in sensitivity. In contrast, the higher noise level associated with the fuel-lean flame meant that, despite an actual increase in the magnitude of the fluorescence signals, the signal-to-noise ratio was considerably reduced.

In all three types of flame, however, the optimum viewing position was found to be at a height of 10 mm above the top of the small blue cones at the base of the flame (that is, some 20 mm above the top of the burner).

Figure 4.4 OPTIMISATION OF OPERATING PARAMETERS FOR SELENIUM





4.3.6. Optimisation of phase

Figure 4.4 shows the output signal produced at various phase settings and was obtained in two ways. The first method, which may be conveniently termed "the method of direct reflection", involves directing the emission from the source into the photomultiplier with the aid of a small plane mirror mounted on top of the burner, while the second approach merely requires the straightforward measurement of the atomic fluorescence signals produced at the various phase settings. Both methods gave similar results and revealed that the maximum signal was obtained at a phase setting of 4.5.

4.3.7. Analytical growth curve and detection limit

The analytical growth curve for selenium shown in Figure 4.5 was obtained by measuring the atomic fluorescence signals produced by a range of solutions of differing concentrations, these solutions being prepared by appropriate dilution of the 1000 ppm stock solution.

Some limitation on the maximum measurable atomic fluorescence signal which could be produced by the instrumentation used in this study was found to exist. More exactly, the maximum output which could be obtained from the amplifier was found to be 1 Volt as this, in turn, produced the maximum output of 10 Volts from the phase-sensitive detector (although this could be increased to 20 Volts, if necessary, with the aid of a backing-off control incorporated into the device). In order to obtain maximum atomic fluorescence signals from a given solution, it was decided that the operating

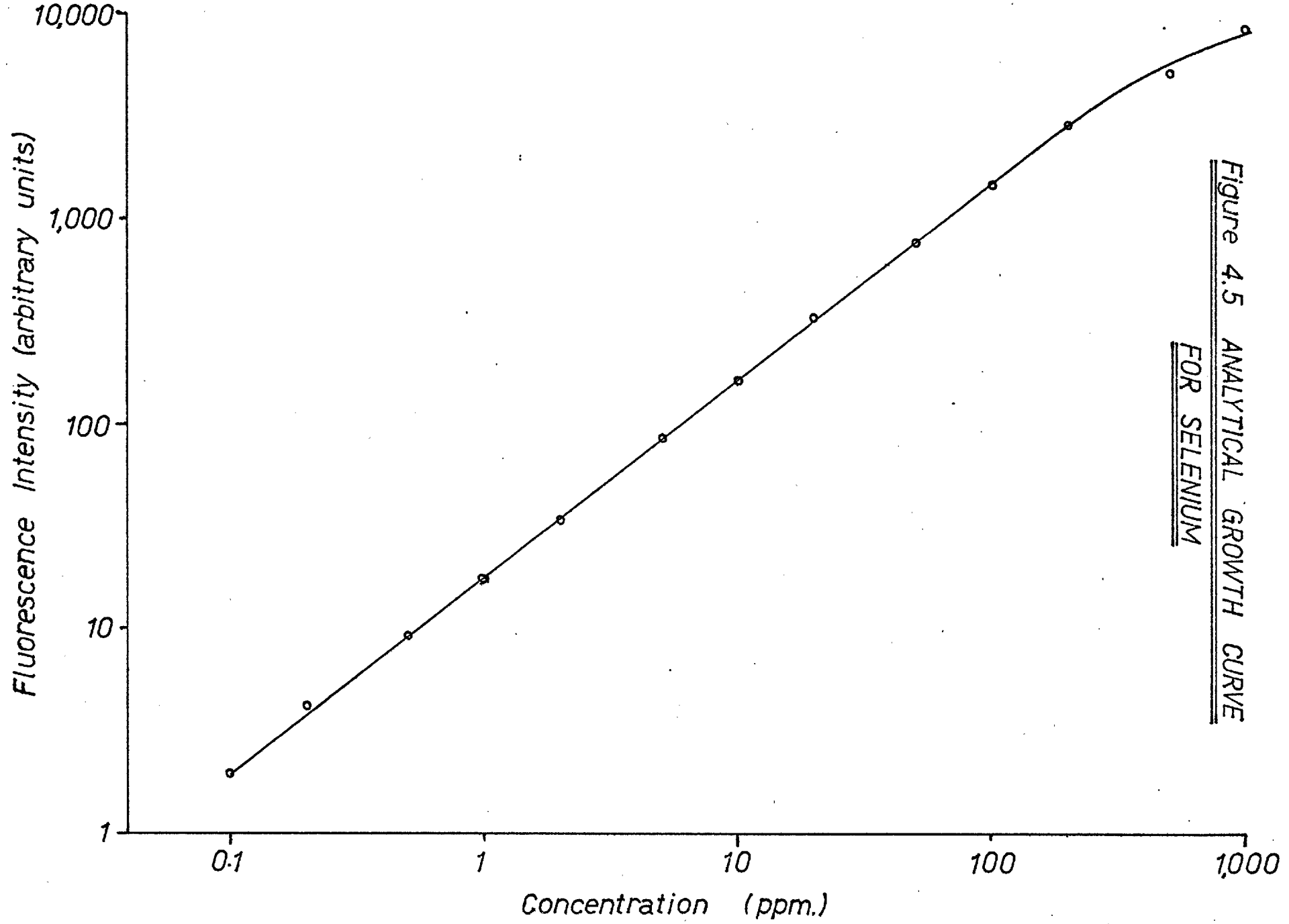


Figure 4.5 ANALYTICAL GROWTH CURVE FOR SELENIUM

voltage of the photomultiplier and the gain of the amplifier should be adjusted such that the most concentrated solution which might normally be encountered (fixed arbitrarily at 1000 ppm) would give a signal of about 10 Volts. This approach ensures that solutions of quite low concentrations would still produce signals which could be easily measured.

Under no circumstances was the photomultiplier operated below 900 Volts (where the signal-to-noise ratio begins to deteriorate) or above 1200 Volts (as damage to the photomultiplier tube could result). In practice, therefore, the operating voltage of the photomultiplier was established with the amplifier set at minimum gain after which, if an inadequate signal was obtained when aspirating a 1000 ppm solution, the amplifier gain was increased until the desired output was produced.

In the case of selenium this was achieved with the photomultiplier operating at 900 Volts and the amplifier set at minimum gain (20 db). Under these conditions a detection limit (signal-to-noise ratio = 2) of 0.20 ppm in aqueous solution was obtained with the linear range of the analytical growth curve extending up to about 300 ppm.

The instrumental operating conditions under which the curve shown in Figure 4.5 was produced may be summarised as follows:

Spectral source:

1. Air-stream temperature - 119^{o}C (at 7.5 litres/min).
2. Applied microwave power - 70 Watts.
3. Modulation frequency - 285 Hz.

4. Degree of modulation - 70%.

Atom cell:

1. Acetylene flow-rate - 1.1 (0.8 litres/min).
2. Nebuliser pressure - 30 psi (0.2 MN/m^2).
3. Viewing height above burner - 20 mm.

Photomultiplier:

1. Operating voltage - 900 Volts.

Amplifier:

1. Input - Normal protected.
2. Frequency limits - 100 Hz to 1000 Hz.
3. Filter - Internal.
4. Meter damping - Off.
5. Gain - 20 db (i.e. 30 db-10 db).

Phase-sensitive detector:

1. Meter - 10 Volt range (negative).
2. Zero - Negative.
3. Time constant - Internal (1 sec).
4. Filter - Off.
5. Reference channel - A.

Phase shifter:

1. Sensitivity - 100 mV.
2. Frequency range - 100 Hz to 1000 Hz.
3. Phase setting - 4.5.

4.3.8. Interferences

In order to investigate the interference effects of iron on selenium, a number of solutions were prepared containing various concentrations of the two elements. Ten systems were examined, the range of concentrations being shown in Figure 4.6, and the following scheme of analysis employed:

1. The atomic fluorescence signal produced by a selenium solution, at a concentration equal to that present in the system under investigation, was measured.
2. The signal produced by an iron solution, at a concentration equal to that present in the system under investigation, was measured.
3. The signal produced by the iron/selenium system itself was measured.
4. The third measurement was repeated.
5. The first measurement was repeated.

Figure 4.6 SELENIUM INTERFERENCES

Iron conc. (ppm.)	Selenium conc. (ppm.)	Relative Signal
10,000	1,000	0·97
10,000	100	1·23
10,000	10	1·39
10,000	1	1·28
1,000	100	1·05
1,000	10	1·12
1,000	1	0·92
100	10	1·00
100	1	1·00
10	1	1·00

Interferent	Apparent Signal			Relative Signal
	Matrix	Steel	0·5 ppm Se	
Fe+Cr+Ni	14	24	9	1·1
Fe+Cr	12	24	10	1·2
Fe+Ni	12	24	10	1·2
Fe	10	24	10	1·4
Cr	2	24	10	2·2
Ni	2	24	10	2·2

6. The signal produced by the iron/selenium system was measured using the iron solution, instead of distilled water, as the reference solution.

In this way, any inaccuracies in measurement due to fluctuations in the performance of the instrument were minimised as the first and fifth measurements and the third and fourth measurements should agree closely, while the sixth measurement should be equal to the difference between the third and second. In all the results quoted, these conditions were fulfilled.

In Figure 4.6 the relative signal for each system is defined as the ratio of the sixth and first measurements. This shows the apparent selenium fluorescence signal, obtained in the presence of the excess concentration of iron, relative to the signal produced by the selenium alone. Thus, a relative signal of unity indicates no interference from the iron matrix.

From these results it may be seen that the absolute amount of interferent rather than the ratio of iron to selenium is of greatest importance so that, in the analysis of a steel sample, the degree of interference can be reduced to some extent by simple dilution of the sample solution. This approach is clearly restricted to samples with fairly high selenium contents, however.

The interference effects of chromium and nickel were also investigated. A simulated stainless steel solution containing 740 ppm iron, 180 ppm chromium, 80 ppm nickel and 0.5 ppm selenium was prepared and examined in accordance with the following scheme:

1. The atomic fluorescence signal produced by a 0.5 ppm selenium solution was measured.

2. The signal produced by a solution of the interferent under investigation (as listed in the interferent column in Figure 4.6), at a concentration equal to that present in the simulated steel sample, was measured.

3. The signal produced by the simulated steel sample was measured.

4. The third measurement was repeated.

5. The first measurement was repeated.

6. The signal produced by the simulated steel sample was measured using the interferent solution, instead of distilled water, as the reference solution.

The results in Figure 4.6 show that, although some correction has to be made for the presence of both chromium and nickel in a steel sample, the overall interference effect is of a similar level to that which would be produced by an equivalent amount of iron. This indicates that, in an actual analysis of a steel sample, any such interferences could be easily eliminated by the appropriate addition of iron to the calibration solutions.

4.3.9. Analysis of steel samples

This section (and similar sections in subsequent chapters) forms the very heart of this work, for only by the analysis of standard materials of known composition may a technique be fully evaluated. In

metallurgical analysis this may be conveniently achieved with the aid of British Chemical Standards (BCS) steel samples which are prepared and issued by the Bureau of Analysed Samples Ltd., Middlesbrough, Cleveland. In this case, however, there were no readily available BCS steel samples containing selenium so that it was necessary to add known volumes of a standard selenium solution to dissolved steel samples to produce appropriate standards.

For the sake of convenience and simplicity a general method of sample dissolution was adopted and was strictly adhered to regardless of the type of steel under investigation. While it is realised that this method is by no means perfect, its main virtue is its practicality and may be considered wholly adequate until shown to be otherwise.

The same philosophy applies to the matching of the sample solution and calibration solutions by the addition of iron. For convenience of operation, and regardless of the type of steel, only iron was added to the calibration solutions in order to simulate any interference effects or scattering of radiation produced by the sample solution. Once again, this approach was felt to be completely satisfactory until proven to be inadequate.

The method of sample dissolution used throughout this work may be summarised as follows:

Approximately 0.5 g of the steel sample was accurately weighed into a 125 ml conical flask. 5 ml of a mixture of concentrated hydrochloric and nitric acids (6:1) was added and the flask warmed slightly on a hotplate. When all the effervescence had ceased, the solution was gently boiled and evaporated to dryness, after which the residue was

heated for a further two minutes. The residue was then re-dissolved in 5 ml of the hydrochloric and nitric acid mixture (6:1) with the aid of gentle heat, if necessary, and transferred, with washing, into a 50 ml volumetric flask. This flask was made up to volume with distilled water and the contents filtered through a No. 41 (7 cm) Whatman filter paper. This filtrate was the sample solution.

Silicon is present in many ferrous alloys and may partly precipitate as gelatinous silica during some dissolution procedures, while silicates in solution can also cause problems during sample atomisation. For these reasons, the sample dissolution method described above features a step in which the steel residue is heated. This facilitates the removal of silica since precipitation will normally occur after this dehydration of the material. After filtration, a step which also removes any particles of carbon present in the solution, atomisation problems are minimised. A possible drawback with this method is that precipitated silica can co-precipitate or co-absorb some of the element to be determined. In this event, the dissolution procedure would have to be modified to include some further treatment of the precipitate in order to overcome such difficulties.

Preparation of suitable standards for selenium was effected by adding appropriate amounts of a standard selenium solution to four BCS steel samples during the dissolution procedure described above (at the re-dissolving of the residue stage). These additions were made as follows:

1. BCS 320 + 2 ml of a 50 ppm selenium solution, diluted to 50 ml = 0.020% selenium in the solid.

2. BCS 324 + 4 ml of a 50 ppm selenium solution, diluted to 50 ml = 0.040% selenium in the solid.

3. BCS 273 + 6 ml of a 50 ppm selenium solution, diluted to 50 ml = 0.060% selenium in the solid.

4. BCS 239/2 + 8 ml of a 50 ppm selenium solution, diluted to 50 ml = 0.080% selenium in the solid.

Five separate weighings of each sample were taken and the results of the analyses presented in Figure 4.7. A blank sample was also included in the analyses and indicated that there was no selenium present in any of the reagents or glassware used in this study.

No elaborate scheme of analysis was used during the measurement of these sample solutions. A range of calibration solutions, containing iron (0.5 g of electrolytic iron powder in 50 ml of solution) and matched for acid content (5 ml of concentrated hydrochloric acid in 50 ml of solution), was prepared and the signal produced by each solution was measured. The signals from the five sample solutions and the blank solution were then measured followed by a re-measurement of each calibration solution. The relative standard deviation for each analysis was calculated from the measurements obtained from the

Figure 4.7 ANALYSIS OF SELENIUM IN STEELS

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 320	MILD STEEL	0.020o, 0.020o, 0.020o, 0.024o, 0.024o	0.0216	10.1	—	—
BCS 324	MILD STEEL	0.036o, 0.044o, 0.040o, 0.040o, 0.044o	0.0408	8.2	—	—
BCS 273	MILD STEEL	0.068o, 0.060o, 0.060o, 0.056o, 0.060o	0.0608	7.2	—	—
BCS 239/2	CARBON STEEL	0.080o, 0.076o, 0.076o, 0.080o, 0.080o	0.0784	2.8	—	—

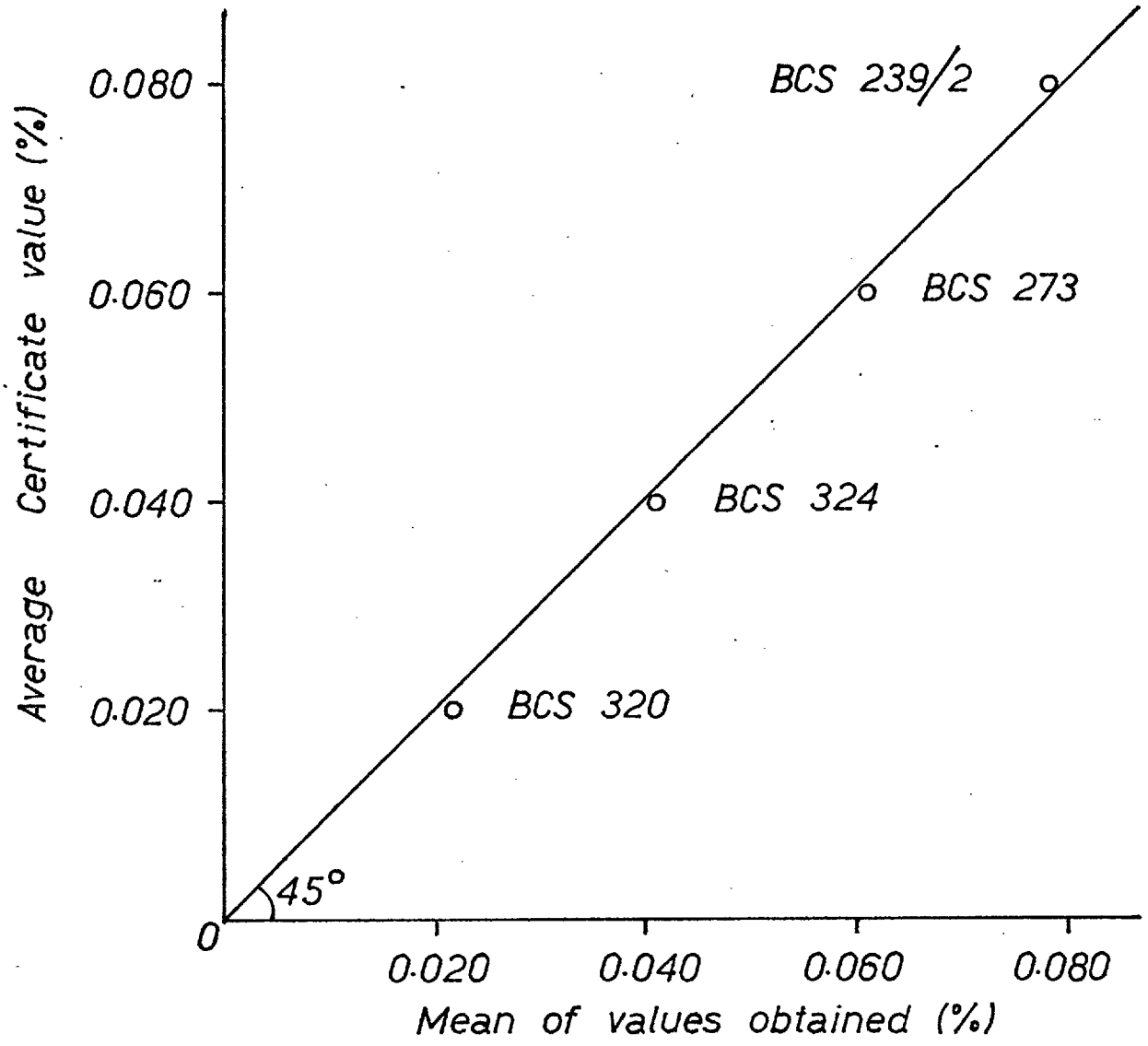
five solutions of each sample rather than from a number of measurements on one sample solution as this approach enables an appraisal of the overall precision of the technique, and not of the measurement step alone, to be made.

The results of the analyses as shown in Figure 4.7 reveal a good degree of accuracy for each of the four steel samples examined. In fact, the accuracy of each analysis may be quickly assessed from Figure 4.8 in which the mean value obtained by measurement of each sample is compared to the expected or average certificate value. Those points below the diagonal line indicate "high" analyses while those above denote that the values obtained were lower than the expected or certificate values. The precision of each analysis was also found to be quite acceptable particularly, as was to be expected, for those samples containing relatively high levels of selenium.

4.4. Conclusions

The results presented in this chapter indicate that the technique of non-dispersive AFS may be used to advantage for the rapid, precise and accurate determination of selenium in ferrous metals. The minimum of sample pre-treatment is required and only iron need be added to the calibration solutions. Good sensitivity and freedom from interferences (other than scatter by the matrix material) are also important features of the non-dispersive AF determination of selenium.

Figure 4.8 ANALYSIS OF SELENIUM IN STEELS



CHAPTER FIVE

THE DETERMINATION OF TELLURIUM BY NON-DISPERSIVE AFS

5.1. Introduction

The determination of tellurium by non-dispersive AFS was first reported by Larkins (46). Using a separated air-acetylene flame and a HCL, he obtained a detection limit of 3 µg/ml in aqueous solution. Prior to this, several workers had determined tellurium by AFS, usually at 214.3 nm, using single or multi-element EDLs and reported limits of detection ranging from 0.006 to 1.5 µg/ml (110, 111, 113, 114, 126).

As with selenium, the most sensitive of the more recent determinations of tellurium by AFS (52, 72, 102, 116, 127-129) has been that of Thompson (72) which utilises the method of hydride generation. Of these, only the determination by King (102), who used a carbon filament atom reservoir and a solar-blind photomultiplier, was in the non-dispersive mode. Thompson and Wildy (117) and Browner and Manning (118) have also included the determination of tellurium in their respective evaluations of the electronically modulated source and the separated air-acetylene flame in AFS.

5.2. Tellurium in ferrous alloys

Like selenium and sulphur, the effect of tellurium on certain alloy steels is to improve the machining properties (119, 130, 131). The introduction of this element confers additional hardness, although heat-treatment hardenability seems to be decreased, and tellurium steels forge well with no marked deterioration in ductility. Tellurium contents of less than 0.01% in cast iron markedly inhibit graphitization (see Section 1.3.) by stabilising much of the iron carbide present.

The AES determination of tellurium in steel down to 0.003%, and in pig iron, have been described by Pravčeva and co-workers (132) and Sturlese, Petrucci and Morello (133) respectively.

The application of AAS to the determination of tellurium in ferrous alloys is quite well documented (73, 122-124, 134-136) with Fleming and Ide (73) quoting the best limit of detection. Using the technique of hydride generation, they have determined tellurium down to levels of 1 ppm in steel.

Coincidentally, this is also the level attained by Dagnall, Taylor and West (13) in the only reported metallurgical application of AFS to the determination of tellurium, in nickel-based alloys.

This chapter describes the first application of non-dispersive AFS to the determination of tellurium in ferrous metals.

5.3. Experimental

5.3.1. Reagents

A 1000 ppm stock solution of tellurium was prepared by dissolving 0.250 g of tellurium in 10 ml of a 5:1 mixture of concentrated nitric and hydrochloric acids and diluting to about 100 ml with glass-distilled, de-ionised water. This solution was made just alkaline by the addition of concentrated ammonia solution to a slight excess and then made up to 250 ml with water. Standard solutions were prepared by the appropriate dilution of this stock solution and were usually prepared freshly each day. Analytical grade reagents were used wherever possible in this work.

5.3.2. The principal tellurium fluorescence lines

The emission spectrum produced by the heated tellurium EDL used throughout this work is shown in Figure 5.1. The radiation from this lamp was focussed onto the entrance slit of a Varian-Techtron AA4 monochromator (the slit width of which was set at 300 microns) scanning at 5 nm/min and detected by an R431 photomultiplier operating at 1100 Volts. The spectrum was recorded by passing the signal from the photomultiplier directly to a potentiometric chart recorder set at 500 mV full-scale deflection.

The pattern of the fluorescence processes which occur for tellurium is similar in nature to that described in Section 4.3.2. for selenium. As before, the $^3P_2$ ground state is part of a fairly closely spaced triplet and this results in there being three main contributions to the overall fluorescence intensity. Since the 214.3 nm resonance line ($^3P_2$ to $^3S^o_1$ transition) absorbs about ten times as strongly as the 238.6 and 238.3 nm lines ($^3P_1$ to $^3S^o_1$ and ^3P_o to $^3S^o_1$ transitions respectively), the major contributions come from resonance fluorescence at 214.3 nm and direct-line fluorescence at 238.6 and 238.3 nm.

In addition, there is some contribution from the 226.0 nm intercombination lines ($^3P_2$ to $^5S^o_2$ transition) but, despite the relatively high intensity of emission from the source as shown in Figure 5.1, the weakly absorbing nature of this line means that this contribution is only very slight. Moreover, there is no contribution to the overall fluorescence intensity from the 253.1 nm intercombination line ($^3P_1$ to $^5S^o_2$ transition), again as

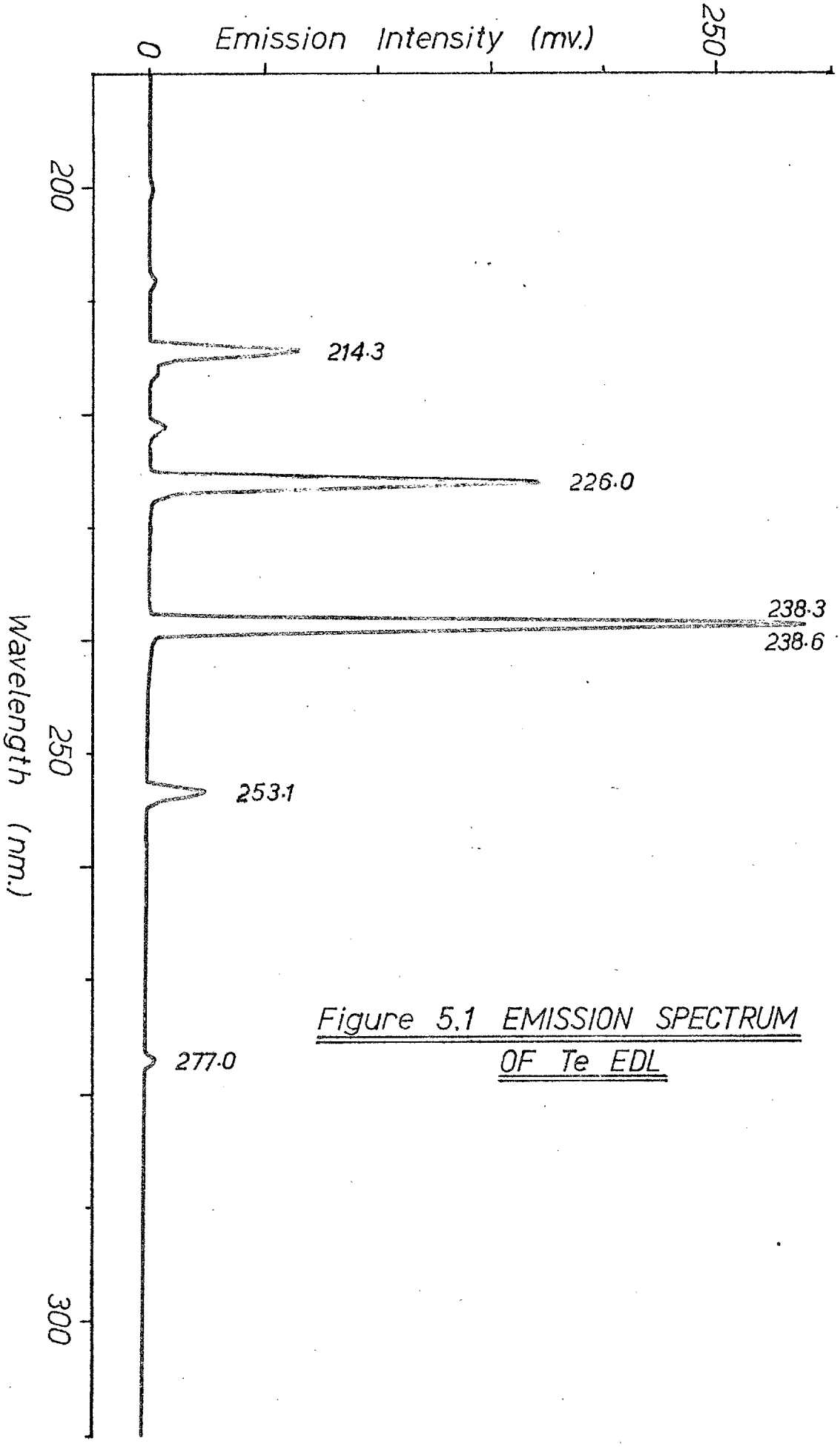


Figure 5.1 EMISSION SPECTRUM OF Te EDL

a result of its weakly absorbing nature (125).

5.3.3. Experimental procedure

The experimental procedure outlined in Section 4.3.3. was adopted in this study. No scatter or atomic emission signals were observed when aspirating aqueous solutions of tellurium, even at concentrations of 1000 ppm.

5.3.4. Preparation and characteristics of the tellurium EDL

At the outset of the work described in this chapter, a tellurium/iodine EDL was examined, but proved to be unsatisfactory for atomic fluorescence studies as sufficient intensity could not be obtained even when the lamp was operated under temperature-controlled conditions. A lamp containing tellurium only was, therefore, used throughout this work, the preparation of which is described elsewhere (52).

As with selenium, no optical components were employed at this stage except during the analysis of steel samples (as described in Section 5.3.9.) when the instrumentation outlined in Section 3.3. was used.

A 10 ppm tellurium solution was used to establish the fluorescence characteristics of the source which are presented in Figures 5.2 and 5.3. The optimum operating conditions for this lamp were found to be at an air-stream temperature of 474^{o}C (with an air flow-rate of 5.0 litres/min) and 70 Watts applied microwave power.

Figure 5.2 CHARACTERISTICS OF Te EDL

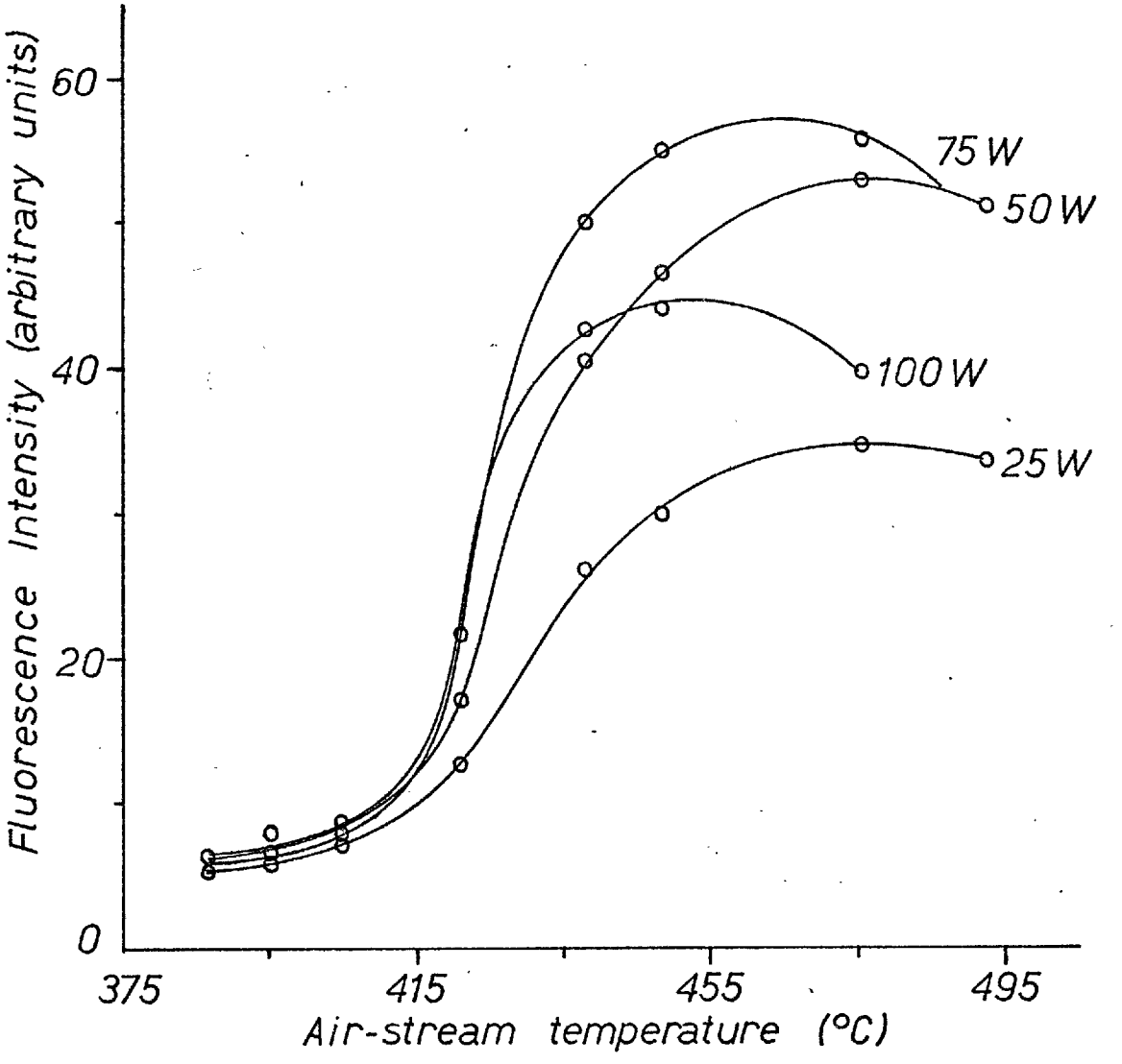
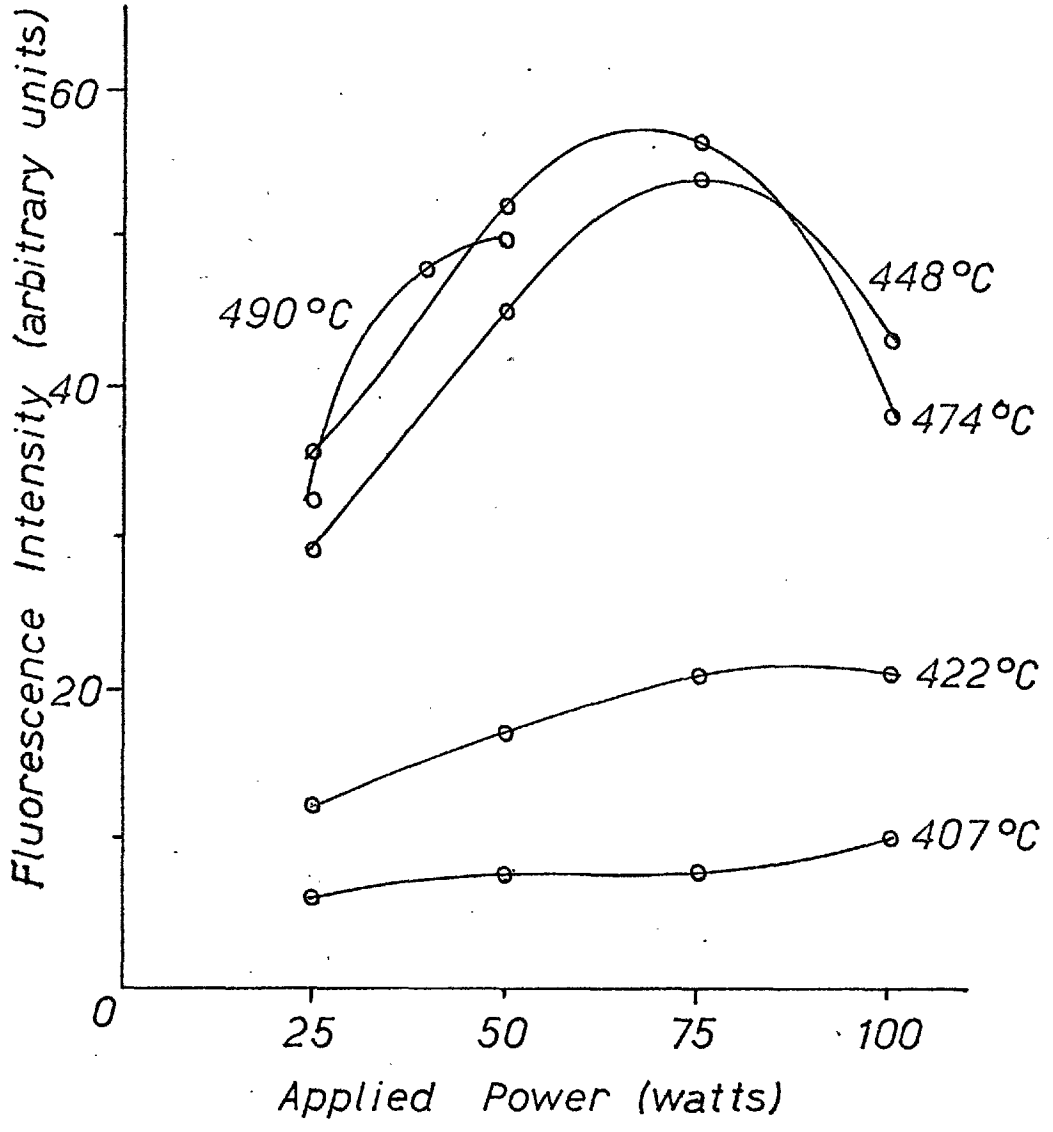


Figure 5.3 CHARACTERISTICS OF Te EDL



5.3.5. Optimisation of flame height and flame composition

A nitrogen-separated air-acetylene flame was used throughout this study. The small increase in sensitivity which could be gained by using argon as the separating-gas was ignored on economic grounds.

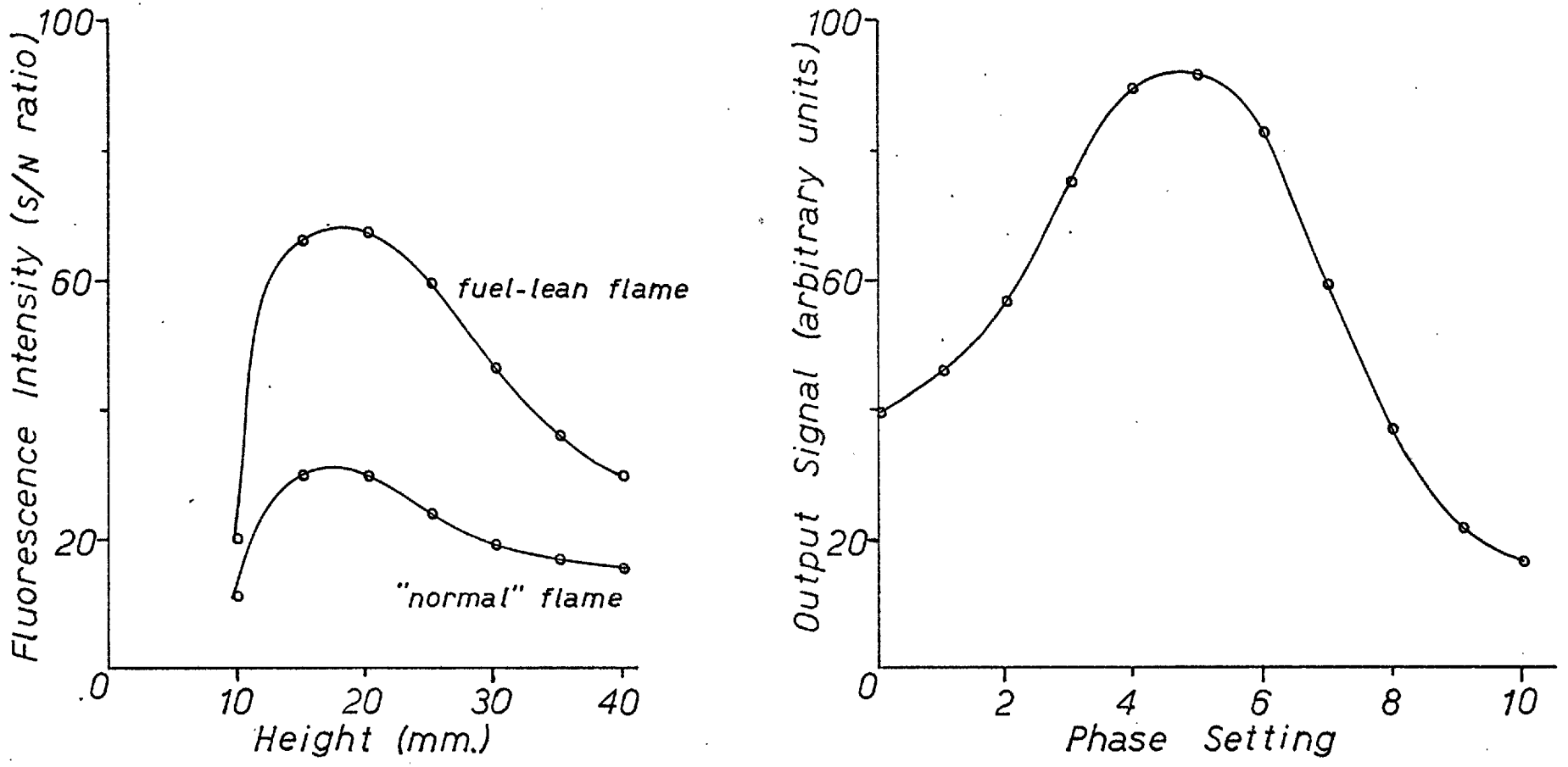
The effect of the various flame conditions on the atomic fluorescence signal-to-noise ratio is shown in Figure 5.4 and reveals that the optimum position for measurement of tellurium atomic fluorescence signals is to be found in a slightly fuel-lean flame, some 20 mm above the top of the burner. This is somewhat surprising as, although the fuel-lean air-acetylene flame usually gives signals of a greater magnitude than those produced by either the "normal" or fuel-rich flames, the increase in the associated noise level generally results in a poorer overall signal-to-noise ratio. In this case, however, the signals produced by the fuel-lean flame seem to be even greater than would normally be envisaged. Perhaps the most likely explanation for this phenomenon is that there are less fluorescence quenching species present in the fuel-lean flame, although it would be wrong to ignore the effect of changes in flame temperature on the degree of atomisation of tellurium.

5.3.6. Optimisation of phase

Figure 5.4 shows the variation in output signal with phase setting and was obtained by both methods described in Section 4.3.6. Maximum output was produced at a phase setting of 5.0.

Optimisation of phase is important because it serves as a useful check that the instrument is functioning correctly. Not only

Figure 5.4 OPTIMISATION OF OPERATING PARAMETERS FOR TELLURIUM



can this exercise ensure that the spectral source, modulation system and detection system are behaving "electronically correctly", but it may also reveal any unusual chemical processes which might occur within the atom cell (i.e. any processes which, unlike atomic fluorescence phenomena, are not instantaneous and might, therefore, produce a phase shift effect).

5.3.7. Analytical growth curve and detection limit

The analytical growth curve for tellurium is shown in Figure 5.5 and was obtained with the amplifier gain set at the minimum value (20 db) and the photomultiplier operating voltage at 1000 Volts. These conditions enabled an aqueous detection limit (signal-to-noise ratio = 2) of 0.28 ppm to be obtained with the linear range of the curve extending up to about 100 ppm.

The instrumental operating conditions under which the analytical growth curve was produced are summarised below:

Spectral source:

1. Air-stream temperature - 474^{o}C (at 5.0 litres/min).
2. Applied microwave power - 70 Watts.
3. Modulation frequency - 285 Hz.
4. Degree of modulation - 70%.

Atom cell:

1. Acetylene flow-rate - 1.0 (0.7 litres/min).
2. Nebuliser pressure - 30 psi (0.2 MN/m^{2}).
3. Viewing height above burner - 20 mm.

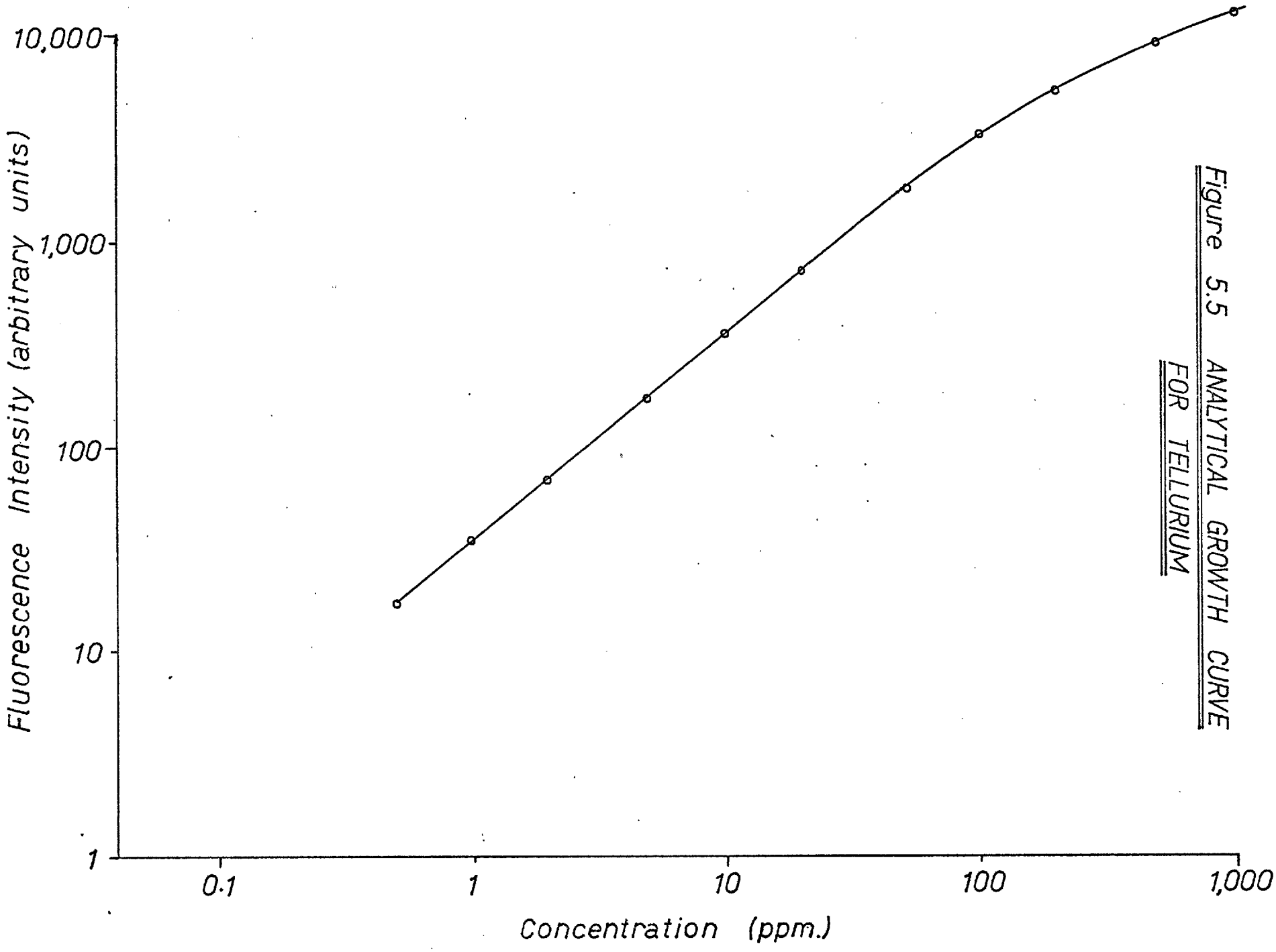


Figure 5.5 ANALYTICAL GROWTH CURVE FOR TELLURIUM

Photomultiplier:

1. Operating voltage - 1000 Volts .

Amplifier:

1. Imput - Normal protected.
2. Frequency limits - 100 Hz to 1000 Hz.
3. Filter - Internal.
4. Meter damping - Off.
5. Gain - 20 db (i.e. 30 db - 10 db).

Phase - sensitive detector:

1. Meter - 10 Volt range (negative).
2. Zero - Negative.
3. Time constant - Internal (1 sec).
4. Filter - Off.
5. Reference channel - A.

Phase shifter:

1. Sensitivity - 100 mV.
2. Frequency range - 100 Hz to 1000 Hz.
3. Phase setting - 5.0.

5.3.8. Interferences

The interference effects of iron on tellurium were examined in accordance with the analysis scheme described in Section 4.3.8. and

the results presented in Figure 5.6. These indicate that, once correction has been made for the scatter signal produced by the iron matrix material, the degree of interference is very small indeed. In fact, even a ten thousand-fold excess iron concentration produced only a 7% enhancement on the fluorescence signal obtained from a 1 ppm tellurium solution.

The chromium and nickel interference effects on tellurium were also investigated using the simulated stainless steel solution referred to in Section 4.3.8. This solution, containing 0.5 ppm tellurium, and the various interferent solutions were examined as before and the results shown in Figure 5.6. From this, it is apparent that it is only necessary to match the iron content of the calibration and sample solutions in order to overcome any interference problems which might be encountered in the analysis of a steel sample.

5.3.9. Analysis of steel samples

In the case of tellurium, no BCS steel samples were found to be available so that suitable standards had to be prepared by adding known volumes of a standard tellurium solution to some dissolved steel samples. The dissolution procedure described in Section 4.3.9. was employed with the tellurium additions being made, during the re-dissolution of the residue, as follows:

1. BCS 320 + 2 ml of a 50 ppm tellurium solution, diluted to 50 ml = 0.020% tellurium in the solid.

Figure 5.6 TELLURIUM INTERFERENCES

Iron conc. (ppm.)	Tellurium conc. (ppm.)	Relative Signal
10,000	1,000	0·95
10,000	100	0·94
10,000	10	0·93
10,000	1	1·07
1,000	100	0·97
1,000	10	0·95
1,000	1	1·07
100	10	1·00
100	1	1·00
10	1	1·00

Interferent	Apparent Signal			Relative Signal
	Matrix	Steel	0·5 ppm Te	
Fe+Cr+Ni	4	13	9	1·0
Fe+Cr	4	14	9	1·1
Fe+Ni	4	14	9	1·1
Fe	4	14	9	1·1
Cr	-	13	9	1·4
Ni	-	13	9	1·4

2. BCS 324 + 4 ml of a 50 ppm tellurium solution, diluted to 50 ml = 0.040% tellurium in the solid.

3. BCS 273 + 6 ml of a 50 ppm tellurium solution, diluted to 50 ml = 0.060% tellurium in the solid.

4. BCS 239/2 + 8 ml of a 50 ppm tellurium solution, diluted to 50 ml = 0.080% tellurium in the solid.

Five separate weighings of each sample were taken and the results of the analyses presented in Figure 5.7. A blank sample was included in these analyses and revealed that all the reagents and glassware used during this study were tellurium-free.

The results presented in Figures 5.7 and 5.8 show a good degree of accuracy and precision for the analyses of the four steel samples which were examined, indicating that the addition of iron alone to the calibration solutions was sufficient to overcome any matrix effects (including the scattering of radiation from the source) which might have occurred during these analyses.

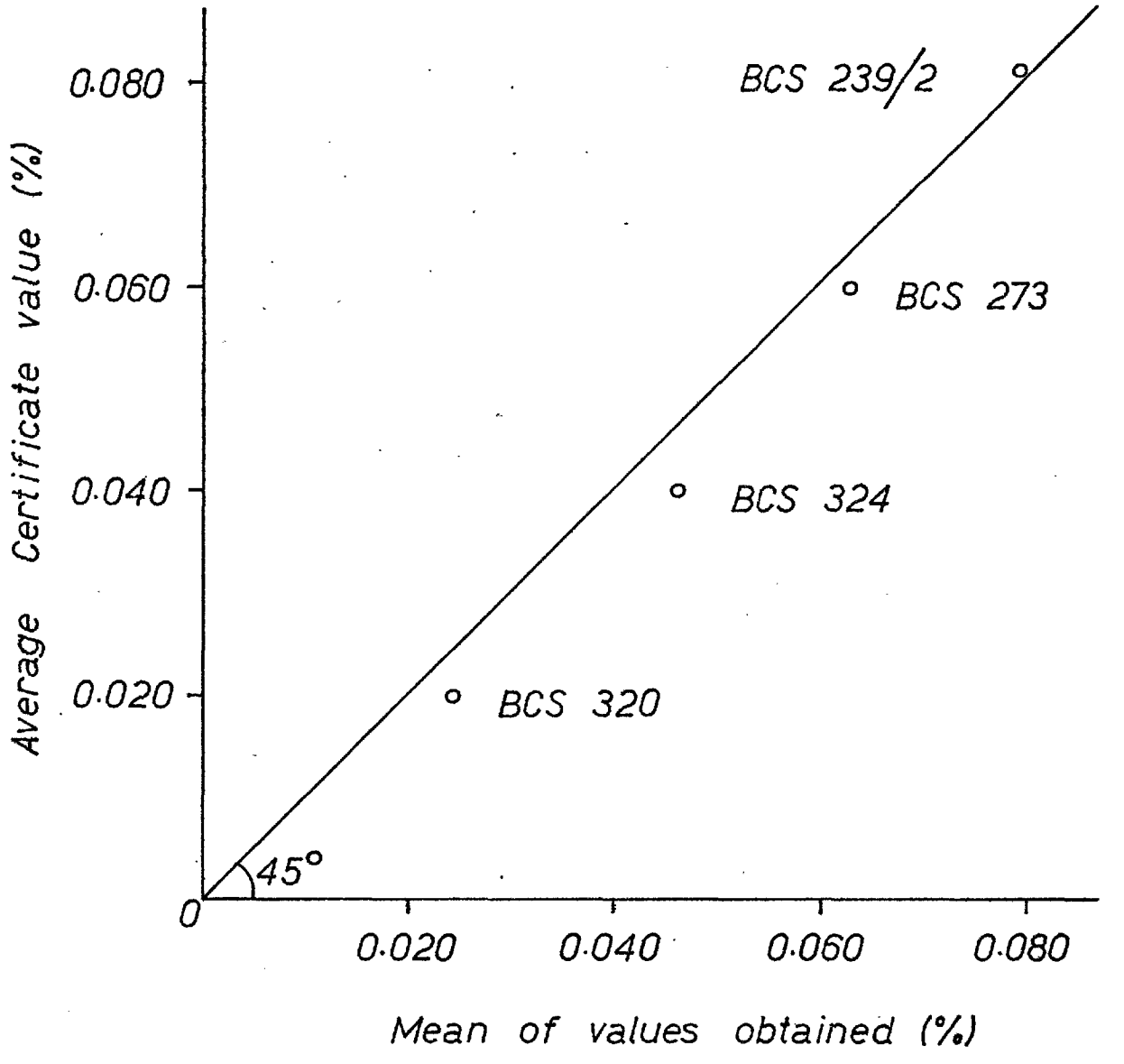
5.4. Conclusions

It is evident that tellurium lends itself particularly well towards a non-dispersive AFS approach and may be easily determined, with good precision and accuracy, in a number of ferrous metals. No elaborate pre-treatment of samples was found to be necessary and

Figure 5.7 ANALYSIS OF TELLURIUM IN STEELS

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 320	MILD STEEL	0.0233, 0.0233, 0.0267, 0.0233, 0.0233	0.0240	6.3	—	—
BCS 324	MILD STEEL	0.0467, 0.0433, 0.0467, 0.0467, 0.0467	0.0460	3.3	—	—
BCS 273	MILD STEEL	0.0667, 0.0667, 0.0600, 0.0600, 0.0600	0.0627	5.9	—	—
BCS 239/2	CARBON STEEL	0.0767, 0.0800, 0.0800, 0.0800, 0.0767	0.0787	2.0	—	—

Figure 5.8 ANALYSIS OF TELLURIUM IN STEELS



the freedom from matrix interference effects is quite remarkable.

In many respects, tellurium (like selenium) seems to act as a model element in non-dispersive AFS, as very few problems are encountered during its determination, so that it is, perhaps, an important feature of the technique that such notoriously "difficult" elements can be determined so conveniently.

CHAPTER SIX

THE DETERMINATION OF LEAD BY NON-DISPERSIVE AFS

6.1. Introduction

In comparison with the other elements dealt with in this work, there exists a veritable plethora of literature on lead. Since the original work by Larkins (46), in which he obtained a detection limit of 0.15 µg/ml in aqueous solution, several workers have reported the determination of lead by non-dispersive AFS, particularly in this department where King (102) and Sanz-Medel (137) have used a carbon filament atom reservoir and Mounce (24) has determined lead in nickel/cobalt alloys using a wire loop atomiser.

Palermo and co-workers (35) have also examined lead as part of their multi-element, non-dispersive AFS studies while, more recently, Kuga and Tsujii (138), in an attempt to reduce the high continuum emission generally associated with non-flame cells, have employed a shielded graphite atomiser and obtained a limit of detection of 0.002 µg/ml.

In the dispersive mode, lead is usually determined at either 405.8 or 283.3 nm. The literature contains such a variety of information, however, that rigorous classification is difficult but it may be said that the published papers (49, 50, 56, 57, 105, 111, 113, 115, 116, 118, 127-129, 139-152) describe many flame and non-flame determinations of lead in which most types of excitation source have been used.

6.2. Lead in ferrous alloys

Lead additions of the order of 0.25% are often made to

both carbon and low-alloy steels to improve their free-cutting properties (119) but, in contrast to sulphur and phosphorus which improve machinability by embrittling the steel, lead does not greatly affect the ductility, toughness or other mechanical properties.

It can be readily inferred from the amount of literature which exists that the presence of lead in ferrous alloys is of considerable importance. In fact, the determination of lead in iron and steel has been included in a number of reviews dealing with the application of AAS to metallurgical analysis (153-157).

In more specific instances (73, 122, 158-184), both the flame and non-flame determinations in iron and steel have been reported and a variety of analytical procedures established. These usually involve some form of preliminary separation of the lead from the iron matrix followed by measurement at 217.0 or 283.3 nm. In addition, the determination of lead by AAS in a number of other ferrous materials has been reported, including stainless steels (185-188), high temperature alloys (123), high-alloy steels (189, 190), ferro-manganese (177, 191, 192) and ferro-silicon (192, 193).

The technique of AES has found application to a similar range of materials, lead in steel having been determined by Pravčeva and co-workers (132), Gegus (194) and Sturlese and co-workers (195), the latter workers having previously centred their attention on lead in stainless steel (196).

A paper by Foster, Molins and Bozon (197), which compares their determination of lead in ferro-manganese by AES to their earlier studies using AAS, is of considerable value in evaluating the capabilities of the two techniques while the remaining literature (198-202) deals with the AES determination of lead in ferrous and high temperature alloys and is again of interest for comparative purposes. Maiboroda and co-workers (203) have also included the determination of lead in their paper dealing with the effect of a "carrier" on the spectral excitation conditions for determining small amounts of impurities in iron-based alloys.

Apart from the work by Mounce (24) referred to above, the only other reported metallurgical application of AFS to the determination of lead is that of Dagnall, Taylor and West (13) who found it necessary to resort to a solvent extraction procedure to eliminate interference problems.

This chapter describes the first application of non-dispersive AFS to the determination of lead in ferrous metals.

6.3. Experimental

6.3.1. Reagents

A 1000 ppm stock solution of lead was prepared by dissolving 0.399 g of lead (II) nitrate in 250 ml of distilled, de-ionised water. Standard solutions were prepared by the appropriate dilution of this stock solution and were usually prepared freshly

each day. Analytical grade reagents were used wherever possible in this work.

6.3.2. The principal lead fluorescence lines

The spectrum emitted by the heated lead/iodine EDL used throughout this work is presented in Figure 6.1 and was obtained with the aid of a Varian-Techtron AA4 monochromator scanning at a rate of 5 nm/min and having a slit width of 100 microns. An R431 photomultiplier operating at 1100 Volts was used to detect the radiation passing through the monochromator and the signal produced was monitored on a potentiometric chart recorder set at 500 mV full-scale deflection.

Lead is not particularly suited to a non-dispersive approach in which a solar-blind photomultiplier is used as the most sensitive line (405.8 nm) lies outside the response range of this type of detector. The most important, but still not particularly sensitive, contributions to the overall fluorescence intensity come from the 283.3 and 217.0 nm resonance lines. Lead exhibits a complex fluorescence spectrum, however, and there are several small contributions from most of the lines shown in Figure 6.1 (147).

6.3.3. Experimental procedure

The procedure used throughout this study has been described in Section 4.3.3. A 1000 ppm aqueous lead solution was used to check for the occurrence of any scatter or atomic emission signals,

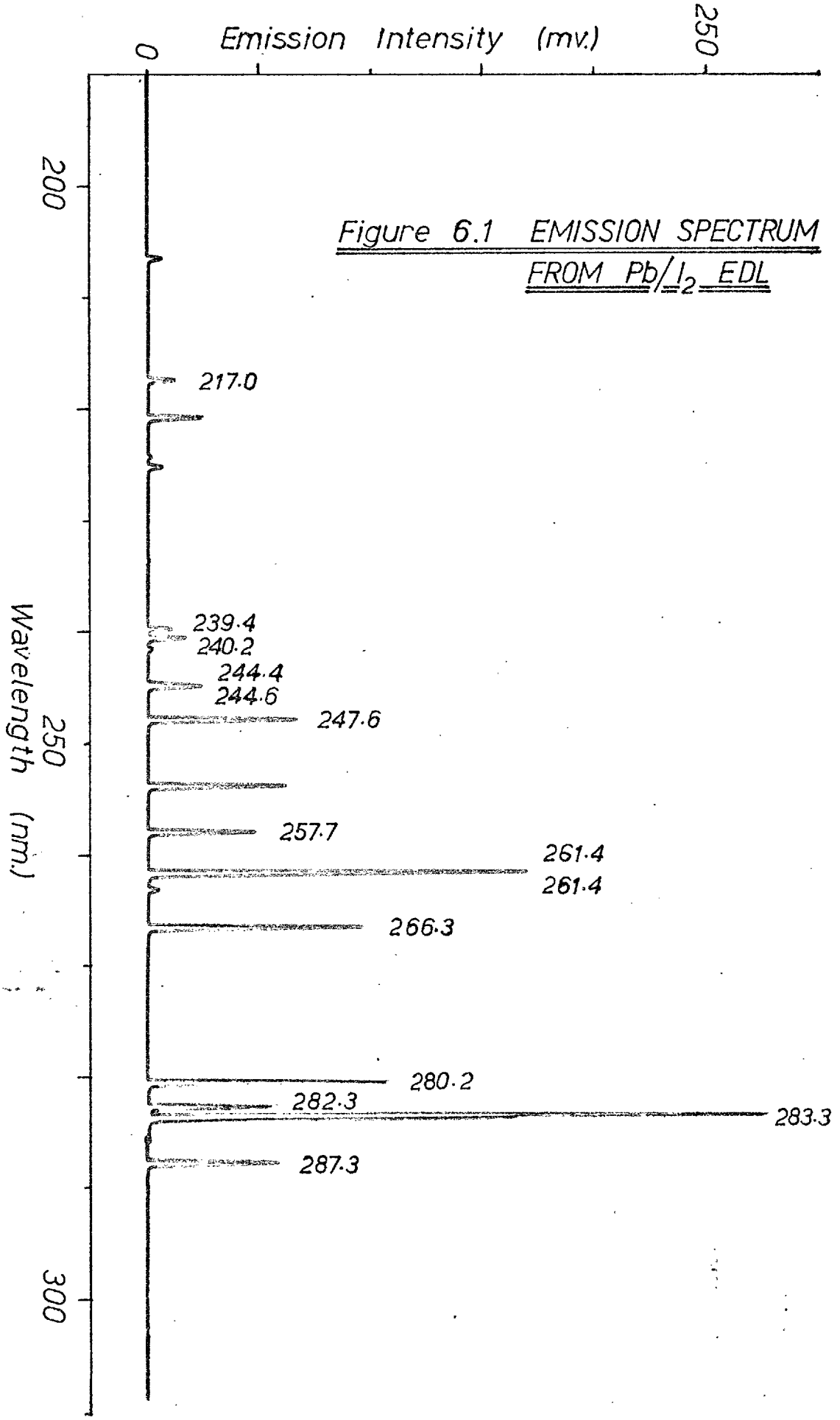


Figure 6.1 EMISSION SPECTRUM FROM Pb/I_2 EDL

neither of which were observed in this investigation.

6.3.4. Preparation and characteristics of the lead EDL

The method of preparation of the lead/iodine EDL used throughout this study has been described in detail elsewhere (102). Such lamps are usually found to be completely satisfactory in terms of emission intensity and stability, which is fortunate because lamps containing lead only give poor intensity, even when operated at high temperatures, due to the comparatively low volatility of this element.

Using the instrumentation described in Section 3.3., although no optical components were employed at this stage, the fluorescence characteristics of the lead/iodine EDL as shown in Figures 6.2 and 6.3 were obtained, a 10 ppm lead solution being aspirated for this purpose. These results reveal that at the optimum operating air-stream temperature of 424^{o}C (with an air flow-rate of 10 litres/min) the fluorescence intensity is almost independent of the applied microwave power (which was optimised at 50 Watts).

6.3.5. Optimisation of flame height and flame composition

A nitrogen-separated air-acetylene flame was used throughout this determination. An improvement in sensitivity (by a factor of about 1.5) was observed when argon was used to separate the flame but this was not felt to be sufficient to outweigh the additional expense involved in using this gas.

Figure 6.2 CHARACTERISTICS OF Pb/I_2 EDL

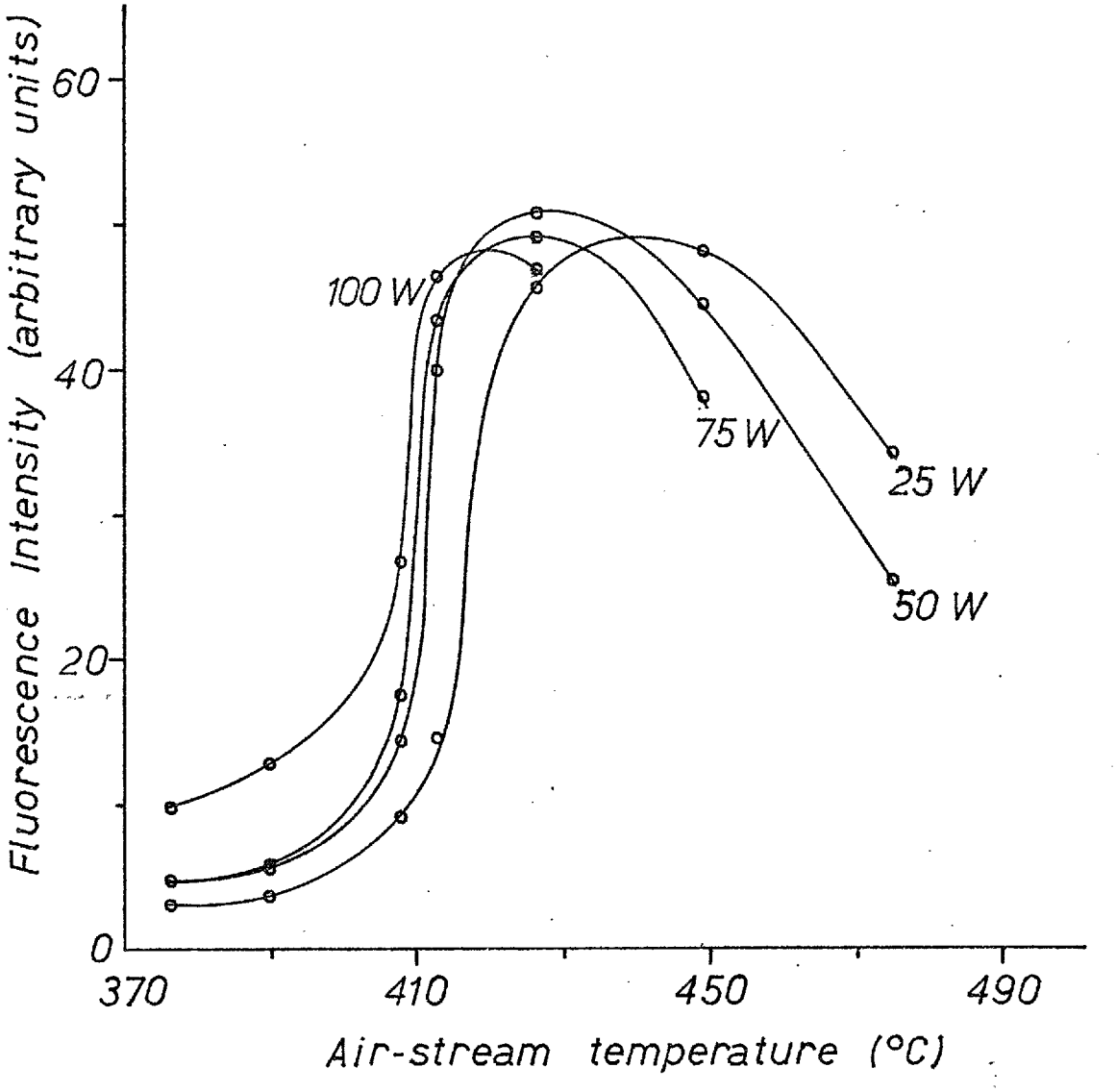


Figure 6.3 CHARACTERISTICS OF Pb/I_2 EDL

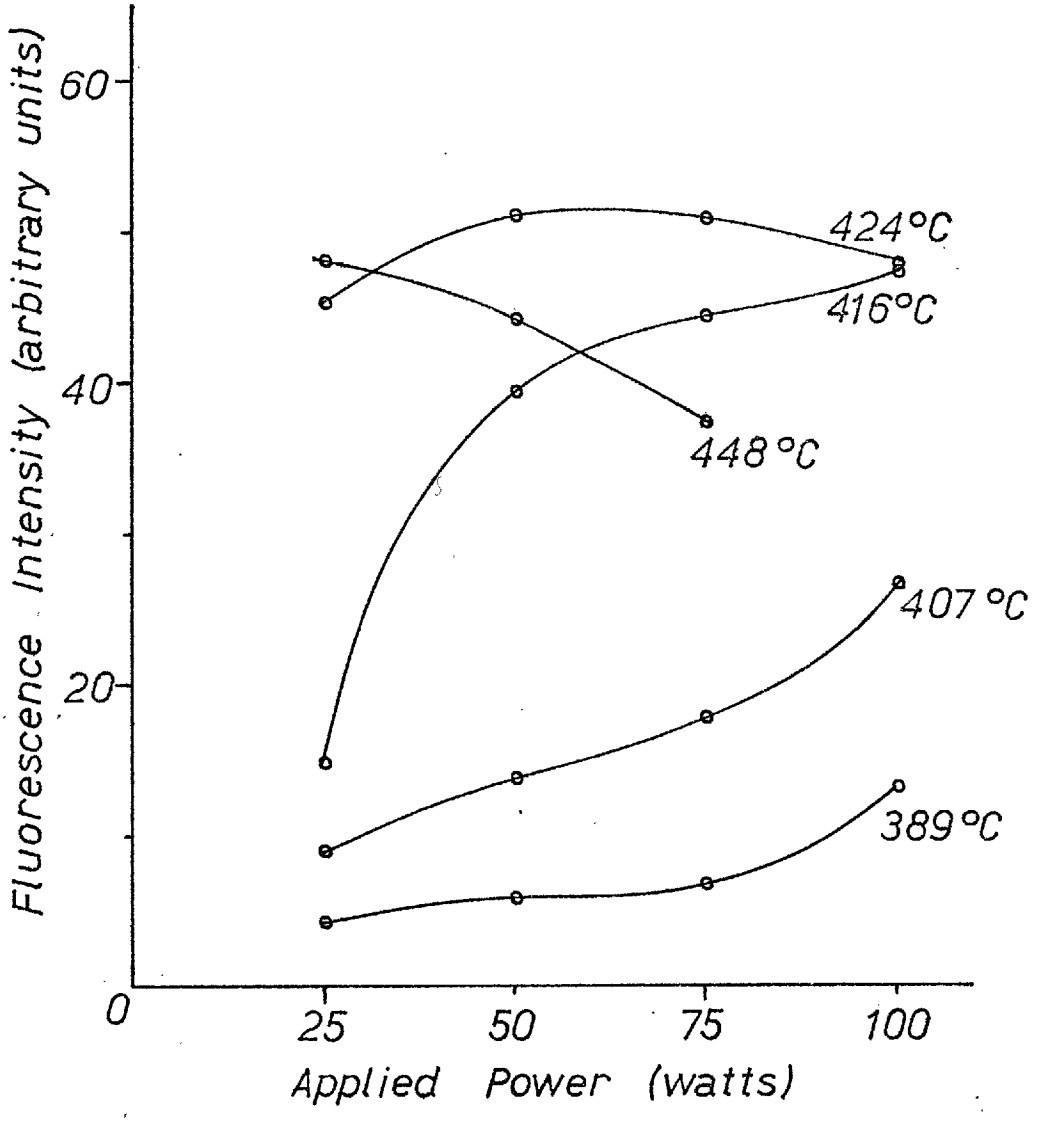


Figure 6.4 shows the atomic fluorescence signal-to-noise ratio produced under various flame conditions. Throughout this study the "normal" flame was chosen, although no loss in sensitivity was observed when using a slightly fuel-rich flame, with the optimum viewing position at a height of about 25 mm above the top of the burner.

6.3.6. Optimisation of phase

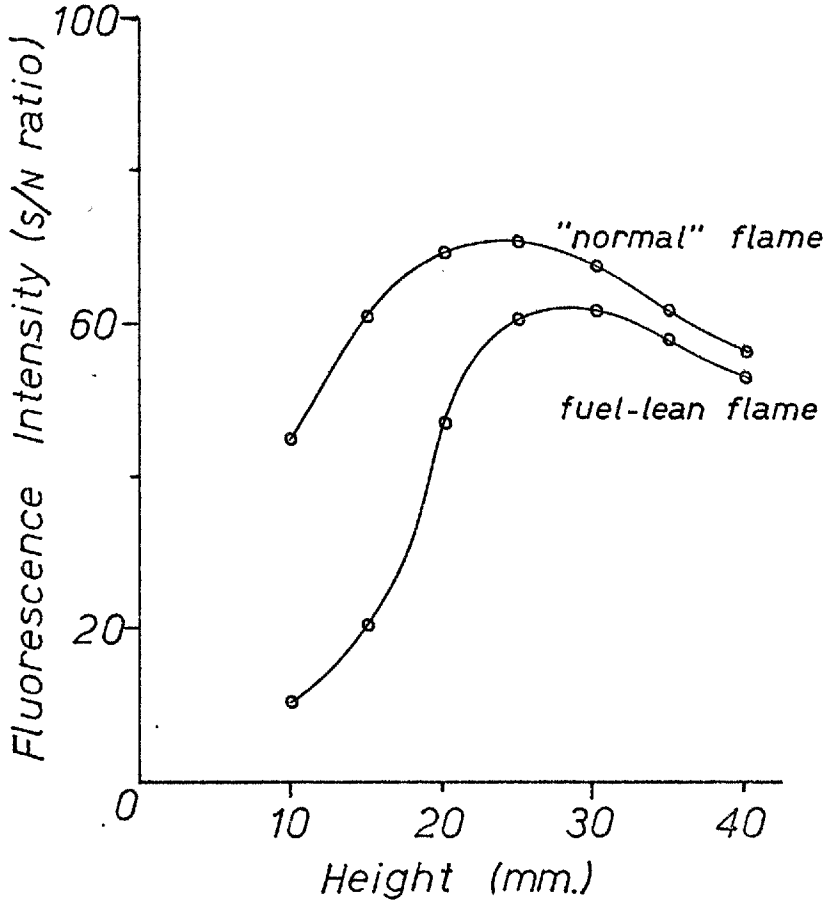
The output signal produced at different phase settings is also shown in Figure 6.4. Both methods described in Section 4.3.6. were used to obtain these results, which indicate that maximum output occurred at a phase setting of 4.5.

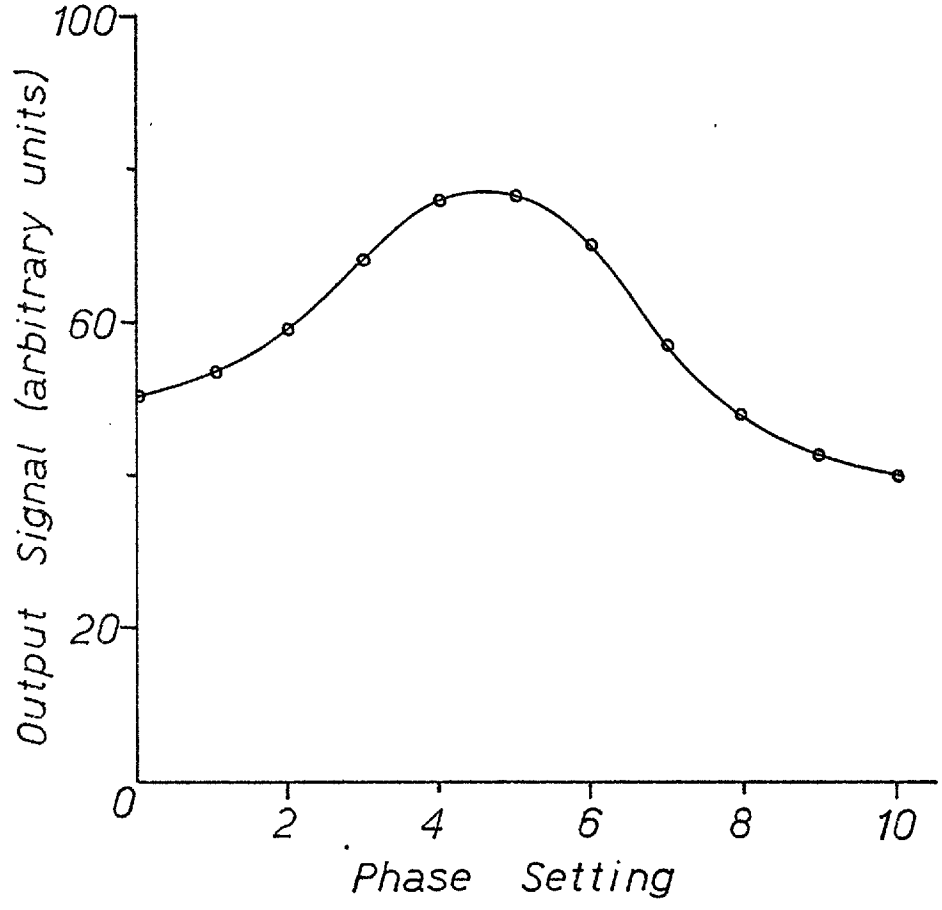
6.3.7. Analytical growth curve and detection limit

Figure 6.5 shows the analytical growth curve for lead obtained with the photomultiplier operating at 1200 Volts and the amplifier gain set at 23 db. These settings indicate the relative insensitivity of the instrument (and of the photomultiplier, in particular) towards lead atomic fluorescence signals and serve to emphasise that no great improvement in detection limit is to be obtained in the case of this element by adopting a non-dispersive approach.

An aqueous detection limit (signal-to-noise ratio = 2) of 0.35 ppm was obtained in this study with the linear range of the analytical growth curve extending up to about 40 ppm. At this point, it was felt that some improvement in sensitivity would be desirable, so the optical components described in

Figure 6.4 OPTIMISATION OF OPERATING PARAMETERS FOR LEAD





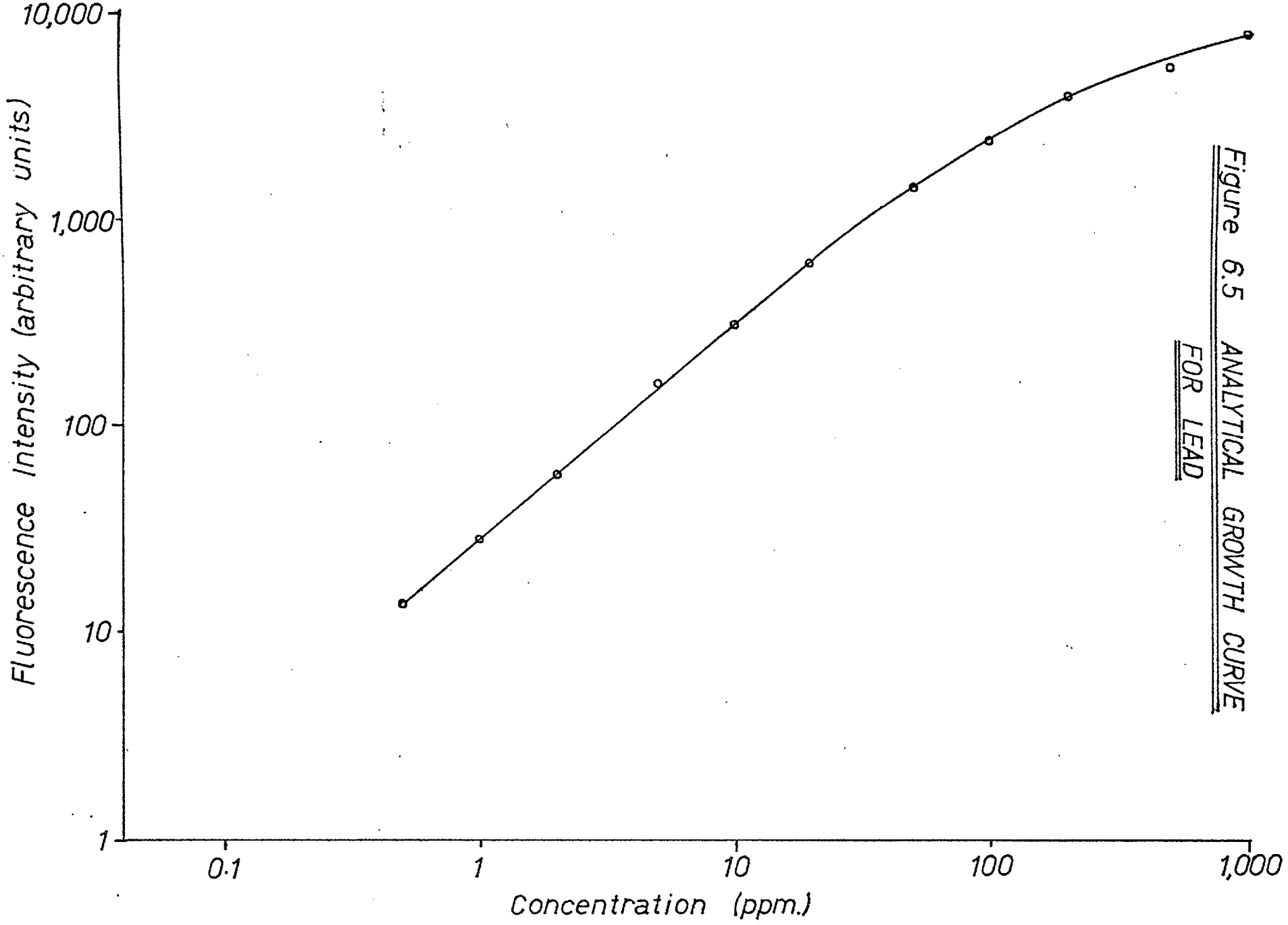


Figure 6.5 ANALYTICAL GROWTH CURVE FOR LEAD

Section 3.3.3. were introduced into the system. The new arrangement was found roughly to halve the detection limit and was, therefore, retained throughout the remainder of the work described in this thesis.

The instrumental operating conditions under which the analytical growth curve shown in Figure 6.5 was obtained are summarised as follows:

Spectral source:

1. Air-stream temperature - 424^{o}C (at 10.0 litres/min).
2. Applied microwave power - 50 Watts.
3. Modulation frequency - 285 Hz.
4. Degree of modulation - 70%.

Atom cell:

1. Acetylene flow-rate - 1.1 (0.8 litres/min).
2. Nebuliser pressure - 30 psi (0.2 MN/m^{2}).
3. Viewing height above burner - 25 mm.

Photomultiplier:

1. Operating voltage - 1200 Volts.

Amplifier:

1. Input - Normal protected.
2. Frequency limits - 100 Hz to 1000 Hz.
3. Filter - Internal.
4. Meter damping - Off.
5. Gain - 23 db (i.e. 30 db - 7 db).

Phase-sensitive detector:

1. Meter - 10 Volt range (negative).
2. Zero - Negative.
3. Time constant - Internal (1 sec).
4. Filter - Off.
5. Reference channel - A.

Phase shifter:

1. Sensitivity - 100 mV.
2. Frequency range - 100 Hz to 1000 Hz.
3. Phase setting - 4.5.

6.3.8. Interferences

The interference effects of iron on lead are shown in Figure 6.6 from which it may be seen that the overall level of interference is small. These results were obtained as described in Section 4.3.8., the correction for the iron scatter signal being made by aspirating a solution of pure iron, as opposed to the more usual distilled water, as the reference material.

The interference effects of chromium and nickel are also presented in Figure 6.6 and indicate that the addition of an appropriate amount of iron to the calibration solutions would avoid any scatter interference problems. The reason for this is that the contribution to the matrix scatter signal from the chromium and nickel contents is of a similar magnitude to that which would be produced by an equivalent amount of iron. Thus, it is unnecessary to match the levels of each matrix element in the sample and calibration solutions, but merely to consider

Figure 6.6 LEAD INTERFERENCES

Iron conc. (ppm.)	Lead conc. (ppm.)	Relative Signal
10,000	1,000	0·98
10,000	100	0·96
10,000	10	1·15
10,000	1	1·00
1,000	100	1·10
1,000	10	1·10
1,000	1	1·00
100	10	1·00
100	1	1·00
10	1	1·00

Interferent	Apparent Signal			Relative Signal
	Matrix	Steel	0·5 ppm Pb	
Fe+Cr+Ni	24	29	5	1·0
Fe+Cr	22	29	5	1·4
Fe+Ni	20	29	5	1·8
Fe	18	29	5	2·2
Cr	4	29	5	5·0
Ni	2	29	5	5·4

how? by wt. or what.

the whole matrix as iron and modify the calibration solutions accordingly.

6.3.9. Analysis of steel samples

Three BCS steel samples containing suitable amounts of lead were analysed in accordance with the scheme described in Section 4.3.9. and the results presented in Figures 6.7 and 6.8. These show excellent agreement between the values obtained and the average certificate value for each steel sample with a good degree of precision for each set of analyses. This suggests that the addition of iron only to the calibration solutions is sufficient to enable accurate and precise determinations of lead in steel samples to be made, although it must be emphasised that in the three BCS steel samples examined, no element, other than iron, was present at a level of greater than about 0.55%.

A blank sample was included during this exercise and indicated that all reagents and glassware were free from traces of lead.

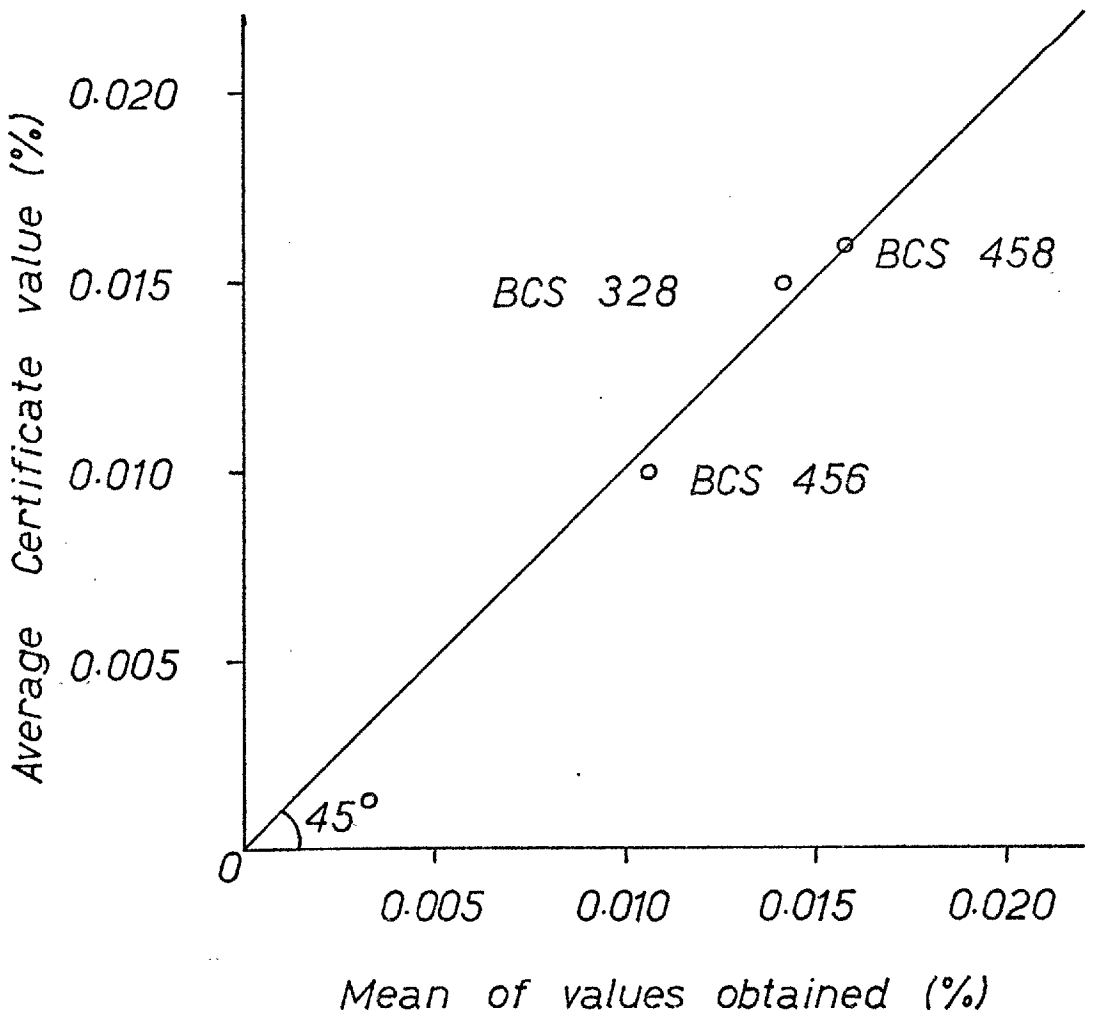
6.4. Conclusions

Although no great advantage is obtained from the point of view of sensitivity, the determination of lead in ferrous metals by non-dispersive AFS seems to be both accurate and precise, with very little interference from the matrix material. Extensive pre-treatment of the steel samples was found to be unnecessary and the addition of iron to the calibration solutions sufficient to enable accurate analyses to be made.

Figure 6.7 ANALYSIS OF LEAD IN STEELS

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 328	MILD STEEL	0.0125 , 0.0155 , 0.0143 , 0.0136 , 0.0131	0.0138	8.4	0.015	0.012 → 0.017
BCS 458	MILD STEEL	0.0155 , 0.0155 , 0.0168 , 0.0150 , 0.0155	0.0157	4.5	0.016	—
BCS 456	MILD STEEL	0.0111 , 0.0117 , 0.0100 , 0.0100 , 0.0100	0.0106	6.7	0.010	—

Figure 6.8 ANALYSIS OF LEAD IN STEELS



CHAPTER SEVEN

THE DETERMINATION OF TIN BY NON-DISPERSIVE AFS

7.1. Introduction

Although there have been several reports of the AFS determination of tin, only those of Larkins (46), who obtained a detection limit of 3 µg/ml in aqueous solution, and Mounce (24), whose wire loop atomiser gave a detection limit of 0.15 µg/ml, employed a non-dispersive approach.

In the dispersive mode, the atomic fluorescence of tin is usually measured at 286.3 or 303.4 nm. Continuum sources and HCLs have been used (118, 142, 152) although, in general, HCLs give better sensitivity. Tin has been determined in a variety of flames (118, 127, 142, 204-206), with the best limits of detection being obtained in the argon-oxygen-hydrogen flame, as well as with non-flame atomisers (105, 128). Molnar and Winefordner (129) have obtained the lowest limit of detection to date, however, quoting a value of 0.002 µg/ml in aqueous solution.

7.2. Tin in ferrous alloys

Additions of tin are often made to plain carbon steel to improve the tensile strength, although the drawing properties can be impaired, even by contents as low as 0.02%. Up to 0.15% tin may be present in mild steel, however, without detrimental effect, although such levels in alloy steels can cause serious forging problems (207). Tin increases the hardenability of steel and inhibits graphitization (see Section 1.3.) in cast iron.

The AFS determination of tin in steels has been reported by Ebdon, Hubbard and Michel (26). Operating at 303.4 nm and using an electronically modulated EDL and an argon-oxygen-hydrogen flame, these workers obtained a detection limit of 0.01 µg/ml in aqueous solution.

Interference problems were eliminated by adding iron (III) chloride to the standard tin solutions.

The application of AAS to the determination of tin in steels is more widespread and has been reviewed by Endo and Nakahara (154), Janousek (155) and Condylis and Mejean (208). More specifically, Kono (209) has determined tin in cast iron down to 0.0002% by direct aspiration of a non-aqueous extract, while Burke (173) used a similar procedure to measure 0.1 ppm tin in iron-based alloys. Tin has also been determined in ferro-manganese (191) and ferro-silicon (193).

Of the several papers concerned with the AAS determination of tin in steel (73, 74, 122, 169, 170, 176, 179, 210-213) the more interesting are those of Fleming and Ide (73), which quotes a detection limit of 2 ppm in steel using hydride generation, and of Thompson and Godden (74), which involves the technique of single-pulse nebulisation and reports a limit of detection of 0.0008% in steel.

In addition, there are a few papers dealing with the AES determination of tin in steel and ferrous alloys (132, 197, 199, 200, 202, 203, 214, 215) which are of interest mainly for comparative purposes.

This chapter describes the first application of non-dispersive AFS to the determination of tin in ferrous metals.

7.3. Experimental

7.3.1. Reagents

A 1000 ppm stock solution of tin was prepared by dissolving 0.250 g of tin in 10 ml of hot concentrated hydrochloric acid and diluting to 250 ml with glass-distilled, de-ionised water. This solution was found to be quite unstable, however, and was, therefore, prepared freshly whenever required. In many cases, this involved discarding solutions, prepared on the previous day, in which precipitation had occurred.

Standard solutions of tin were prepared by the appropriate dilution of this stock solution and, once again, were freshly prepared immediately before use. Analytical grade reagents were used wherever possible in this work.

7.3.2. The principal tin fluorescence lines

Figure 7.1 shows the emission spectrum produced by the heated tin/iodine EDL used throughout this work. This was obtained by focussing the radiation from the lamp onto the entrance slit (100 microns) of a Varian-Techtron AA4 monochromator scanning at 5 nm/min. The radiation passing through the monochromator was detected by an R431 photomultiplier operating at 1100 Volts and the signal produced was displayed on a potentiometric chart recorder set at 200 mV full-scale deflection.

Tin exhibits a complex spectrum which results in there being many contributions to the overall fluorescence intensity. The most important

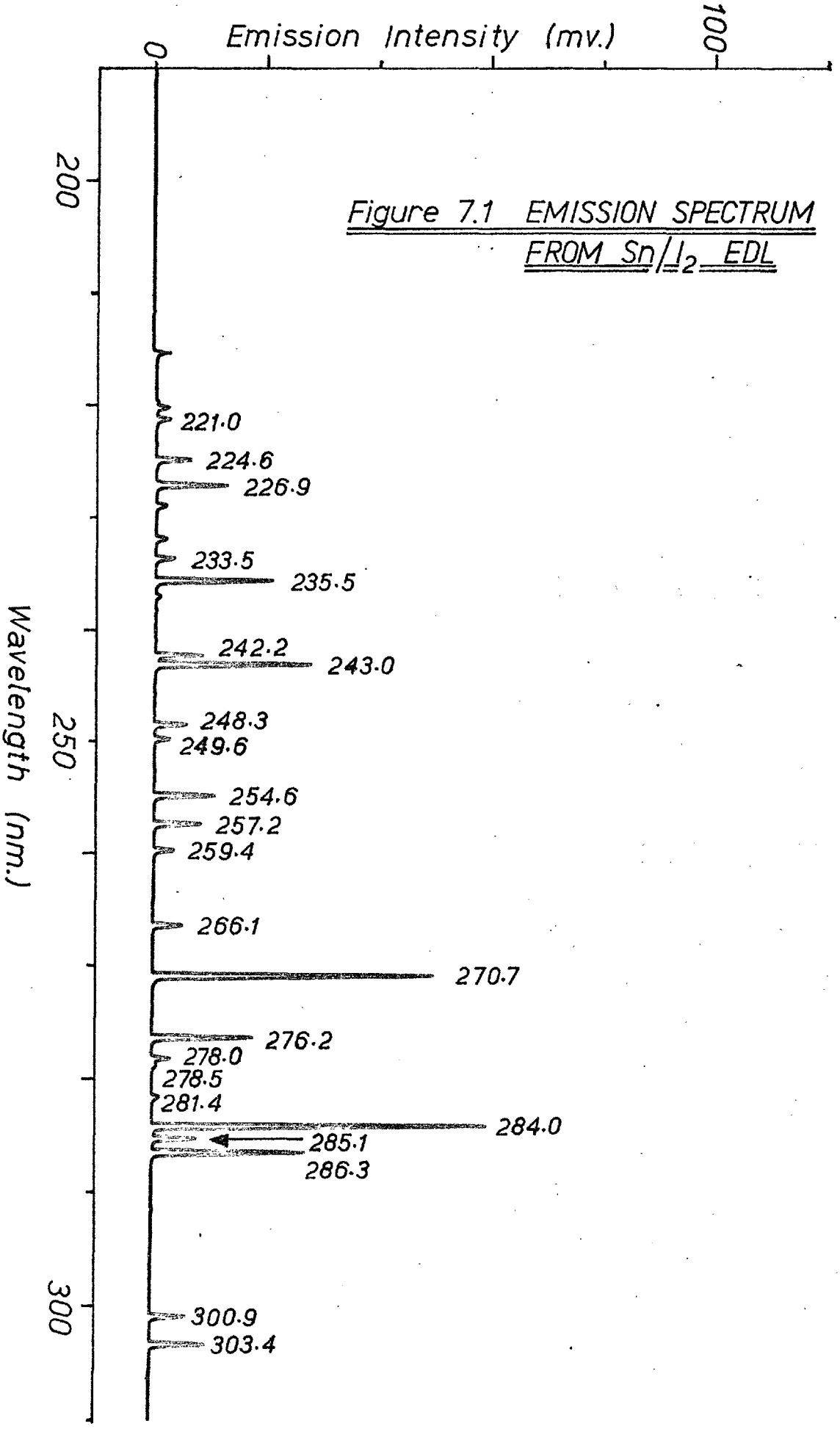


Figure 7.1 EMISSION SPECTRUM FROM Sn/I_2 EDL

of these, however, come from the resonance lines at 286.3, 224.6 and 254.6 nm, although in the hotter type flames (nitrous oxide-acetylene etc.) deactivation to energy levels above the ^3P_o ground state plays a significant part in the overall fluorescence process.

It is unfortunate that tin is not so well suited to a non-dispersive approach as might be imagined from the complexity of the emission spectrum. The reason for this is that, although the spectrum features many lines which contribute to the overall atomic fluorescence signal, most of these are to be found in the region in which the R431 photomultiplier is relatively insensitive. Thus, while reasonable sensitivity might be anticipated, examination of Figure 7.1 would indicate that no great improvement in detection limit would be obtained by the adoption of a non-dispersive approach.

7.3.3. Experimental procedure

The procedure described in Section 4.3.3. was adopted throughout the determination of tin. No scatter or atomic emission signals were observed in this work when aspirating a 1000 ppm aqueous tin solution.

7.3.4. Preparation and characteristics of the tin EDL

Originally a lamp containing tin only was made but was found to give insufficient intensity for atomic fluorescence studies even when operated at high air-stream temperatures. To overcome this problem of involatility, a lamp containing tin and iodine was

made, in accordance with the general method of preparation described in Section 3.3.1.(a). Briefly, this involved the introduction of a small piece of tin into the bulb of a suitably treated EDL blank which was then flushed several times with argon. In this inert atmosphere, the metal was gently heated and driven out of the bulb, whence it was allowed to condense on the wall of the blank. A small amount of this condensate was then driven back into the bulb, which was flushed with argon and allowed to cool. A drop of a dilute solution of iodine in chloroform was then introduced into the lamp blank and the chloroform evaporated off under vacuum. After extensive flushing with argon, the pressure was reduced to about 5 Torr and the bulb rapidly sealed.

An initial "running-in" period of a few hours was allowed for this lamp to ensure that the tin and iodine had chance to equilibrate before use, after which the fluorescence characteristics shown in Figures 7.2 and 7.3 were determined. A 10 ppm tin solution and a nitrogen-separated air-hydrogen flame were used for this purpose as no appreciable atomic fluorescence signals could be obtained with the customary air-acetylene flame.

The lamp was operated at an air-stream temperature of 210^{o}C (with an air flow-rate of 10 litres/min) and 50 Watts applied microwave power. Under these conditions, the temperature-dependence of the lamp was negligible, but fluctuations in microwave power were sometimes found to present problems, so that the stability of this lamp was occasionally found to be unsatisfactory. In most cases, however, no source difficulties were encountered during the determination of tin.

Figure 7.2 CHARACTERISTICS OF Sn/I_2 EDL

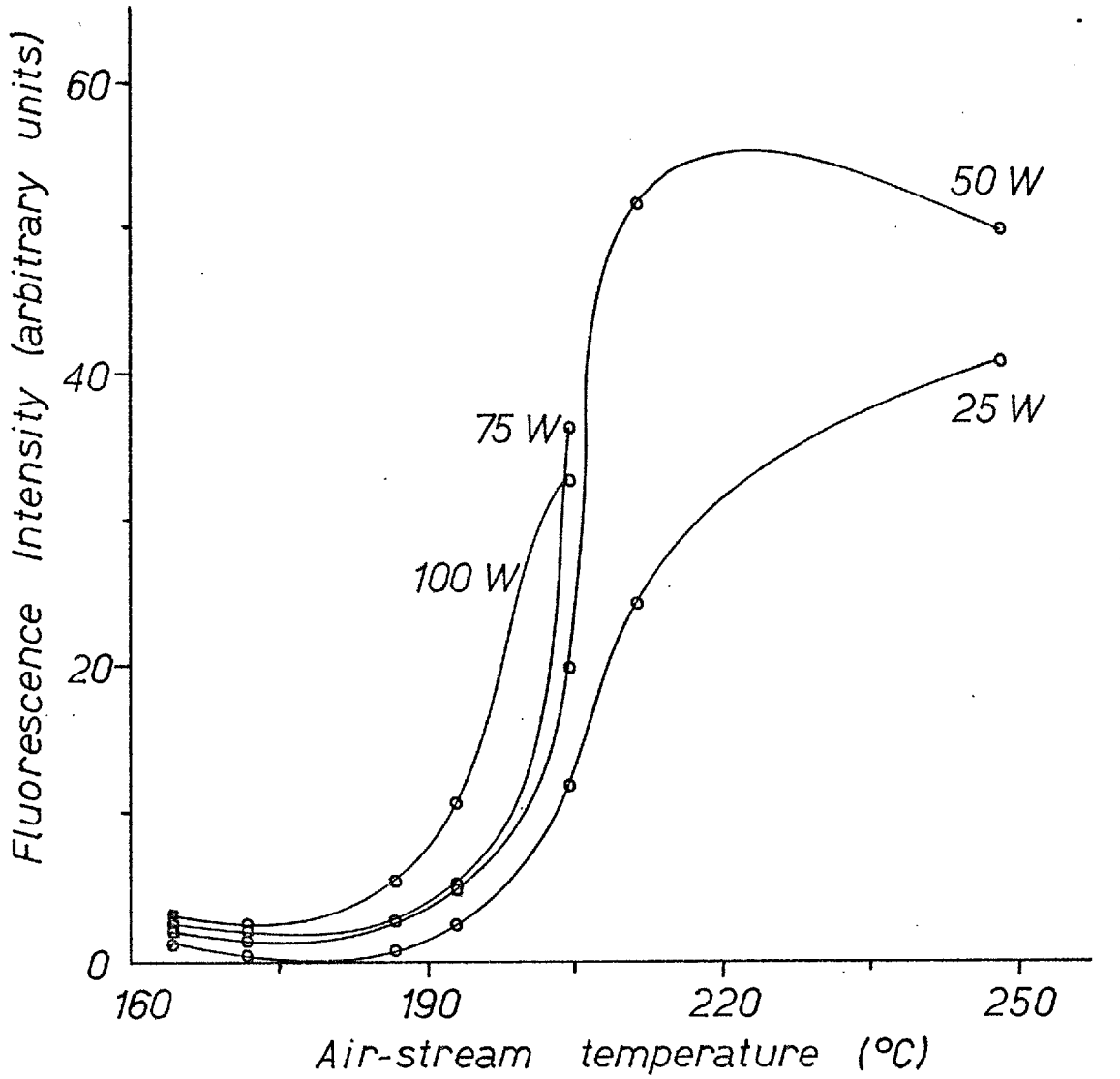
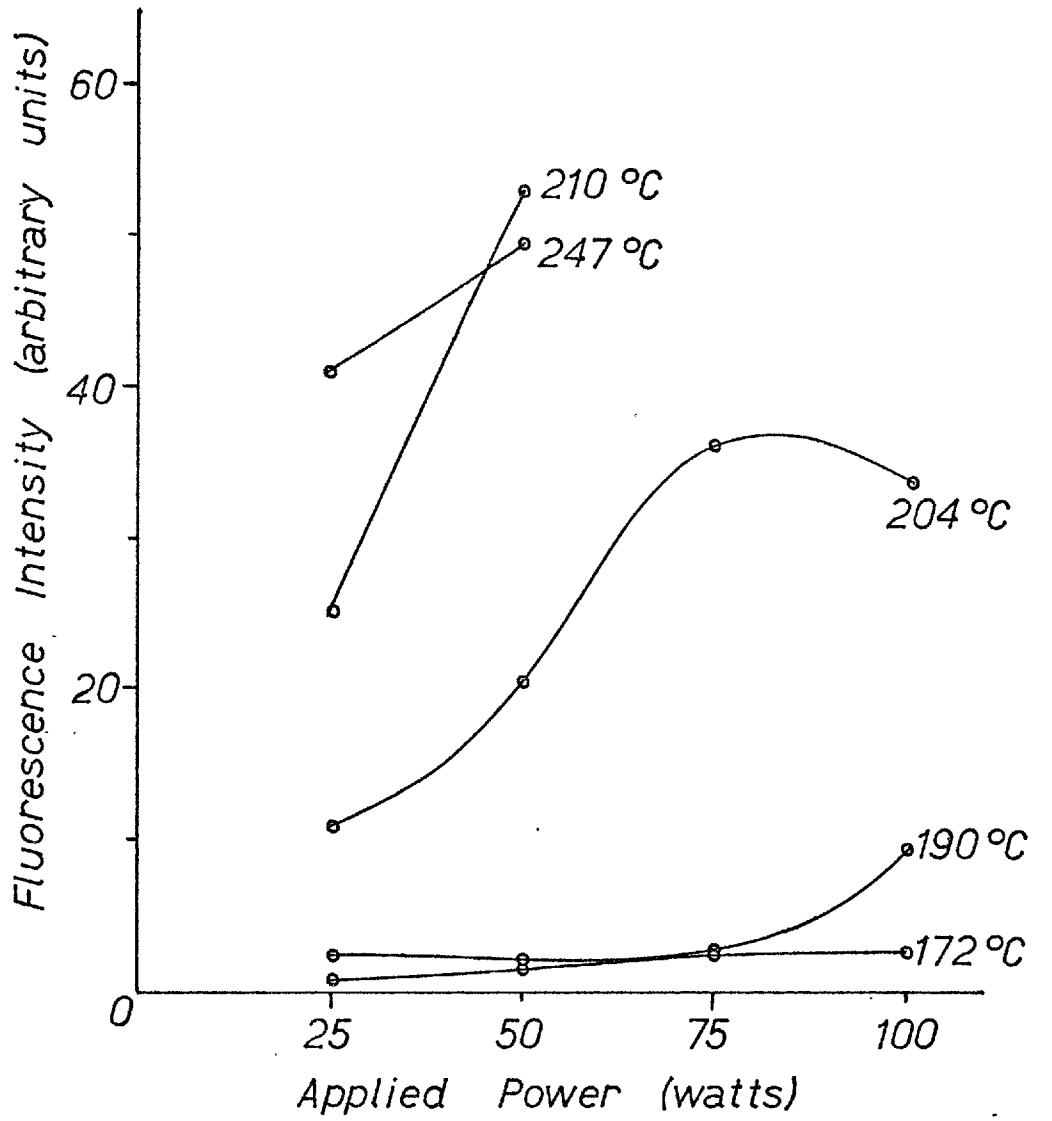


Figure 7.3 CHARACTERISTICS OF Sn/I_2 EDL



7.3.5. Optimisation of flame height and flame composition

Poor sensitivity was obtained for the determination of tin even when a fuel-rich air-acetylene flame was used (presumably because of the inability of this flame to break down the very stable SnO species). A fuel-rich air-hydrogen flame was, therefore, used throughout the determination as this gave a considerable improvement in sensitivity. This would seem to be due to the highly reducing nature of this flame which results in the easily dissociated SnH species being predominantly formed.

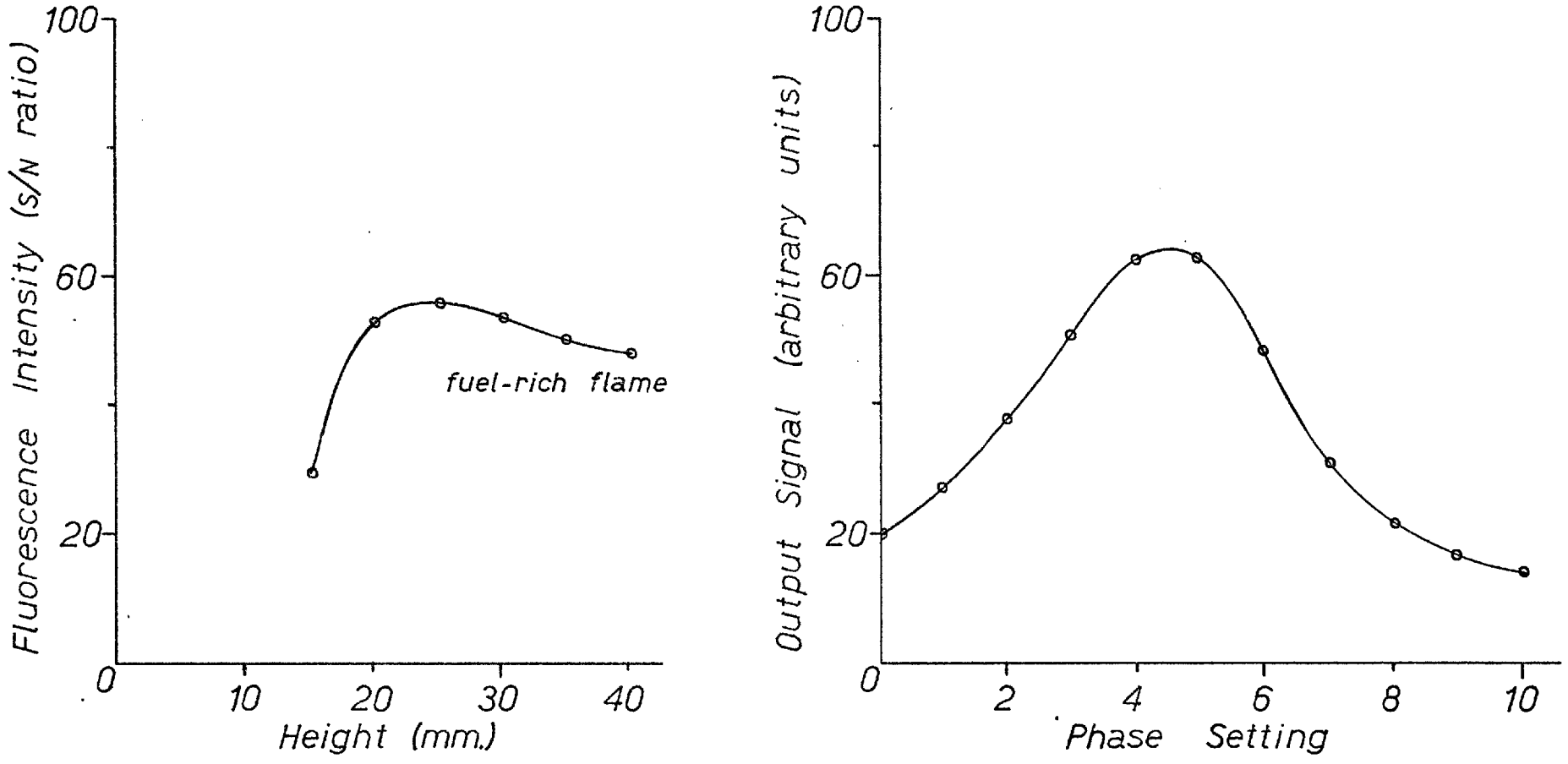
Only the fuel-rich air-hydrogen flame was examined in this work as this was evidently the most suitable composition from the point of view of sensitivity. Figure 7.4 shows the atomic fluorescence signal-to-noise ratio at various viewing heights in this type of flame, the optimum viewing position being some 25 mm above the top of the burner.

A slight improvement in sensitivity was observed when argon was used as the flame separating-gas but was felt to be insufficient to outweigh the extra expense involved.

7.3.6. Optimisation of phase

Maximum output was observed at a phase setting of 4.5 as may be seen from Figure 7.4. These results were obtained by both methods described in Section 4.3.6, and indicate no anomalous behaviour within the system.

Figure 7.4 OPTIMISATION OF OPERATING PARAMETERS FOR TIN



7.3.7. Analytical growth curve and detection limit

The analytical growth curve for tin shown in Figure 7.5 was obtained with the photomultiplier operating voltage set at 1000 Volts and the amplifier gain at 20 db. An aqueous detection limit (signal-to-noise ratio = 2) of 0.40 ppm was obtained and the linear range found to extend up to about 500 ppm.

The instrumental operating conditions used to produce the curve shown in Figure 7.5 are summarised as follows:

Spectral source:

1. Air-stream temperature - 210^{o}C (at 10.0 litres/min).
2. Applied microwave power - 50 Watts.
3. Modulation frequency - 285 Hz.
4. Degree of modulation - 70%.

Atom cell:

1. Hydrogen flow-rate - 3.0 (9.0 litres/min).
2. Nebuliser pressure - 30 psi (0.2MN/m^{2}).
3. Viewing height above burner - 25 mm.

Photomultiplier:

1. Operating voltage - 1000 Volts.

Amplifier:

1. Input - Normal protected.

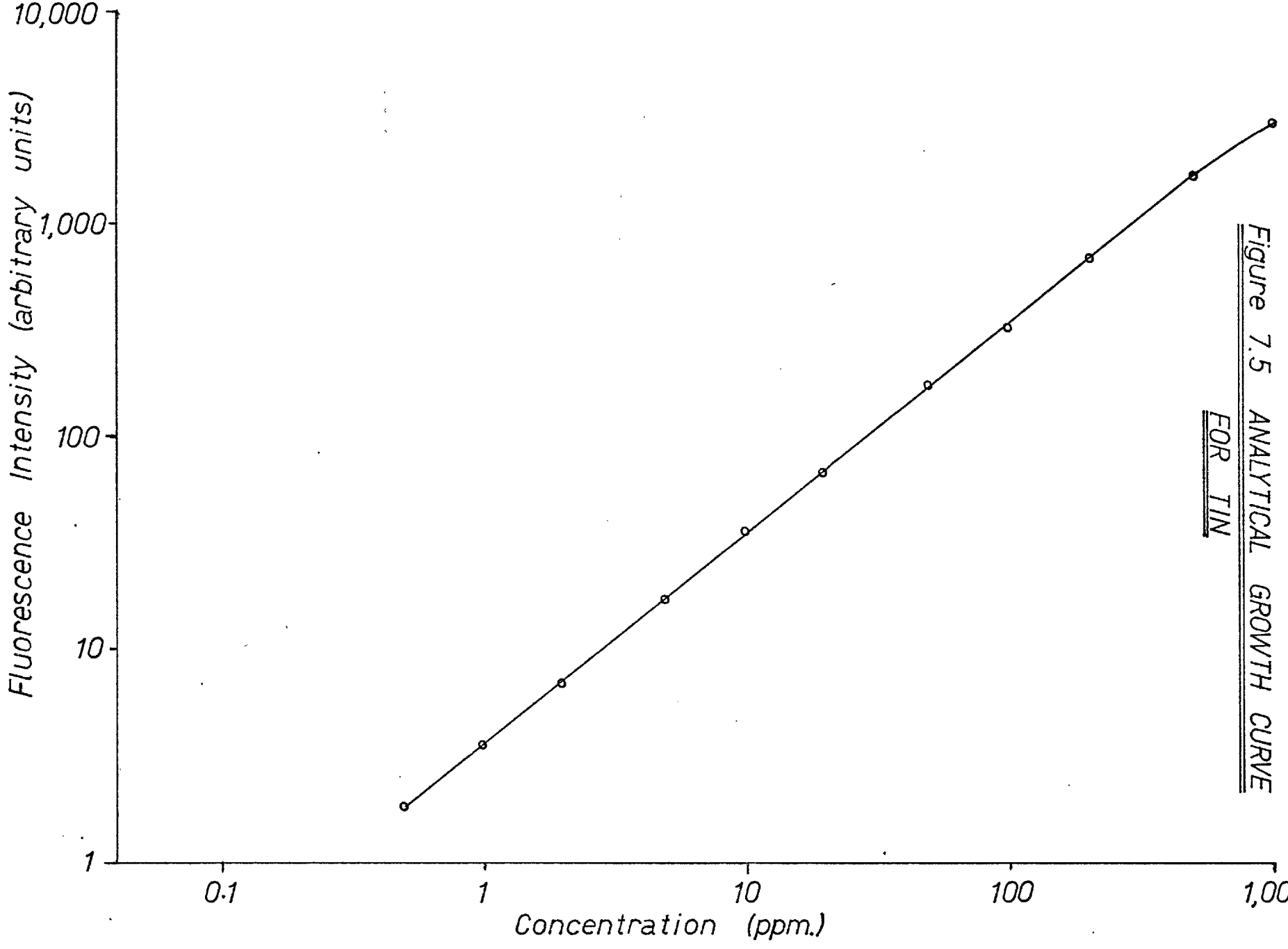


Figure 7.5 ANALYTICAL GROWTH CURVE FOR TIN

2. Frequency limits - 100 Hz to 1000 Hz.
3. Filter - Internal.
4. Meter damping - Off.
5. Gain - 20 db (i.e. 30 db - 10 db).

Phase-sensitive detector:

1. Meter - 10 Volt range (negative).
2. Zero - Negative.
3. Time constant - Internal (1 sec).
4. Filter - Off.
5. Reference channel - A.

Phase shifter:

1. Sensitivity - 100 mV.
2. Frequency range - 100 Hz to 1000 Hz.
3. Phase setting - 4.5.

7.3.8. Interferences

The interference effect of various excess concentrations of iron on tin were examined in accordance with the analysis scheme described in Section 4.3.8. The results obtained are presented in Figure 7.6, from which it may be seen that, in general, the degree of interference is quite small. This is very encouraging because it was felt that the use of the relatively cool air-hydrogen flame, while perfectly satisfactory in terms of sensitivity, might give rise to some matrix interference problems which would not normally have been expected to occur in the air-acetylene flame.

Figure 7.6 TIN INTERFERENCES

Iron conc. (ppm.)	Tin conc. (ppm.)	Relative Signal
10,000	1,000	0·95
10,000	100	1·02
10,000	10	1·00
10,000	1	1·00
1,000	100	0·97
1,000	10	1·16
1,000	1	1·00
100	10	1·04
100	1	1·00
10	1	1·00

Interferent	Apparent Signal			Relative Signal
	Matrix	Steel	0·5 ppm Sn	
Fe+Cr+Ni	63	66	3	1·0
Fe+Cr	60	67	3	2·3
Fe+Ni	51	66	3	5·0
Fe	48	67	3	6·3
Cr	13	65	3	17·3
Ni	4	65	3	20·3

However, the most important aspect of the determination of tin, particularly at low concentrations, in the presence of large excesses of iron is the relative magnitude of the tin atomic fluorescence signal compared to the scatter signal produced by the matrix material. In such cases, this scatter signal was often found to be some twenty times larger than the actual tin atomic fluorescence signal. Thus, when correcting for scatter by subtracting the signal produced by the matrix material alone from the apparent atomic fluorescence signal, considerable inaccuracies and imprecision are introduced in establishing the magnitude of the actual atomic fluorescence signal, as this involves estimating the small difference between two large signals. It is felt, therefore, that difficulties would be encountered in the determination of tin in steels at very low levels.

The interference effects of chromium and nickel were also investigated and the results presented in Figure 7.6. These show that similar scatter problems occur with these matrix elements, although the overall effect is identical to that produced by an equivalent amount of iron. In the analysis of standard steel samples, therefore, the addition of iron at the appropriate concentration to the calibration solutions would be sufficient to simulate the scatter effect of the matrix elements.

During the determination of tin described in this chapter, a method of scatter correction using a cadmium EDL was examined. This involved the measurement of a range of solutions with different ratios of iron-to-tin concentrations using the normal

tin/iodine lamp and then with a cadmium lamp adjusted to give the same emission intensity level. Under these conditions it was felt that both lamps would give the same scatter signal from the matrix element while tin atomic fluorescence signals would only be seen when using the tin/iodine lamp. This method seemed quite encouraging, particularly in terms of practicality, although still somewhat inaccurate and imprecise.

7.3.9. Analysis of steel samples

The results of the determination of tin in eight BCS steel samples are presented in Figures 7.7 and 7.8. The analysis scheme outlined in Section 4.3.9. was employed throughout these determinations, five separate weighings of each sample being taken and a blank sample included. No traces of tin were found in any of the reagents or glassware used during this study.

The striking feature of the results of these analyses is the poor level of precision, especially in those steel samples which contain low levels of tin. This indicates, as discussed earlier, that the determination of tin in steels at very low concentrations (i.e. up to about ten times the aqueous detection limit) may not be satisfactorily achieved using non-dispersive AFS. At higher concentrations, however, the precision of the analyses improves markedly and the technique seems wholly satisfactory under these circumstances.

In most cases, the degree of accuracy of these analyses (see Figure 7.8) was found to be quite good (although this seems a

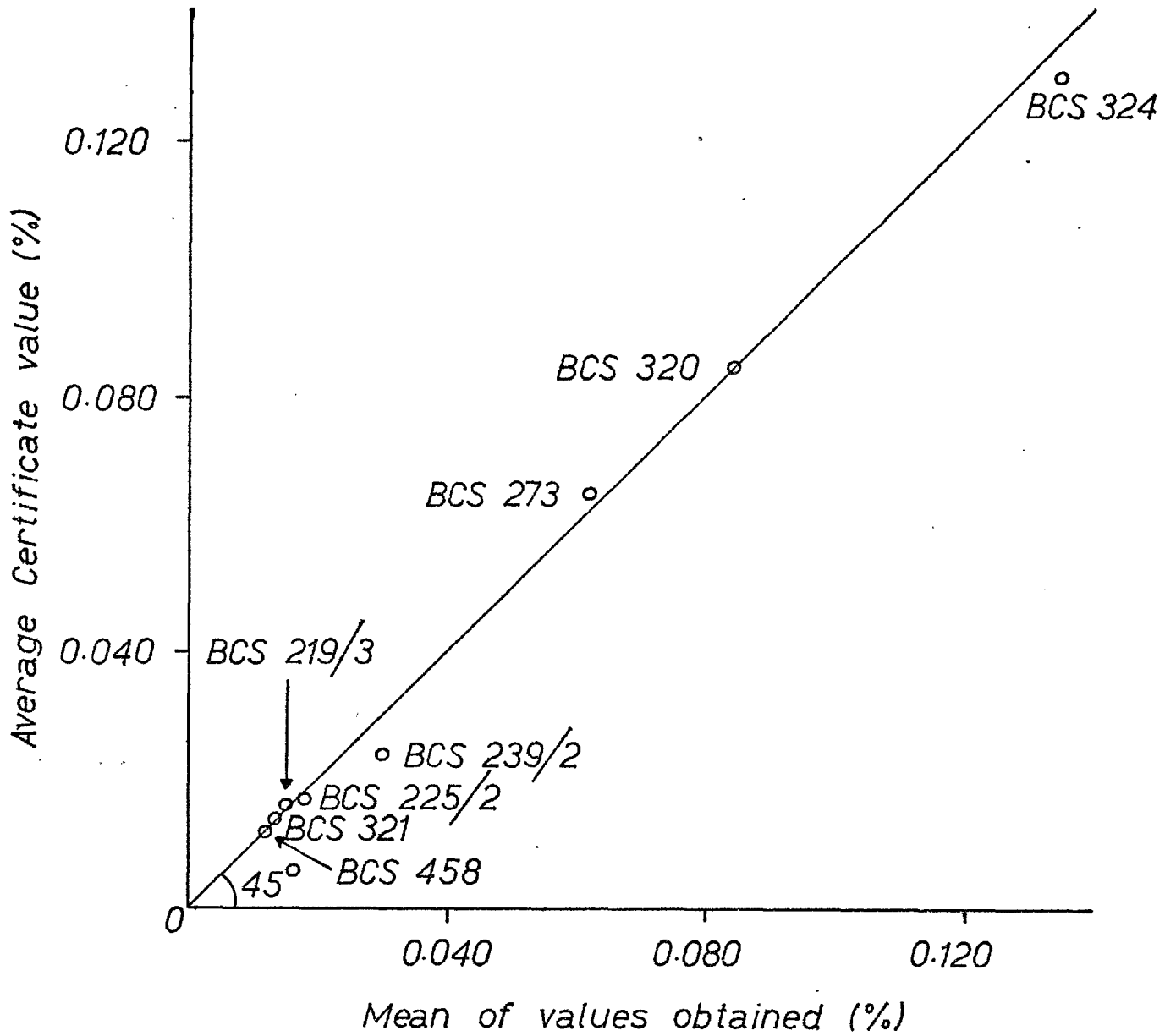
Figure 7.7 ANALYSIS OF TIN IN STEELS

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 321	MILD STEEL	0.0075 , 0.0150 , 0.0075 , 0.0225 , 0.0150	0.0133	47.2	0.014	0.013 → 0.015
BCS 458	MILD STEEL	0.0150 , 0.0075 , 0.0075 , 0.0150 , 0.0150	0.0120	34.2	0.012	—
BCS 225/2	Ni-Cr-Mo STEEL	0.0225 , 0.0225 , 0.0150 , 0.0075 , 0.0225	0.0180	37.3	0.017	—
BCS 219/3	Ni-Cr-Mo STEEL	0.0150 , 0.0150 , 0.0225 , 0.0075 , 0.0150	0.0150	35.3	0.016	—

Figure 7.7(cont.) ANALYSIS OF TIN IN STEELS

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 320	MILD STEEL	0.0825 , 0.0825 , 0.0825 , 0.0900 , 0.0825	0.0840	4.0	0.085	0.082 → 0.089
BCS 324	MILD STEEL	0.1350 , 0.1425 , 0.1350 , 0.1275 , 0.1350	0.1350	3.9	0.13	0.12 → 0.14
BCS 273	MILD STEEL	0.0675 , 0.0600 , 0.0675 , 0.0600 , 0.0525	0.0615	10.2	0.065	0.060 → 0.068
BCS 239/2	CARBON STEEL	0.0375 , 0.0300 , 0.0300 , 0.0225 , 0.0300	0.0300	17.7	0.024	0.021 → 0.030

Figure 7.8 ANALYSIS OF TIN IN STEELS



little fortuitous in those samples containing low levels of tin), indicating that the addition of the appropriate level of iron to the calibration solutions is sufficient to avoid the majority of the matrix interference effects.

7.4. Conclusions

In many instances, the application of non-dispersive AFS to the determination of tin in ferrous metals is rapid, accurate and precise. The use of the nitrogen-separated air-hydrogen flame was found to be necessary to obtain good sensitivity, however, and some difficulty was encountered in trying to obtain good precision during the analysis of some steel samples containing low levels of tin. This was not felt to be directly due to the use of this flame, however, but rather to the relatively high scatter signals produced by the matrix elements. The instability of tin in solution was also felt to be a contributory factor to this problem.

Thus, non-dispersive AFS is not particularly suited to the determination of low levels of tin in ferrous metals. Some sample pre-treatment may help to overcome the problems described above but this type of approach would detract from the convenience of the technique. At higher concentrations, however, the determination of tin in ferrous metals by non-dispersive AFS may be carried out both rapidly and effectively. Few matrix interference problems are encountered and accurate and precise results may be obtained without having to resort to any elaborate sample pre-treatment procedures.

CHAPTER EIGHT

THE DETERMINATION OF ARSENIC BY NON-DISPERSIVE AFS

8.1. Introduction

Since the original work by Larkins (46), in which he obtained an aqueous detection limit of 6 µg/ml in an air-acetylene flame, there have been two further reported determinations of arsenic by non-dispersive AFS. Vickers and co-workers (39) used an arsenic EDL and an argon-hydrogen flame to obtain a detection limit of 0.3 µg/ml, while the work of Tsujii and Kuga (71) involved the generation of arsine followed by fluorescence measurements in a hydrogen-argon-entrained air flame. Again an arsenic EDL was used, the absolute limit of detection being 2 ng.

In the dispersive mode, the AFS determination of arsenic is carried out at 189.0 or, more usually, 193.7 nm, although Fulton and co-workers (8) reported a detection limit of 25 µg/ml at 235.0 nm using an arsenic-antimony dual-element EDL. A dual-element EDL containing arsenic and selenium has been used by Cresser and West (113), giving a detection limit of 25 µg/ml at 193.7 nm.

Of the remaining reports (72, 117, 141, 216), the technique of hydride generation used by Thompson (72) quotes the best limit of detection, 0.0001 µg/ml, obtained to date.

8.2. Arsenic in ferrous alloys

Deliberate additions of arsenic are seldom made as the element has a harmful influence on the mechanical properties of iron and steel but, being present in iron ores, it is a common, naturally occurring constituent. The content in cast iron does not normally exceed 0.05%

and steels usually contain between 0.01 and 0.04%. Levels up to about 0.15% are sometimes required in mild steel, however, to improve the resistance to atmospheric corrosion. Arsenic can also have a deleterious effect on the hot workability of steels which contain copper (207).

The application of AFS to the determination of arsenic in steels has been reported by Michel, Ebdon and Hubbard (12). In their study, a nitrogen-flushed monochromator was used to obtain an aqueous detection limit of 0.01 µg/ml at 189.0 nm and, of the various types of flame used, the separated air-acetylene flame was found to be virtually free from matrix interference effects. In addition, Dagnall, Taylor and West (13) have determined arsenic down to 1 ppm in nickel-based alloys by AFS, eliminating interference problems by solvent extraction.

The AAS determination of arsenic in iron and steel is more common, having been reviewed by Janousek (155) and Endo and Nakahara (154). Menis and Rains (217) have determined arsenic in cast iron after preliminary solvent extraction into chloroform. The arsenic was then returned to aqueous medium and nebulised into an argon-hydrogen-entrained air flame, the best detection limit of 0.1 µg/ml being obtained at both 189.0 and 193.7 nm. Hwang and co-workers (121) have also determined arsenic in cast iron by AAS using the technique of hydride generation, quoting a sensitivity of 4 ng at 193.7 nm.

Of the flame determinations of arsenic in steels (74, 122, 169) the most sensitive, and most recent, is that of Thompson and Godden (74) who have used the single-pulse nebulisation technique to obtain

a detection limit of 0.002% in steel. A flameless determination has also been reported by Ratcliffe and co-workers (213) in which the steel sample was dissolved in nitric acid and a 5 µl aliquot atomised directly using a carbon furnace. This procedure gave an absolute detection limit of 1 ng at 193.7 nm.

The technique of hydride generation for the AAS determination of arsenic in steel has been used by Tsujino and co-workers (218) who have reported a procedure in which the arsenic in the steel sample is reduced to arsine (by stannous chloride and potassium iodide) and then introduced into an argon-hydrogen flame, while Fleming and Ide (73) have obtained a limit of detection of 1 ppm in steel.

In addition, Nakahara and co-workers (219) have reported the AAS determination of arsenic in stainless steel, while Hill (220) has centred his attention on carbon and high-alloy steels. Gŏmez-Coedo and Dorado (221) have reported the determination of arsenic by AAS down to 0.001% in iron alloys using a procedure which involves the preliminary separation of arsenic from the iron matrix by a benzene extraction.

The technique of AES has also been applied to the determination of arsenic in steels by Prăvčeva and co-workers (132), in ferrous alloys by Morello, de Gregorio and Savastano (199) and in ferro-molybdenum by Delijska and Prăvčeva (202), while Maiboroda and co-workers (203) have included the AES determination of arsenic in their study of the effect of a "carrier" on the spectral excitation conditions for determining small amounts of impurities in iron-based alloys.

This chapter describes the first application of non-dispersive AFS to the determination of arsenic in ferrous metals.

8.3. Experimental

8.3.1. Reagents

A 1000 ppm stock solution of arsenic was prepared by dissolving, with the aid of gentle heating, 0.330 g of arsenic trioxide in 250 ml of glass-distilled, de-ionised water. Standard solutions were prepared immediately before use by the appropriate dilution of this stock solution, analytical grade reagents being used wherever possible in this work.

8.3.2. The principal arsenic fluorescence lines

The emission spectrum of the heated arsenic EDL used throughout this study is shown in Figure 8.1 and was obtained by focussing the radiation from the lamp onto the entrance slit (200 microns) of a Varian-Techtron AA4 monochromator scanning at a rate of 5 nm/min. An R431 photomultiplier operating at 1100 Volts was used to detect the radiation passing through the monochromator and the spectrum recorded on a potentiometric chart recorder set at 100 mV full-scale deflection.

The relative intensities of the lines shown in Figure 8.1 are probably modified to some extent by the response characteristics of the R431 photomultiplier, as the main arsenic resonance lines are 189.0 nm ($^4P_{2\frac{1}{2}}$ to $^4S^o_{1\frac{1}{2}}$ transition), 193.7 nm ($^4P_{1\frac{1}{2}}$ to $^4S^o_{1\frac{1}{2}}$ transition)

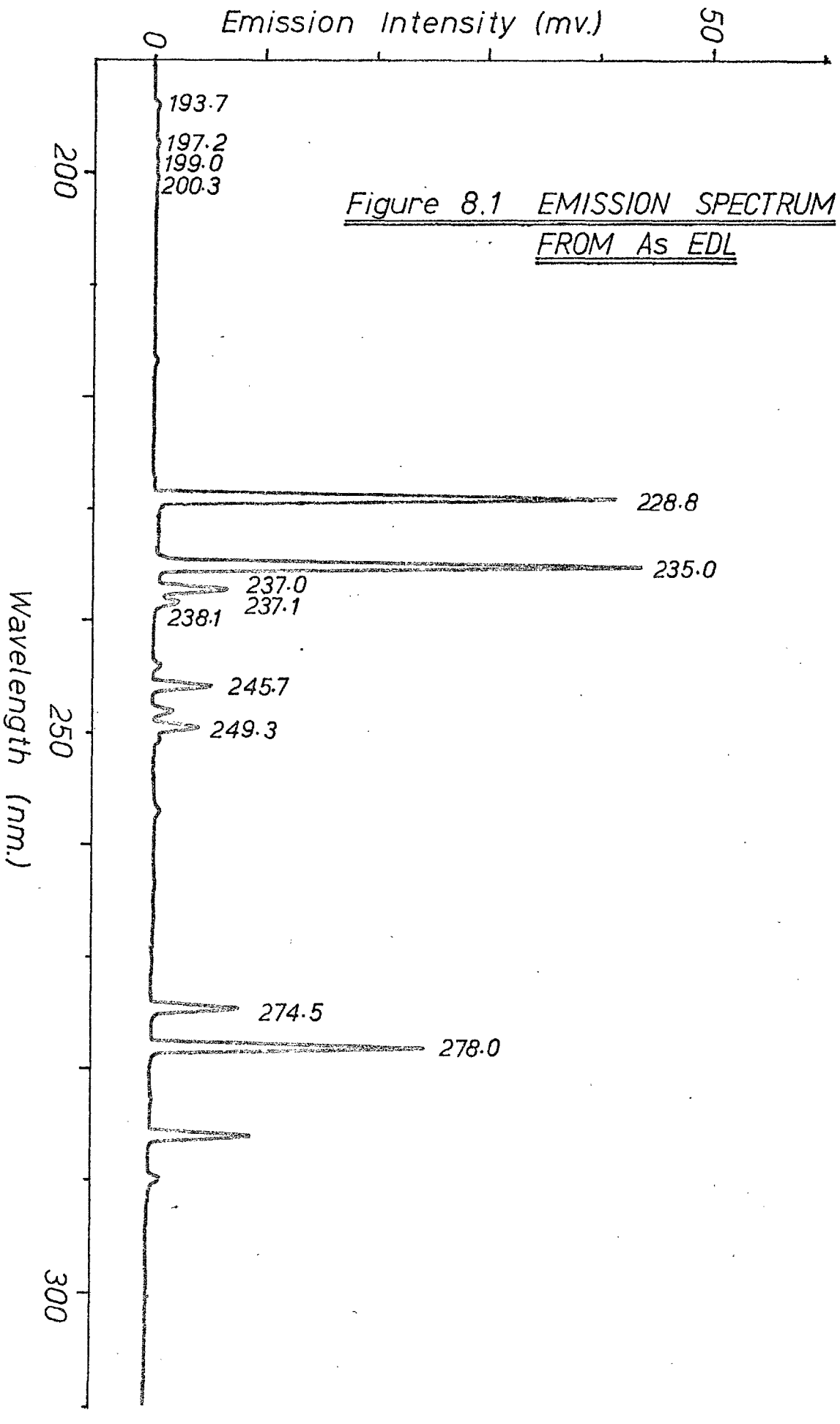


Figure 8.1 EMISSION SPECTRUM FROM As EDL

and 197.2 nm ($^4P_{\frac{1}{2}}$ to $^4S^o_{1\frac{1}{2}}$ transition). Most of the lines shown contribute towards the overall fluorescence intensity, however, the most important being the 235.0 nm ($^2P_{\frac{1}{2}}$ to $^2D^o_{1\frac{1}{2}}$ transition) and the 228.8 nm ($^2P_{1\frac{1}{2}}$ to $^2D^o_{2\frac{1}{2}}$ transition) thermally-assisted direct-line fluorescence, the 238.1 nm ($^4P_{2\frac{1}{2}}$ to $^2D^o_{2\frac{1}{2}}$ transition) intercombination line and the 245.7 nm ($^4P_{1\frac{1}{2}}$ to $^2D^o_{2\frac{1}{2}}$ transition) and 249.3 nm ($^4P_{\frac{1}{2}}$ to $^2D^o_{1\frac{1}{2}}$ transition) lines, as well as the main resonance lines mentioned previously, of course. Thompson (125) has given an excellent and detailed account of the atomic fluorescence characteristics of arsenic in both the air-acetylene flame and the nitrogen-hydrogen diffusion flame (for which he has included the arsenic atomic fluorescence spectrum).

8.3.3. Experimental procedure

The experimental procedure adopted during this study has been described previously (see Section 4.3.3.). No scatter or atomic emission signals were observed even when aspirating a 1000 ppm aqueous solution of arsenic.

8.3.4. Preparation and characteristics of the arsenic EDL

Lamps containing arsenic only and arsenic and iodine were examined at the outset of this study and it was concluded that, from the point of view of intensity, the former type of EDL was to be preferred. The preparation of this lamp, which was used throughout this determination, has been described elsewhere (52).

Arsenic EDLs, in general, are somewhat unusual as they tend

to extinguish before reaching any plateau in the atomic fluorescence intensity versus air-stream temperature curve (see Figure 8.2). This means that they have to be operated on the almost vertical part of the curve which makes them much more susceptible than the other lamps mentioned in this thesis to small fluctuations in air-stream temperature and applied microwave power. Careful control of these operating conditions is essential, therefore, if inaccurate measurements are to be avoided.

A 10 ppm arsenic solution was used to establish the fluorescence characteristics of the lamp and are depicted in Figures 8.2 and 8.3. The optimum operating conditions were found to be at an air-stream temperature of 252^{o}C (with an air flow-rate of 11.25 litres/min) and 70 Watts applied microwave power.

8.3.5. Optimisation of flame height and flame composition

The determination of arsenic was carried out using a nitrogen-separated air-acetylene flame. An improvement in sensitivity by a factor of about 1.5 was observed when argon was used as the flame separating-gas, but this was not felt to be sufficient to justify the increased expense involved in using this gas.

The variation in atomic fluorescence signal-to-noise ratio with different flame compositions and viewing heights is shown in Figure 8.4. From this it may be seen that the use of the "normal" flame (or, alternatively, the fuel-rich flame, which exhibited a very similar response) represents a considerable increase in signal-to-noise ratio over the fuel-lean flame. This type of flame was

Figure 8.2 CHARACTERISTICS OF As EDL

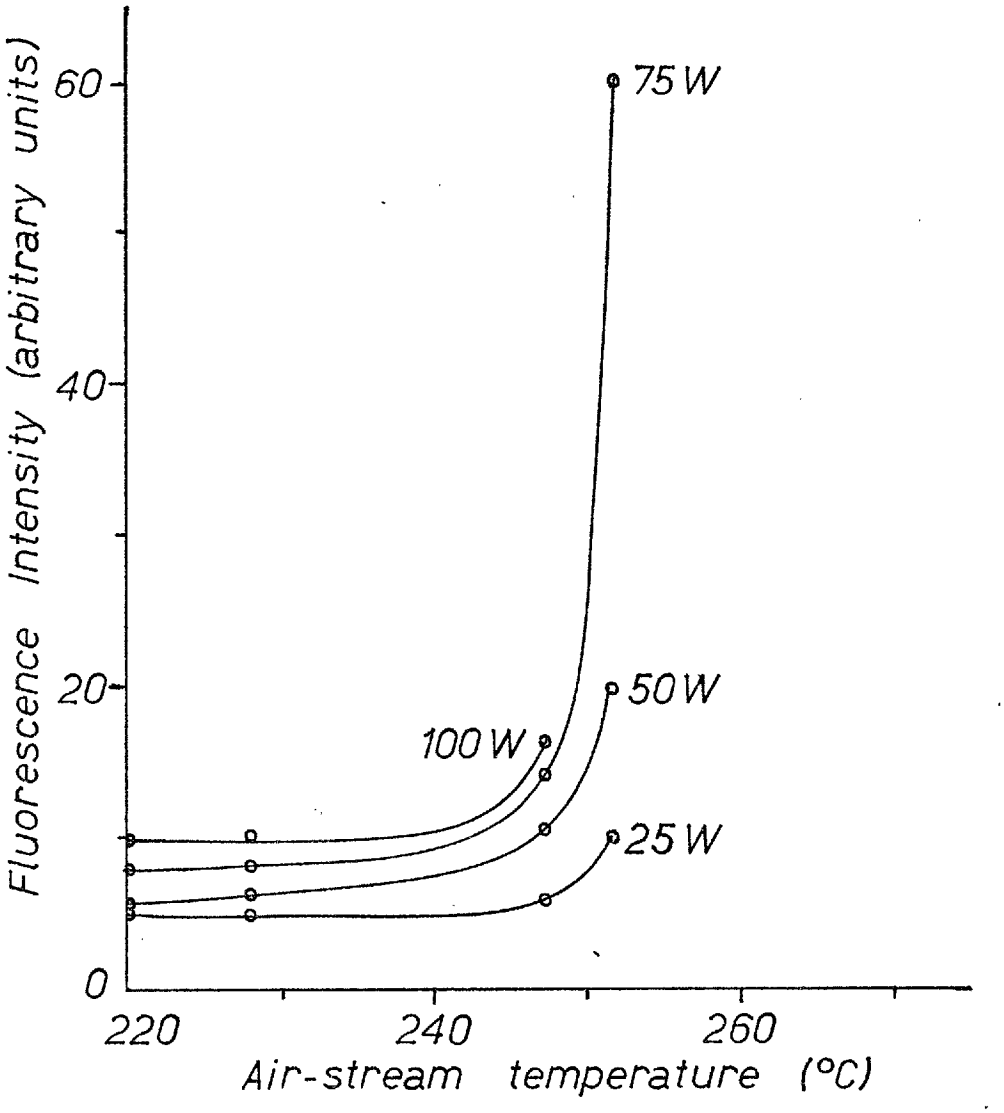


Figure 8.3 CHARACTERISTICS OF As EDL

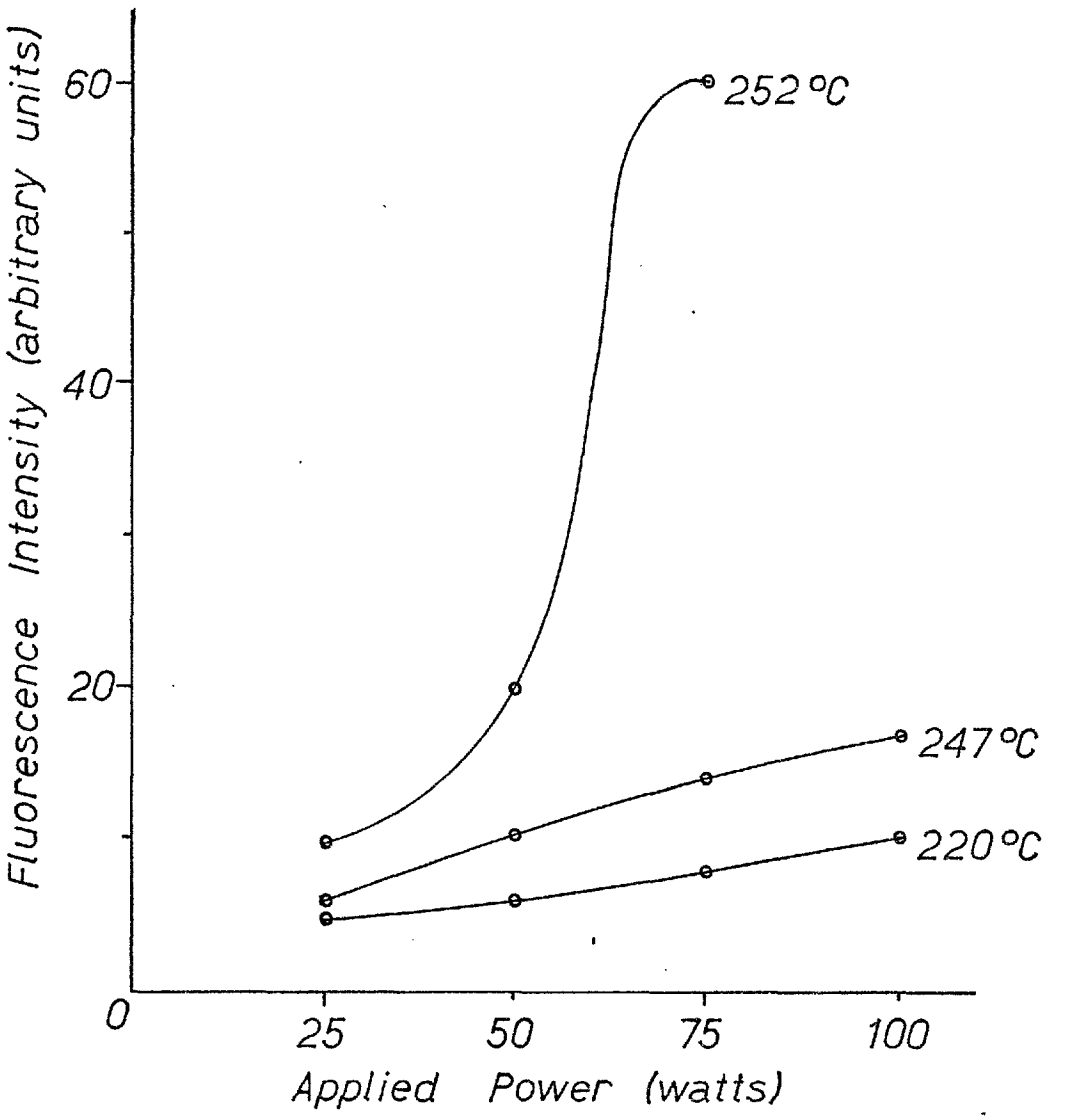
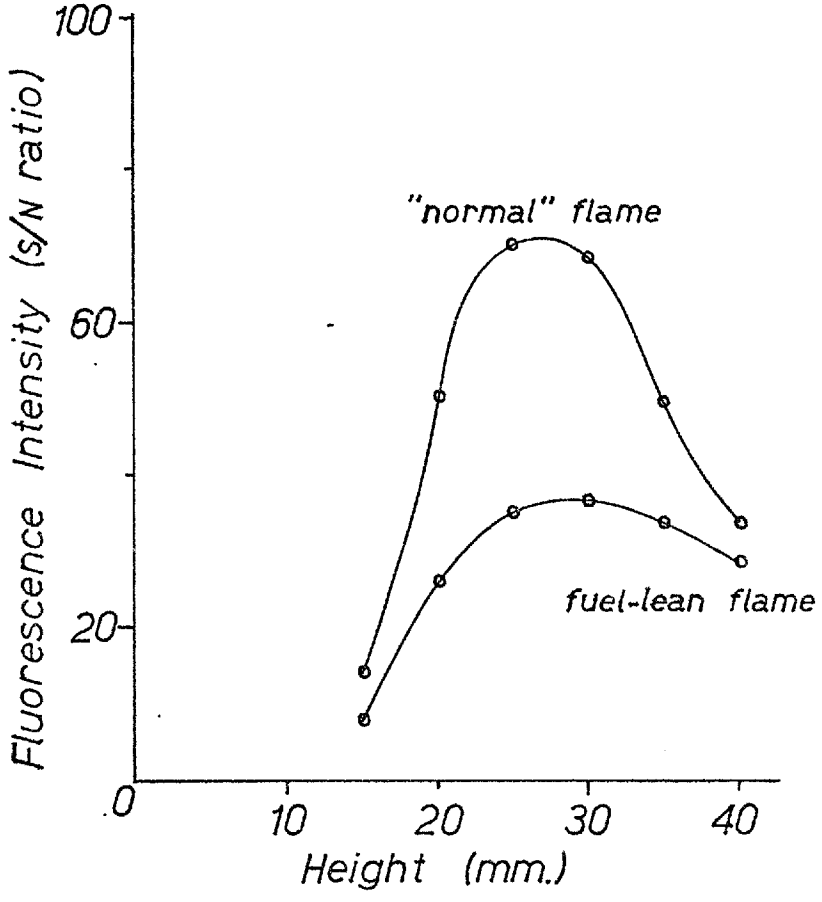
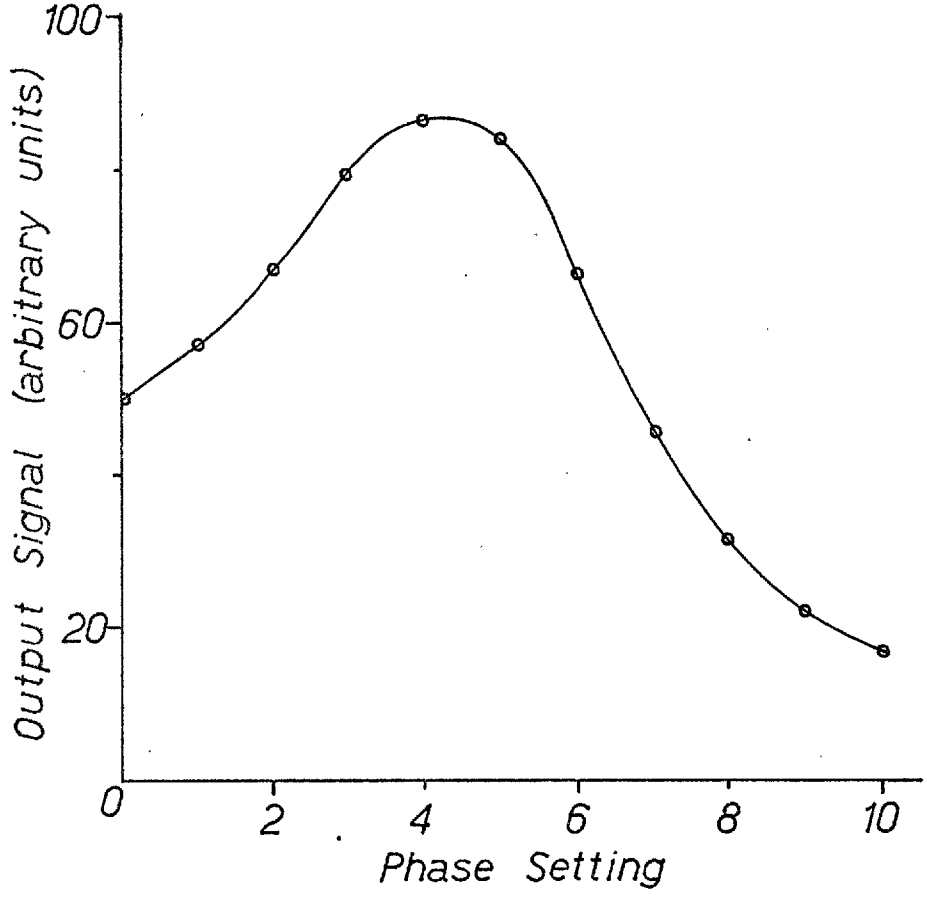


Figure 8.4 OPTIMISATION OF OPERATING PARAMETERS FOR ARSENIC





used throughout the determination of arsenic, the optimum viewing position being about 25 mm above the top of the burner.

8.3.6. Optimisation of phase

Both methods described in Section 4.3.6. were used to optimise the phase setting. Similar results were obtained in each case and are presented in Figure 8.4. Maximum output was produced at a phase setting of about 4.5.

8.3.7. Analytical growth curve and detection limit

The analytical growth curve for arsenic shown in Figure 8.5 was obtained with the photomultiplier operating at 1200 Volts and the amplifier gain set at 30 db. These operating conditions indicate that the intensity of the arsenic atomic fluorescence signals was comparatively low (as the sensitivity of the photomultiplier towards most of the lines discussed in Section 8.3.2. is felt to be quite high).

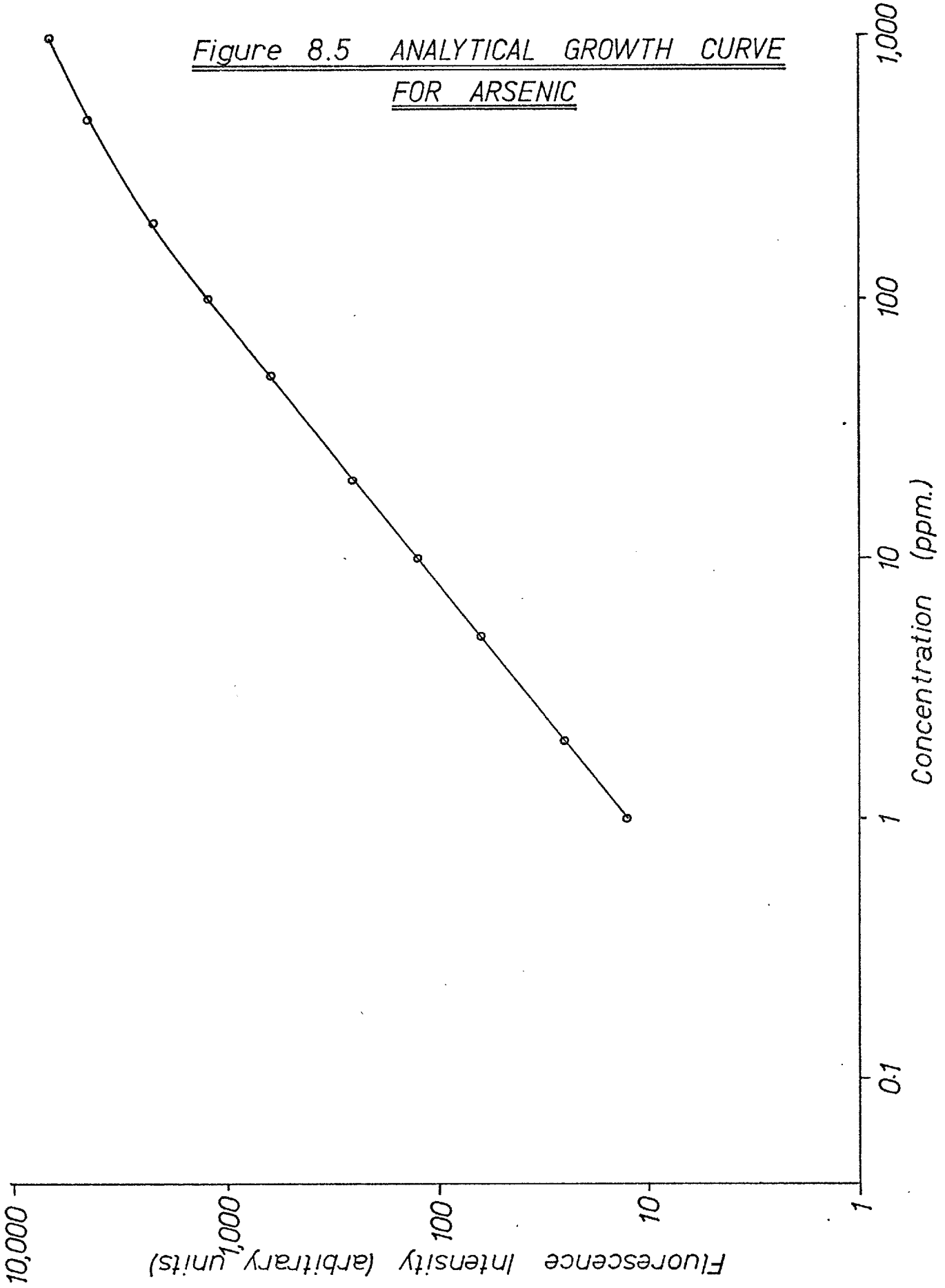
An aqueous detection limit (signal-to-noise ratio = 2) of 0.77 ppm was obtained with the linear portion of the curve extending up to about 200 ppm.

The instrumental operating conditions under which the analytical growth curve shown in Figure 8.5 was produced are summarised below:

Spectral source:

1. Air-stream temperature - 252^{o}C (at 11.25 litres/min).

Figure 8.5 ANALYTICAL GROWTH CURVE FOR ARSENIC



2. Applied microwave power - 70 Watts.
3. Modulation frequency - 285 Hz.
4. Degree of modulation - 70%.

Atom cell:

1. Acetylene flow-rate - 1.1 (0.8 litres/min).
2. Nebuliser pressure - 30 psi (0.2 MN/m^2).
3. Viewing height above burner - 25 mm.

Photomultiplier:

1. Operating voltage - 1200 Volts.

Amplifier:

1. Input - Normal protected.
2. Frequency limits - 100 Hz to 1000 Hz.
3. Filter - Internal.
4. Meter damping - Off.
5. Gain - 30 db (i.e. 30 db - 0 db).

Phase-sensitive detector:

1. Meter - 10 Volt range (negative).
2. Zero - Negative.
3. Time constant - Internal (1 sec).
4. Filter - Off.
5. Reference channel - A.

Phase shifter:

1. Sensitivity - 100 mV.
2. Frequency range - 100 Hz to 1000 Hz.
3. Phase setting - 4.5.

8.3.8. Interferences

Using the scheme of analysis outlined in Section 4.3.8., the interference effects of various excess concentrations of iron on arsenic were examined and the results presented in Figure 8.6. The lowest concentration of arsenic which was used during this exercise was 2 ppm (cf. the 1 ppm concentration used during the determination of the other elements considered in this work) because of the relatively poor detection limit obtained. This poor sensitivity would have made the measurement of solutions containing less than about 1.5 ppm arsenic rather difficult and unreliable.

Some significant interference effects are revealed in Figure 8.6, although no obvious trends are established. The most important feature of these interferences is that they do not occur as a result of radiation scattering by the matrix material. In fact, the magnitude of most of the scatter signals from the iron solutions aspirated during this determination was found to be almost immeasurable. It is evident from these results, however, that careful matching of the calibration solutions and sample solutions is necessary during the analysis of actual steel samples in order to simulate any matrix interference effects which might occur.

The interference effects of chromium and nickel were also

Figure 8.6 ARSENIC INTERFERENCES

Iron conc. (ppm.)	Arsenic conc. (ppm.)	Relative Signal
10,000	1,000	1·02
10,000	100	0·79
10,000	10	0·93
10,000	2	1·00
1,000	100	0·78
1,000	10	1·05
1,000	2	1·00
100	10	1·05
100	2	1·00
10	2	1·00

Interferent	Apparent Signal			Relative Signal
	Matrix	Steel	5 ppm As	
Fe+Cr+Ni	3	20	17	1·0
Fe+Cr	2	20	17	1·1
Fe+Ni	2	19	16	1·1
Fe	1	17	14	1·1
Cr	1	17	15	1·1
Ni	1	18	15	1·1

investigated using a simulated stainless steel solution containing 5 ppm arsenic. Once again, no significant scatter signals were observed and the overall levels of interference from these matrix elements found to be quite small. Figure 8.6 shows the results obtained during this examination and indicates that the addition of iron to the calibration solutions is sufficient to avoid any matrix interference problems.

The method of scatter correction outlined in Section 7.3.8. was also applied to the determination of arsenic. A cadmium EDL was used to measure the matrix scatter contribution to the apparent arsenic atomic fluorescence signal produced by a range of solutions, in order that the true atomic fluorescence signal could be obtained. This procedure was found to give quite good results, although it was felt that some improvement in the accuracy and precision would be desirable.

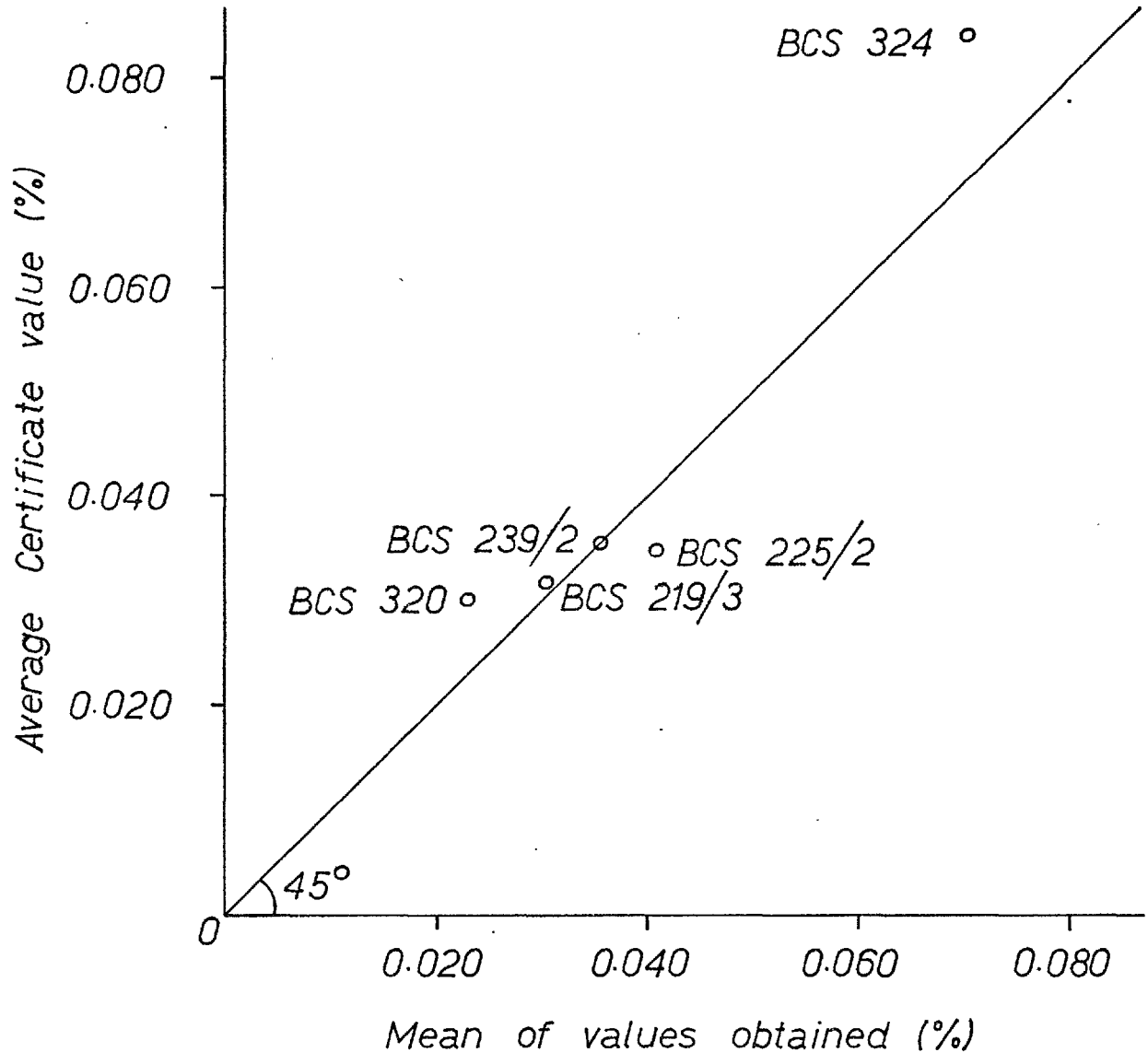
8.3.9. Analysis of steel samples

Five BCS steel samples were examined in accordance with the scheme of analysis detailed in Section 4.3.9. The results for the determination of arsenic are shown in Figures 8.7 and 8.8 from which it may be seen that, although a good level of precision was observed for each analysis, a poor degree of accuracy was obtained for three samples. This is difficult to explain, although the source instability problems mentioned earlier could account for part of these inaccuracies. In this event, the precision of the analyses would have been expected to be much poorer, however. Some loss of arsenic during the dissolution of the samples would seem to be a

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 320	MILD STEEL	0.0233, 0.0200, 0.0233, 0.0233, 0.0233	0.0226	6.5	0.031	0.029 → 0.032
BCS 324	MILD STEEL	0.0667, 0.0667, 0.0667, 0.0733, 0.0733	0.0693	5.2	0.084	0.079 → 0.087
BCS 225/2	Ni-Cr-Mo STEEL	0.0400, 0.0400, 0.0400, 0.0400, 0.0467	0.0413	7.3	0.035	—
BCS 239/2	CARBON STEEL	0.0358, 0.0384, 0.0350, 0.0366, 0.0350	0.0362	3.9	0.036	0.030 → 0.039
BCS 219/3	Ni-Cr-Mo STEEL	0.0324, 0.0292, 0.0300, 0.0308, 0.0300	0.0305	4.0	0.032	—

Figure 8.7 ANALYSIS OF ARSENIC IN STEELS

Figure 8.8 ANALYSIS OF ARSENIC IN STEELS



likely explanation for the low results obtained during the analysis of BCS 320 and 324, but this argument fails to account for the high figure obtained for BCS 225/2, particularly as no traces of arsenic were found in any of the reagents or glassware used in this work. Moreover, excellent results were obtained for the determination of arsenic in BCS 239/2 and 219/3 using the same dissolution procedure, equipment and reagents.

Perhaps a combination of these explanations could account for the relatively poor performance of the technique in this case. It is clear though that, despite the problems encountered, the determination of arsenic in steels is certainly possible under favourable circumstances.

8.4. Conclusions

The determination of arsenic was probably the least successful part of the work described in this thesis. Source instability was sometimes found to be a problem, a relatively poor aqueous detection limit was obtained and interference from matrix material was encountered on some occasions. Additionally, the general method of sample dissolution adopted throughout this work was felt to require some modification to enable arsenic to be determined accurately in steels.

Nevertheless, some satisfactory results were obtained despite the problems outlined above, and this indicates that non-dispersive AFS could be applied to the determination of arsenic in ferrous metals quite successfully, once these difficulties are overcome.

CHAPTER NINE

THE DETERMINATION OF ANTIMONY BY NON-DISPERSIVE AFS

9.1. Introduction

Although there have been several reports of the AFS determination of antimony, only those of Larkins (46) and Tsujii and co-workers (222) have been in the non-dispersive mode. Larkins used a high intensity HCL to obtain an aqueous detection limit of 0.04 µg/ml in a separated air-acetylene flame, while Tsujii employed the technique of hydride generation and an antimony EDL to obtain an absolute detection limit of 2 ng in a hydrogen-argon-entrained air flame.

In the dispersive mode, antimony atomic fluorescence is usually monitored at 231.1 or 217.6 nm. The best limits of detection have been obtained with single-element EDLs (11, 111, 117, 127, 129, 223), although Cresser and West (113) have used a dual-element EDL, containing antimony and bismuth, to obtain a detection limit of 6 µg/ml. Fulton and co-workers (8) obtained 0.9 µg/ml with an arsenic-antimony dual-element EDL.

Massmann (144) has reported the flameless determination of antimony by AFS, attaining an absolute detection limit of 0.2 ng. Flame determinations are more common, however, with Manning and Heneage (142) using an air-hydrogen flame and Atanov and co-workers (115) an air-propane flame. In fact, Kolihová and Sychra (224) have examined the atomic fluorescence of antimony in a variety of pre-mixed flames, concluding that the hydrogen-argon diffusion flame gives the best limit of detection.

Kanunnikova and Maizil (116) have also determined antimony

by AFS with a VSB-2 high-frequency power tube as their spectral source and a quartz prism dispersive device. In addition to this, Thompson (72) has reported a detection limit of 0.0001 µg/ml at 231.1 nm using the hydride generation technique.

9.2. Antimony in ferrous alloys

Although a fairly rare constituent naturally, small amounts of antimony are sometimes present in steel. This element is occasionally added to cast iron as a graphitization inhibitor (see Section 1.3.) and to low-alloy copper steels where, although having a detrimental effect on the hot workability (207), it improves the corrosion resistance in acid environments (225).

The only reported application of AFS to the determination of antimony in metallurgical samples has been that of Norris and West (11), specifically copper-based alloys, in which a detection limit of 0.02 µg/ml was obtained using an argon-hydrogen flame.

In contrast, there are a number of papers dealing with the application of AAS, Headridge (226), Condylis and Mejean (208) and Janousek (155) having included antimony in their respective reviews of AAS in the analysis of metallic materials. More particularly, the non-flame AAS determination of antimony in steel has been reported by Frech (227), Ashy and co-workers (212) and Ratcliffe and co-workers (213), the chief advantage of their methods being that sample pre-treatment is avoided. Shaw and Ottaway (184) have also recently outlined a method for the AAS determination of antimony in iron and steel using carbon furnace atomisation.

The more conventional flame determinations (122, 169, 228) usually involve the use of an air-acetylene flame and include a demonstration of the advantages of background correction by Barnett and Kerber (122). The technique of hydride generation has also been used to determine antimony in both cast iron, where Hwang and co-workers (121) have obtained an absolute detection limit of 30 ng, and in steel, in which Fleming and Ide (73) have been able to measure levels of 1 ppm.

In addition, Burke (173) has reported a procedure in which a non-aqueous extract is nebulised directly to determine antimony in iron-based alloys, while Foster and co-workers (191) have measured levels of 0.002% in ferro-manganese.

The technique of AES has also been applied to the determination of antimony in ferrous alloys (199, 202, 203) and in high-temperature alloys and steel (200, 229), this work being of interest in evaluating the various techniques and methods described above.

This chapter describes the first application of non-dispersive AFS to the determination of antimony in ferrous metals.

9.3. Experimental

9.3.1. Reagents

A 1000 ppm stock solution of antimony was prepared by dissolving 0.667 g of potassium antimony tartrate ($KSbO.C_4H_4O_6$) in 250 ml of distilled, de-ionised water. Standard solutions were freshly prepared

immediately before use by the appropriate dilution of this stock solution, analytical grade reagents being used wherever possible in this work.

9.3.2. The principal antimony fluorescence lines

Figure 9.1 shows the emission spectrum produced by the antimony/iodine EDL used through this work and was obtained by focussing the radiation from the lamp onto the entrance slit (200 microns) of a Varian-Techtron AA4 monochromator scanning at 5 nm/min. The radiation passing through the monochromator was detected by an R431 photomultiplier operating at 1100 Volts and the resulting signal displayed on a potentiometric chart recorder set at 100 mV full-scale deflection.

Antimony would seem to lend itself quite well to a non-dispersive approach as there are a number of significant contributions to the overall fluorescence intensity. The principal resonance lines associated with the $^4S_{1\frac{1}{2}}$ ground state (231.1, 217.6 and 206.8 nm) play an important part, with further major contributions coming from the 259.8 nm ($^4P_{2\frac{1}{2}}$ to $^2D_{2\frac{1}{2}}$ transition), 287.8 nm ($^4P_{\frac{1}{2}}$ to $^2D_{1\frac{1}{2}}$ transition), 277.0 nm ($^4P_{1\frac{1}{2}}$ to $^2D_{2\frac{1}{2}}$ transition) and 267.1 nm ($^4P_{1\frac{1}{2}}$ to $^2D_{1\frac{1}{2}}$ transition) lines. As the R431 solar-blind photomultiplier is very sensitive towards most of these lines, a considerable improvement in detection limit is to be expected when using the non-dispersive technique, rather than the more conventional dispersive system.

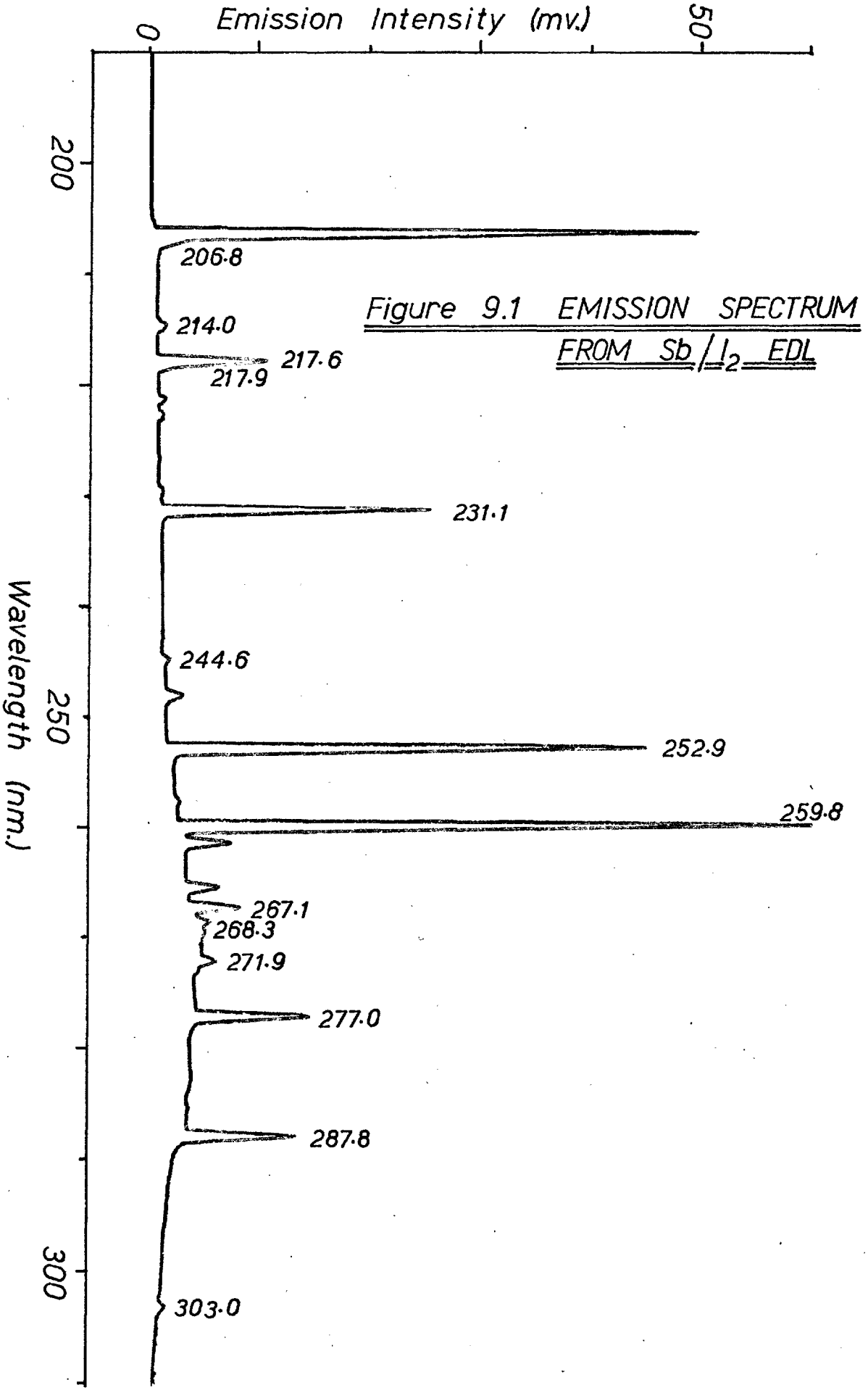


Figure 9.1 EMISSION SPECTRUM FROM Sb/I_2 EDL

9.3.3. Experimental procedure

The experimental procedure described in Section 4.3.3. was strictly adhered to in this study. Even when aspirating a 1000 ppm aqueous antimony solution, no scatter or atomic emission signals were observed.

9.3.4. Preparation and characteristics of the antimony EDL

A lamp containing antimony only was examined at the outset of the work described in this chapter but was found to be of no use for atomic fluorescence studies owing to the relatively low volatility of the element. A number of lamps containing antimony and iodine were, therefore, constructed (as outlined in Section 7.3.4.), each with a slightly different antimony-to-iodine ratio, although in all cases an excess amount of antimony over iodine was maintained. After an initial "running-in" period, the most satisfactory performance was obtained from the source to which the greatest amount of iodine had been added and this lamp was, therefore, used throughout the determination described in this chapter.

A 10 ppm antimony solution was used to obtain the fluorescence characteristics of the antimony/iodine EDL, and these are presented in Figures 9.2 and 9.3. Optimum operating conditions were found to be at an air-stream temperature of 85^{o}C (with an air flow-rate of 12.5 litres/min) and 50 Watts applied microwave power. Careful control of these parameters was found to be necessary in order to avoid minor fluctuations in the intensity of the lamp but, in general, source instability was not found to be a major problem.

Figure 9.2 CHARACTERISTICS OF Sb/I_2 EDL

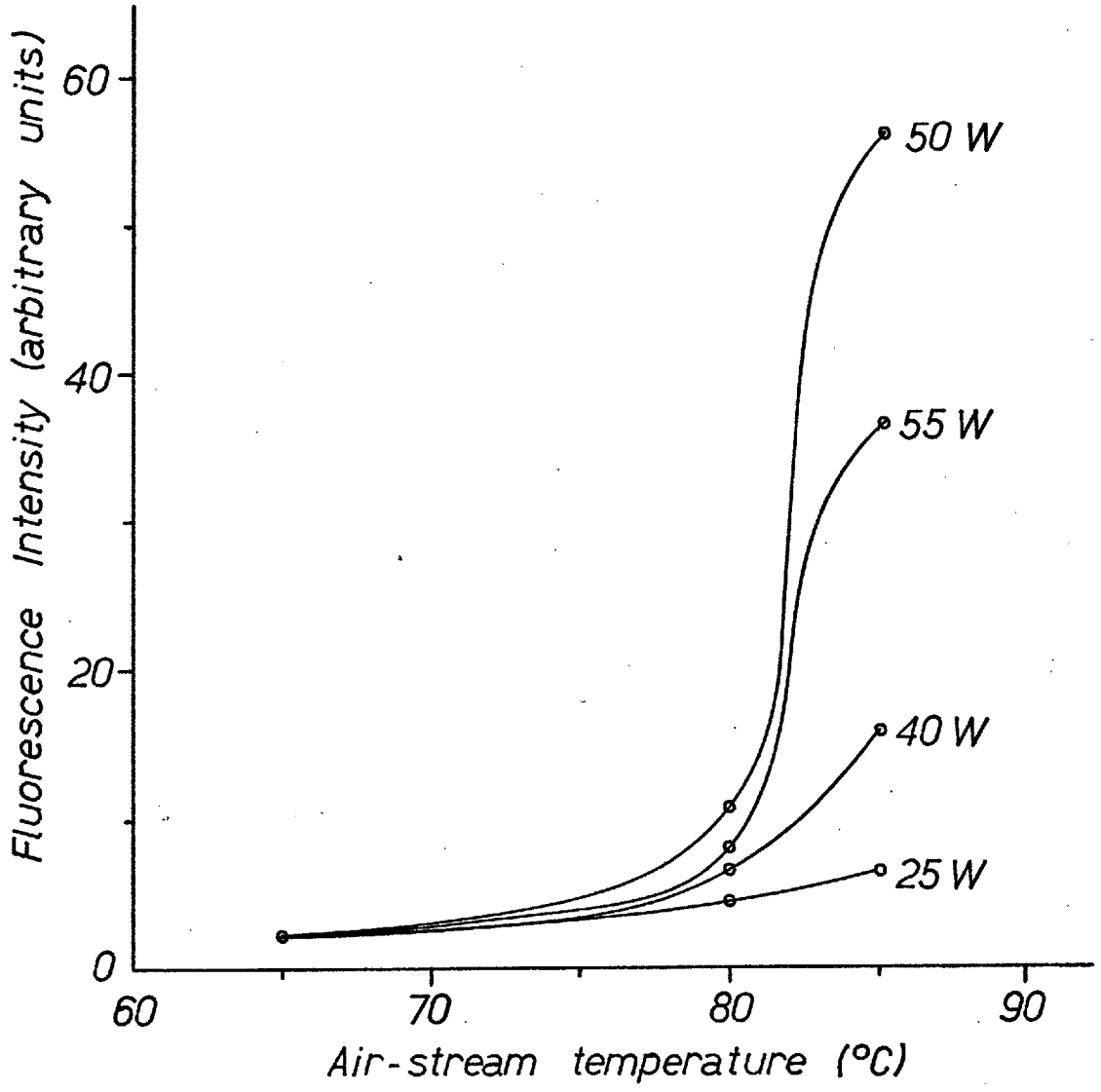
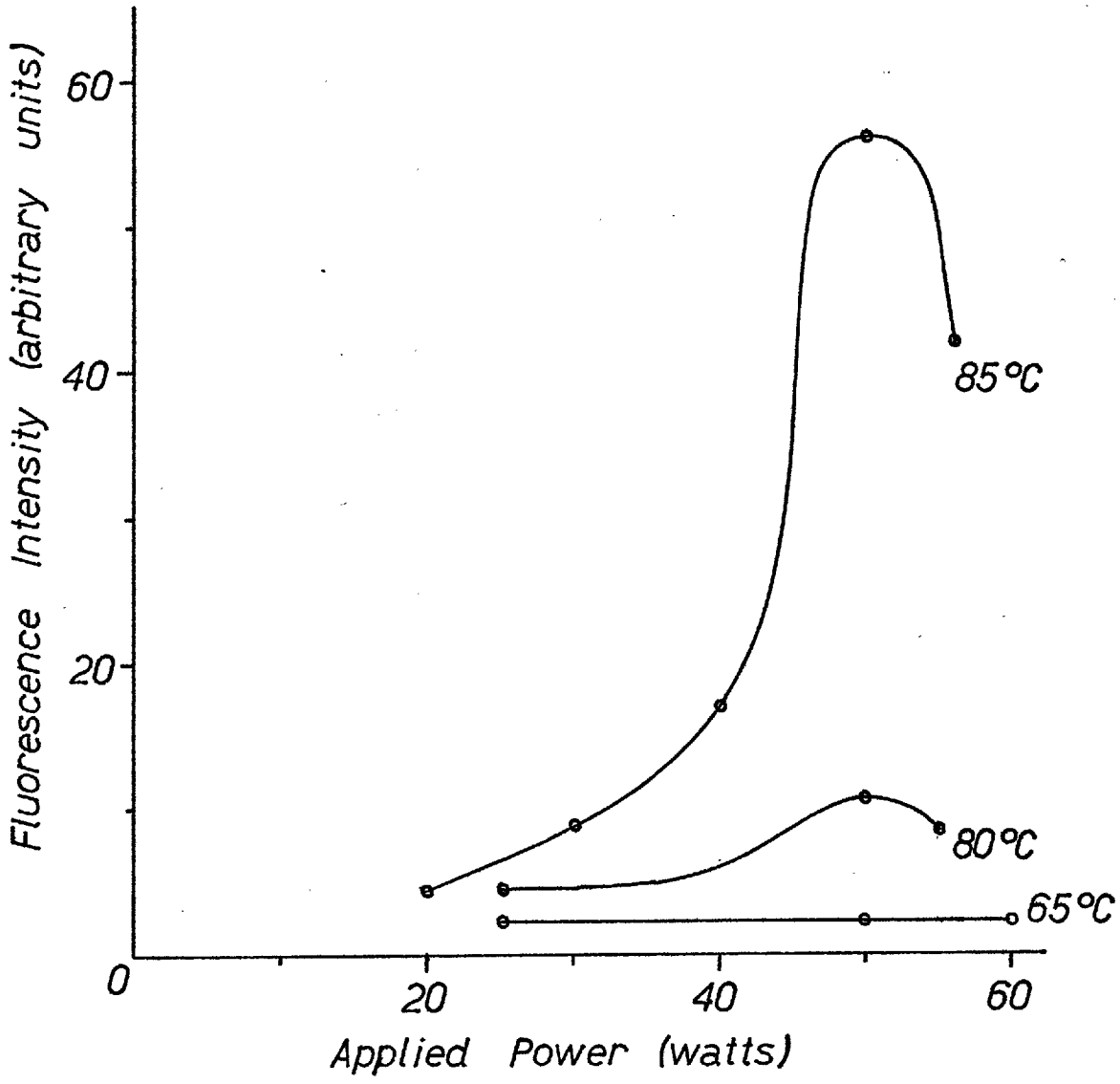


Figure 9.3 CHARACTERISTICS OF Sb/I_2 EDL



9.3.5. Optimisation of flame height and flame composition

Throughout this determination a nitrogen-separated air-acetylene flame was used. No significant improvement in sensitivity was observed when using argon as the separating-gas.

Figure 9.4 shows the variation of the atomic fluorescence signal-to-noise ratio with different flame compositions and viewing positions, and indicates that the maximum signal-to-noise ratio is obtained when using the "normal" flame and viewing some 30 mm above the top of the burner. In fact, the slightly fuel-rich air-acetylene flame could also be used with no great loss of sensitivity.

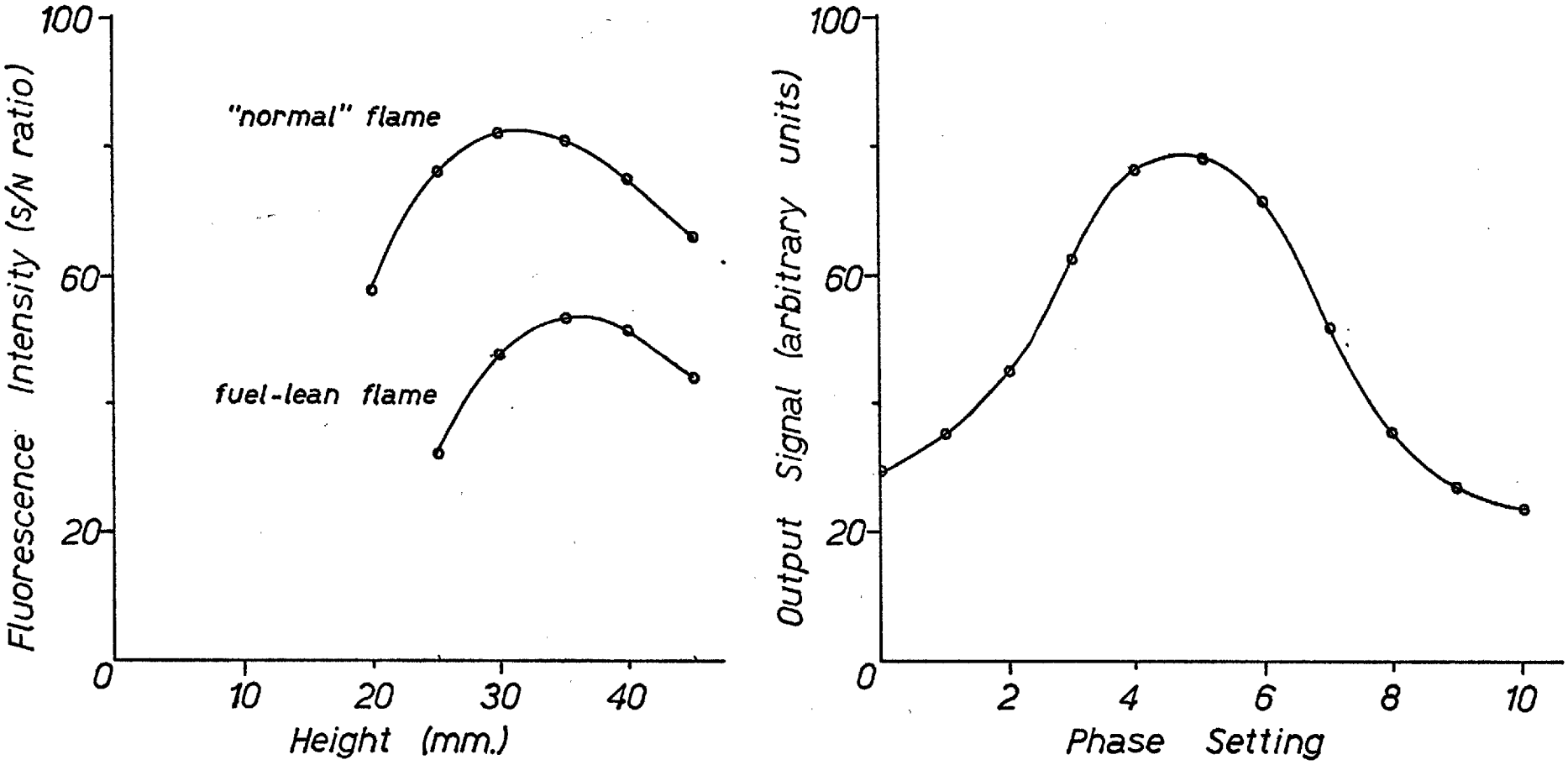
9.3.6. Optimisation of phase

Using both methods described in Section 4.3.6., the variation of output signal with phase setting was established, and is shown in Figure 9.4. This reveals that maximum output was obtained at a phase setting of about 4.5 which, in turn, shows that the instrumentation was functioning correctly during this determination.

9.3.7. Analytical growth curve and detection limit

Figure 9.5 shows the analytical growth curve for antimony and was produced with the photomultiplier operating at 940 Volts and the amplifier gain set at the minimum of 20 db. These settings enabled an aqueous detection limit (signal-to-noise ratio = 2) of 0.33 ppm to be obtained with the linear portion of the analytical growth curve extending up to about 300 ppm.

Figure 9.4 OPTIMISATION OF OPERATING PARAMETERS FOR ANTIMONY



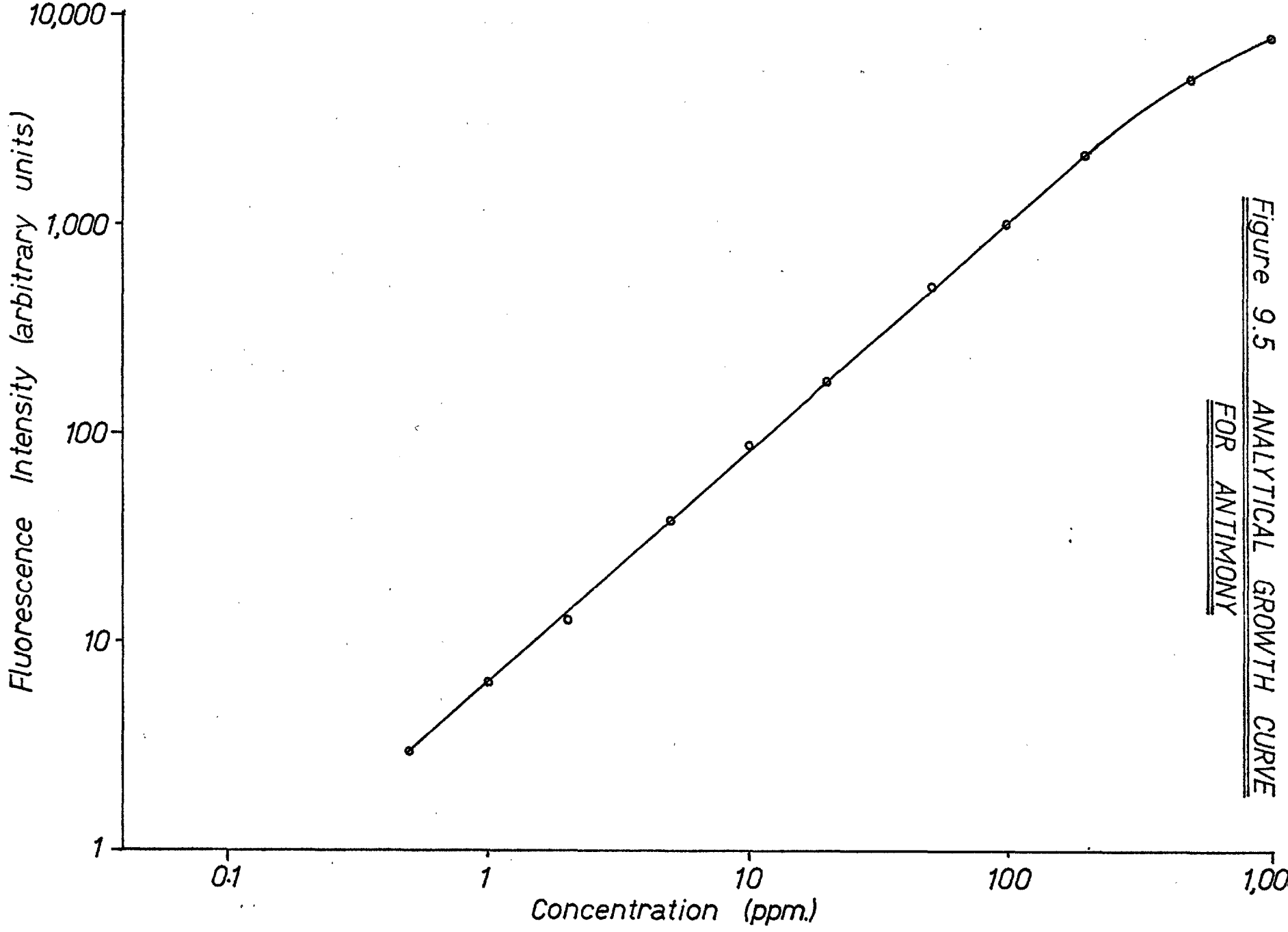


Figure 9.5 ANALYTICAL GROWTH CURVE FOR ANTIMONY

The instrumental operating conditions under which this growth curve was obtained may be summarised as follows:

Spectral source:

1. Air-stream temperature - 85^{o}C (at 12.5 litres/min).
2. Applied microwave power - 50 Watts.
3. Modulation frequency - 285 Hz.
4. Degree of modulation - 70%.

Atom cell:

1. Acetylene flow-rate - 1.1 (0.8 litres/min).
2. Nebuliser pressure - 30 psi (0.2 MN/m^{2}).
3. Viewing height above burner - 30 mm.

Photomultiplier:

1. Operating voltage - 940 Volts.

Amplifier:

1. Input - Normal protected.
2. Frequency limits - 100 Hz to 1000 Hz.
3. Filter - Internal.
4. Meter damping - Off.
5. Gain - 20 db (i.e. 30 db - 10 db).

Phase-sensitive detector:

1. Meter - 10 Volt range (negative).
2. Zero - Negative.
3. Time constant - Internal (1 sec).
4. Filter - Off.
5. Reference channel - A.

Phase shifter:

1. Sensitivity - 100 mV.
2. Frequency range - 100 Hz to 1000 Hz.
3. Phase setting - 4.5.

9.3.8. Interferences

The interference effects of iron on antimony were investigated using the scheme of analysis described in Section 4.3.8. and are presented in Figure 9.6. The results obtained show that, apart from the contribution to the measured atomic fluorescence signal as a result of the scattering of source radiation by the matrix material, the interference effects of iron are, in general, quite small. There are two exceptions to this - notably those systems which contain high concentrations of both iron and antimony - and in at least one of these cases, a definite chemical reaction appeared to have taken place when the respective solutions of the two elements were combined. Immediately after preparation, the solution containing 10,000 ppm iron and 1000 ppm antimony became distinctly white and opaque and, on standing, a white precipitate

Figure 9.6 ANTIMONY INTERFERENCES

Iron conc. (ppm.)	Antimony conc. (ppm.)	Relative Signal
10,000	1,000	0.85
10,000	100	0.89
10,000	10	1.00
10,000	1	1.00
1,000	100	0.97
1,000	10	1.05
1,000	1	1.00
100	10	1.05
100	1	1.00
10	1	1.00

Interferent	Apparent Signal			Relative Signal
	Matrix	Steel	0.5 ppm Sb	
Fe+Cr+Ni	8	11	3	1.0
Fe+Cr	8	11	3	1.0
Fe+Ni	6	11	3	1.7
Fe	6	12	3	2.0
Cr	2	12	3	3.3
Ni	-	13	3	4.3

was observed in the bottom of the solution container.

Such an occurrence must obviously affect the reliability of any measurements made on these solutions and it is felt that this behaviour might help to explain the observed interference effects of iron. In fact, it is possible that this effect is not due to the addition of iron at all, rather to the addition of a highly acidic solution (since, of necessity, the iron solution contains a large amount of hydrochloric acid) to the antimony solution. A similar white, opaque solution was certainly formed when hydrochloric acid was added to quite highly concentrated solutions of antimony, and a similar depression in the atomic fluorescence signal was also observed. Consequently, it should be borne in mind during the analysis of steel samples that some instability of relatively high concentrations of antimony in solution might occur when large amounts of acid are also present.

Figure 9.6 also shows the interference effects of chromium and nickel on antimony at levels which might typically be encountered in stainless steels. These results indicate that the addition of iron at the appropriate concentration to the calibration solutions would be sufficient to overcome any matrix interference problems which might be encountered during the analysis of steel samples.

During this examination of interference effects, the method of scatter correction outlined in Section 7.3.8. was employed for the determination of antimony in the presence of iron. As before, a cadmium EDL was used to measure the actual magnitude

of the matrix scatter signals so that correction could be made on the measured atomic fluorescence signals. The results obtained certainly indicated that some success could be achieved with this kind of approach, but that the precision and accuracy of measurement were somewhat inferior to that which could be obtained by the addition of matrix material to the calibration solutions.

9.3.9. Analysis of steel samples

The results of the analyses of four BCS steel samples containing antimony are presented in Figures 9.7 and 9.8. The dissolution procedure and scheme of analysis outlined in Section 4.3.9. were used during these determinations and included a blank sample which indicated that there were no traces of antimony present in any of the reagents or glassware used.

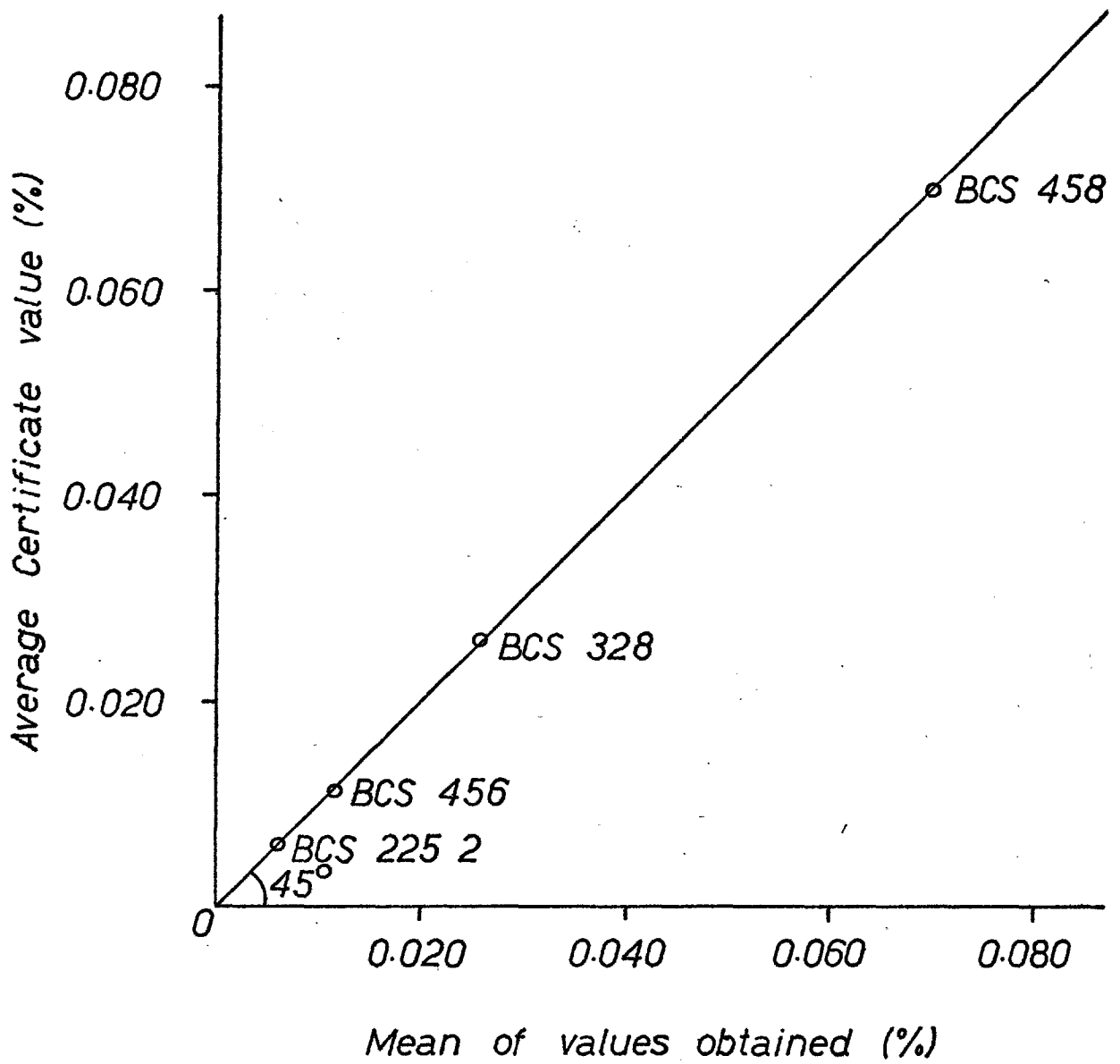
The accuracy of the results obtained was excellent with almost total agreement between the mean value and the average certificate value for each steel sample. Furthermore, the precision of each analysis was found to be very good indeed, with the single exception of BCS 225/2. However, as this sample contains a level of antimony of only about twice the aqueous detection limit obtained in this work, a relative standard deviation of 16.1% for this determination was felt to be quite acceptable.

Overall, it is apparent that the addition of iron to the calibration solutions is usually sufficient to avoid any matrix

Figure 9.7 ANALYSIS OF ANTIMONY IN STEELS

SAMPLE	TYPE	VALUES OBTAINED (%)	MEAN (%)	RSD (%)	AVERAGE CERTIFICATE VALUE (%)	CERTIFICATE RANGE (%)
BCS 458	MILD STEEL	0.0697, 0.0683, 0.0697, 0.0713, 0.0713	0.0701	1.8	0.070	—
BCS 328	MILD STEEL	0.0255, 0.0255, 0.0270, 0.0247, 0.0247	0.0255	3.7	0.026	0.023 → 0.027
BCS 456	MILD STEEL	0.0120, 0.0120, 0.0113, 0.0113, 0.0113	0.0116	3.4	0.011	—
BCS 225/2	Ni-Cr-Mo STEEL	0.0053, 0.0060, 0.0075, 0.0053, 0.0053	0.0059	16.1	0.006	—

Figure 9.8 ANALYSIS OF ANTIMONY IN STEELS



interference problems which might be encountered during the determination of antimony in steel samples.

9.4. Conclusions

This chapter has shown that non-dispersive AFS may be successfully applied to the determination of antimony in ferrous metals. Good sensitivity may be obtained as a result of adopting a non-dispersive approach and excellent precision and accuracy are the features of the analyses of steel samples. The minimum of sample pre-treatment is required and matrix interference effects may be overcome simply by adding the appropriate amount of iron to the calibration solutions. When samples which contain relatively high levels of antimony are to be examined, however, some dissolution problems may arise as high concentrations of antimony seem to be fairly unstable in strongly acidic solutions. In this event, it may be necessary to modify the general sample dissolution procedure used throughout this work in order to avoid inaccurate results.

CHAPTER TEN

CONCLUSIONS

THE PRACTICABILITY OF THE TECHNIQUE

10.1. Introduction

In assessing any analytical technique, the major concern should be that of suitability. It is pointless to consider those aspects of a technique which play little or no part in overcoming a particular analytical problem. For example, a high degree of sensitivity is of little use to the analyst who wishes to measure levels of, perhaps, several per cent.

There is no such thing as the "ideal" analytical technique - merely the most suitable for a particular application - and such is the case with non-dispersive AFS. In outlining the advantages and limitations of the technique for the determination of trace metals in steels, particular emphasis will be placed upon those features which make non-dispersive AFS so suitable and how the disadvantages may be overcome or avoided.

10.2. Assessment of the technique

In the introductory chapter of this thesis, a discussion of analytical requirements was included to facilitate the selection of the most suitable technique for ferrous analysis. Using the general headings under which these requirements were considered, the special features of non-dispersive AFS may be discussed and the technique as a whole evaluated:

1) Selectivity

Since non-dispersive AFS features no form of wavelength selection, this requirement depends wholly on the spectral purity

of the excitation source. Fortunately, satisfactory sources are readily available and provide the technique with more than adequate selectivity for most practical purposes. Indeed, the built-in selectivity provided by excitation sources of sufficient spectral purity contributes greatly to the sequential multi-element capabilities of the technique as a number of elements may be rapidly determined by simply inserting the appropriate sources. No re-alignment or adjustment of the detection system is required during the analytical procedure, making it difficult to imagine a more dedicated, and yet easily re-dedicated instrument.

Although the occurrence of spectral overlap interferences is more likely with a non-dispersive approach than with a more conventional AF system, no such interference problems were encountered during the determination of those elements dealt with in this work. Indeed, the instances in which this type of interference may be met are felt to be sufficiently few in number not to be a major source of difficulty. It is important, however, to consider the likelihood of spectral overlap during the determination of any element by non-dispersive AFS. Of course, even if such overlaps are possible it is still necessary for the interfering element (or elements) to be present in the sample solution before any difficulties can arise. Where samples of unknown composition are to be examined it is wise to employ a philosophy of "guilty until proven innocent" should there be any suspicion of spectral overlap interferences occurring. Fortunately, the few cases of this type of interference which occur in non-dispersive AFS are well-known, enabling the appropriate steps (should they be necessary) to be taken to

avoid inaccurate results. These precautions might include some form of sample pre-treatment to remove the interfering species or adjustment of the instrumental operating conditions.

2) Sensitivity

At the outset of this work it was felt that non-dispersive AFS could provide the best limits of detection for a number of the elements of interest in the field of ferrous analysis and, to some extent, this point remains unestablished. The main feature of this work is one of practicability - more importance was attached to being able to determine the elements in steels at levels at which they might typically be expected to occur, rather than in trying to obtain the very best detection limit possible. That is not to say that no attempt was made to optimise the instrumentation, merely that optimum instrumentation was not used. There can be no question that the limits of detection quoted in this work could be substantially improved simply by using better or more efficient instrumental units. AF instrumentation usually consists of a conglomeration of modified or improvised component parts, few of which have been specifically designed for the application in which they find themselves, and this frequently limits the performance of the instrument. However, beyond trying to produce the best possible performance from the available instrumentation, provided adequate sensitivity could be obtained, it was felt unnecessary to look for better limits of detection by improving or replacing the individual components.

The technique of non-dispersive AFS provides good sensitivity for all of the elements dealt with in this work. This feature facilitates the determination of these elements in steels at typically occurring levels without having to resort to elaborate extraction or pre-concentration procedures.

In comparison with the other flame spectroscopic techniques, non-dispersive AFS enables similar or slightly better limits of detection to be obtained, particularly for those elements whose main resonance lines lie in the ultra-violet region of the spectrum. In addition, the linear dynamic ranges of the growth curves usually extend over at least three orders of magnitude, enabling the analysis of a number of samples of widely differing concentrations to be made much more rapidly and conveniently than by AAS, for example. This is an important practical feature of AFS generally, especially if an automatic or semi-automatic instrument is desired, as it is obviously useful to be able to present the range of sample solutions to an instrument capable of performing all the measurements without having to re-adjust the instrumental settings.

It must be stressed, however, that a number of elements of metallurgical interest cannot be easily determined by non-dispersive AFS. During the course of this work, the determination of aluminium was attempted but, despite having produced a satisfactory aluminium EDL, no atomic fluorescence signals could be obtained. This was felt to be due to the difficulty in producing an adequate atomic population in the nitrogen-separated air-acetylene flame, even though a strongly reducing fuel-rich flame was employed to break

down the stable aluminium oxide molecules. This type of difficulty will clearly be encountered in attempting to determine any element which forms highly stable oxides in the air-acetylene flame. The determination of tin in the air-acetylene flame was similarly found to be insufficiently sensitive but adequate sensitivity was eventually obtained using the more strongly reducing air-hydrogen flame.

The ploy of using different flames for each element is not to be recommended, however. With the principal advantage of non-dispersive AFS being the ease with which it lends itself to rapid, sequential multi-element analysis, the necessity for a number of different flameswould be a serious drawback. It is for this reason that the convenient and versatile air-acetylene flame is so attractive. Nevertheless, in choosing this flame the capabilities of the technique immediately become limited and the determination of elements such as aluminium, niobium and tantalum can no longer be considered. Of course, before any element can be determined by AFS a suitable spectral source must be available and the extreme difficulty involved in preparing satisfactory EDLs containing niobium or tantalum etc. overrides any atomisation problems concerning the choice of flame. Thus, the limitations of non-dispersive AFS in terms of sensitivity must not all be ascribed to poor atomisation - inadequate excitation may play the more significant part.

Some elements of interest in ferrous analysis are difficult to determine by non-dispersive AFS for reasons other than those considered above. These are the elements whose main fluorescence

resonance lines lie outside the spectral range of the detection system used. Since non-dispersive AF spectrometers usually employ photomultipliers sensitive only to radiation from the ultra-violet region of the spectrum, elements such as chromium, copper and silver, whose main resonance lines are in the visible region, cannot be determined. However, this problem can be overcome fairly easily by using a photomultiplier with different response characteristics, although this in turn may require the use of a different flame giving little or no background emission in the new spectral region, and consequently detracts from the convenience of the technique. Where particular difficulty is encountered in determining any element by non-dispersive AFS, it is likely that an alternative analytical technique would prove to be more suitable. Nevertheless, a great many elements of interest in the metallurgical field can be determined by non-dispersive AFS, especially some of the more "difficult" elements such as arsenic, selenium and antimony, although in some cases quite rigorous operating conditions may be required.

3) Cost of instrumentation

By its very nature, non-dispersive AF instrumentation is very simple with only a few, readily available basic units being needed to produce a typical spectrometer. In comparison with an atomic absorption or atomic emission spectrometer of similar capability, the cost of a non-dispersive AF instrument would be considerably lower. This means that, for a given outlay, the non-dispersive AF spectrometer represents the better value for money as a more

sophisticated, more capable instrument can be obtained. Commercial EDLs too, are relatively inexpensive and good sources can even be prepared in the laboratory, with a little practice, at virtually no cost.

4) Cost of operation

There are many contributions to the overall cost of an analysis, not least of which is that due to the time taken for its completion. In terms of speed and simplicity of operation, it is hard to imagine a more suitable technique for ferrous analysis than non-dispersive AFS. Beyond the simple dissolution of the steel, no form of sample pre-treatment is necessary before measurement may be made and a whole series of elements may be determined in any one sample solution, on a sequential basis, simply by inserting the appropriate excitation sources into the instrument. Moreover, the long linear dynamic ranges associated with this technique enable a large number of analyses to be made at any one time.

10.3. Additional features

Having examined the extent to which non-dispersive AFS fulfills, in practice, the general features required of a suitable analytical technique for ferrous analysis, a number of points remain unconsidered:

a) Scatter correction

The scattering of incident radiation by particulate material in the flame is a serious form of interference in non-dispersive AFS as the instrumental detection system is unable to distinguish between

this and the true atomic fluorescence signal. In ferrous analysis especially, the high iron concentrations present in the nebulised sample solutions give rise to quite large scatter signals which can become particularly significant when low levels of analyte are being measured.

A number of methods were used during the course of this work to overcome or eliminate the scattering of radiation and all met with a certain amount of success. The first, and most satisfactory method consisted of incorporating an approximately equivalent amount of iron into the calibration solutions as was present in the sample solutions. In this way the scatter signal obtained from a steel sample solution was produced to an identical extent by the calibration solutions, enabling the analyte concentration to be accurately gauged. An important feature of this approach is that it automatically corrects for any other type of interference which might also occur as a result of the large excesses of matrix material present in the sample solutions. For example, the viscosity of solutions of high dissolved solid content may affect the rate of aspiration into the flame cell giving rise to decreased atomic fluorescence signals. By matching the calibration solutions as described above, however, any such viscosity effects are accurately simulated and, hence, corrected for.

The only disadvantage with this method of scatter correction is that it requires the preparation of slightly more complex calibration solutions than would normally be needed. This detracts somewhat from the convenience of operation making it a little more laborious, although it must be pointed out that it is unnecessary to

simulate the levels of matrix material exactly. Indeed, when dealing with stainless steels, for example, where the iron level is considerably reduced because of quite large levels of chromium and nickel, it is perfectly adequate to regard all the matrix material as iron and match the calibration solutions accordingly. Thus, although this method requires more complex standard solutions than usual, no great degree of accuracy is needed in their preparation.

The second approach to the problem of light scattering was found to be satisfactory only in certain instances. Where such scattering is the only form of interference occurring, the preparation of elaborate calibration solutions as described above, becomes unnecessary. Instead, a single, pure solution of iron, at the appropriate concentration, may be used either as the reference solution or to measure the scatter signal produced by the iron matrix. It is then a simple matter to "back-off" this scatter signal from the apparent fluorescence signal obtained from each sample solution.

It is evident that this sort of approach takes no account of any other form of interference. Nevertheless, in many cases, where no other types of interference significantly affect the analytical signal, this method of scatter correction may prove to be quite satisfactory and may be preferred, from the point of view of convenience, to the slightly more laborious approach described previously.

The inability to correct for types of interference other

than scatter is also a major disadvantage with the third and final method of scatter correction considered in the course of this work. This method is based on the fact that, while the production of atomic fluorescence requires characteristic excitation, scatter from the iron matrix is dependent upon the emission intensity, rather than the nature, of the spectral source. Thus, any apparent fluorescence signals obtained using a spectral source of any element of which the samples are known to be free will be nothing more than scatter from the matrix material, assuming no spectral overlap interferences can occur. Based on these points, this procedure for scatter correction involves normal measurement of the samples and calibration solutions using a spectral source characteristic of whichever element is under consideration, whence apparent fluorescence signals are obtained, part of which are due to matrix scatter. The same solutions are then re-measured using a source of an element known not to be present in the samples (in this work a cadmium EDL was used), the intensity of which must be adjusted to be equivalent to that of the previous source, in order to determine the scatter contribution to the apparent fluorescence signals. In this way the true atomic fluorescence signal from each sample may be obtained without having to add matrix material to the calibration solutions.

A number of major disadvantages make this approach to the problem of scatter correction the least favourable of those considered in this work. As mentioned previously, it fails to take into account the effects of any forms of interference other

than scatter, and this immediately limits the usefulness of the method. In addition, unless the instrument is adapted such that both sources may be operated simultaneously, it is necessary to measure each sample solution twice, which severely detracts from the convenience of operation of the technique. Lastly, it has been demonstrated that light scattering shows some wavelength-dependence, which could result in over- or under-correction of the apparent fluorescence signals. Despite these drawbacks, however, it is felt that if any form of automatic scatter correction is to be incorporated into the instrument this kind of approach should be adopted.

Thus, to summarise this discussion on scatter correction, it is concluded that the most favourable, if slightly inconvenient, approach is to prepare calibration solutions containing matrix material at levels reasonably similar (perhaps, $\pm$ 2% of the sample content) to those found in the sample solutions. In many instances, however, equally good results may be obtained by using the appropriate solution of pure matrix material simply to "back-off" the scatter signal. The remaining method, in which two spectral sources are employed, is the least useful of all but may find some application in the form of an automatic scatter correction unit.

b) Precision and accuracy

Of all the features to be considered in assessing a quantitative analytical technique, this aspect is usually the most important. Speed of operation, simplicity of instrumentation,

multi-element capabilities etc. are all of little consequence if the technique is unable to provide accurate and precise answers.

In order to assess the performance of the technique, a number of BCS steel samples were examined for each of the elements dealt with in this work. In the cases of selenium and tellurium, standard steel samples were not available but this difficulty was surmounted by adding known amounts of these elements to a range of dissolved BCS steel samples. In total, twenty eight determinations covering the six elements of interest in this work were made and, of the results obtained, only three failed to fall within the appropriate certificate range (or, where no range was quoted, within a "typical" certificate range). Moreover, each of these inaccurate results was obtained during the determination of arsenic where source instability can sometimes be a problem (see Section 8.3.4.) and it is felt that a slightly more sophisticated thermostatting device than the one used in this work could eliminate this minor, yet irritating difficulty. Additionally, some modification of the sample dissolution procedure would probably improve the level of accuracy obtained so that, although inconvenient, these problems could be overcome fairly easily.

The purpose of this work is to demonstrate the practicability of non-dispersive AFS for the determination of trace metals in steels. With this in mind, any considerations of precision should relate to the overall analytical procedure rather than merely to the measurement step. Thus, in each determination, five separate weighings of each sample were taken to enable the overall precision

of the technique to be assessed. (While it is realised that a truer statistical picture could have been obtained by taking a greater number of weighings, it was felt that a reasonable appreciation of the capabilities of the technique could be gained without having to prepare an excessive number of samples).

In general, the relative standard deviation for each determination was less than 10%, and frequently less than 5%, except in the case of tin where some determinations of levels of about three or four times the limit of detection gave relative standard deviations of around 40%. One possible explanation for this curious behaviour is the relative instability of tin in solution. Precipitation can occur even in quite highly acidic solutions of tin and this may affect the efficiency of nebulisation and atomisation during the measurement step of the analytical procedure. More important, however, is the relative magnitude of the tin atomic fluorescence signal compared to the scatter signal produced by the matrix elements. Correction for this scatter effect involves the estimation of the small difference between two large signals and this may adversely affect the precision (and accuracy) of the determination. Although tin was the only element to be determined in the course of this work in an air-hydrogen flame, it seems unlikely that the observed deterioration of precision can be attributed directly to the use of this flame. Indeed, a number of determinations of tin in steels, although admittedly at quite high levels, using an air-hydrogen flame gave very

acceptable results in terms of both precision and accuracy, indicating that the choice of this flame would not adversely affect the performance of the technique.

Thus, non-dispersive AFS seems to be capable of making sufficiently accurate and precise determinations of a number of elements of interest in the field of ferrous analysis. Beyond simple dissolution, no sample pre-treatment is necessary (although samples containing tin may require a little more consideration) making the technique particularly suited to practical analysis.

10.4. Additional instrumentation

This final section, which might also be termed, "Suggestions for future work", contains a few indications of how the instrumentation used in this work might be developed. No attempt is made to discuss how this development should be tackled, merely that these are the areas in which the technique might usefully be improved:

a) Simultaneous multi-element analysis

The rapid, sequential multi-element capabilities of the technique ought to be adequate for most applications but the ease with which AFS, in general, lends itself to simultaneous multi-element analysis (using an array of pulsed EDLs, perhaps) makes this aspect worthy of examination. The additional expense involved in developing this aspect might easily outweigh any advantages gained, however.

b) Automatic scatter correction

Despite the limitations discussed previously, the use of a second spectral source as an automatic scatter corrector has some attraction, particularly as development in this area may help to obviate the need for the matching of calibration and sample solutions.

c) Automation

Most analytical procedures can benefit by becoming, at least, partly automated. As an instrument intended for use on a routine basis, a non-dispersive AF spectrometer employing an automatic sample changer and an automatic read-out device would require the minimum of attention during operation. Furthermore, such features would not add greatly to the overall cost of the instrument and serve to underline the suitability of the technique for ferrous analysis.

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