SOME ASPECTS OF ATOMIC FLUORESCENCE SPECTROSCOPY

by

JOHN DONALD NORRIS, M.Sc., A.R.I.C.

A Thesis submitted for the Degree of Doctor
of Philosophy of the University of London

OCTOBER 1972

Chemistry Department,
Imperial College of Science and Technology,
London, S.W.7.

ABSTRACT

The general theory, instrumentation and role in chemical analysis of atomic fluorescence spectroscopy is reviewed.

The atomic fluorescence characteristics and analytical determination of chromium in an argon-separated air-acetylene flame, using an electrodeless discharge lamp, are described. The overlap of neon and chromium spectral lines has been utilised to produce the atomic fluorescence and atomic absorption of chromium with a neon electrodeless discharge lamp. The atomic fluorescence determination of antimony in copper-base alloys in an argon-hydrogen diffusion flame is reported.

An investigation of the preparation and operation of a number of multi-element electrodeless discharge lamps has been undertaken. These lamps have been used as spectral sources for the atomic fluorescence determination of chromium, cobalt, manganese and nickel in a variety of different types of steel. A scanning technique, employing these lamps, has been developed for rapid sequential multi-element determinations by atomic fluorescence spectroscopy.

A non-dispersive atomic fluorescence spectrometer has been constructed for use with the carbon filament atom reservoir and a flame cell. This has been used for the determination of mercury with the carbon filament, and zinc in soils and a variety of non-ferrous metal alloys with a flame. Instrumentation for the continuous operation of the carbon filament atom reservoir is described.

ACKNOWLEDGEMENTS

The work described in this thesis is entirely original except where due reference is made. No part of the work has been previously submitted for any other degree. The work was carried out in the Chemistry Department of the Imperial College of Science and Technology between October 1970 and September 1972.

I should like to thank my supervisor, Professor T.S.West, for the help and encouragement he has given me throughout this work. Thanks are also due to many members of the Analytical Chemistry research group for helpful discussions.

I should also like to thank the Science Research Council for the award of a research studentship.

CONTENTS

CHAPTER I

THEORETICAL BASIS OF ATOMIC FLUORESCENCE SPECTROSCOPY

1.1 HISTORICAL INTRODUCTION

The first work to include the observation of atomic fluorescence was carried out in the latter half of the nineteenth century, and was concerned with the astrophysical study of the composition of stellar and solar atmospheres. At the beginning of the present century, several groups of spectroscopists examined the atomic fluorescence spectra of a number of elements, produced by the atomic vapours contained in quartz cells (1,2). In the case of sodium, Wood (3) succeeded in exciting the D line atomic fluorescence by irradiating an atomic vapour of the element with the atomic line emission from a flame containing sodium chloride. Following Wood's experiments, the atomic fluorescence spectra of antimony (4), bismuth (4), cadmium (4), caesium (5), lead (4), lithium (6), manganese (7), mercury (8), thallium (4) and zinc (9) were all observed, after irradiation by a variety of spectral sources.

It was not until the 1920's that Nichols and Howes (10, 11) conducted the first atomic fluorescence studies in flame cells. The elements examined in this work were barium, caesium, calcium, lithium, rubidium, sodium, strontium and thallium. Further investigations, using flame cells, were made by Badger (12), who observed the atomic fluorescence spectra of cadmium, copper, magnesium, mercury, silver, sodium and thallium, and by Mankopff (13). More recently atomic fluorescence observations were made by Alkemade and co-workers (14-17) and Jenkins (18-22), in order to obtain data about excitation mechanisms and fluorescence quantum efficiencies.

The potential application of atomic fluorescence spectroscopy to chemical analysis was first considered in 1961, after Robinson (23), during an atomic absorption study, had observed the atomic fluorescence emitted at 285.2 nm. by a 1000 ppm. solution of magnesium, in an oxy-hydrogen flame, using a hollow cathode lamp as the source of excitation. In 1964, Winefordner and Vickers (24) described the theory, instrumentation and procedure

for the analytical technique, and Winefordner and Staab (25) gave results for the determination of cadmium, mercury and zinc by atomic fluorescence spectroscopy. Despite using what would now be regarded as far from ideal equipment, they obtained superior detection limits to those which could be obtained by atomic absorption, using the same instrumentation.

Since then, atomic fluorescence spectroscopy has been applied to the determination of nearly forty elements, some of the early extravagant claims for the advantages of the technique have been moderated, a comprehensive theoretical treatment of quantitative atomic fluorescence spectroscopy has been produced, and significant improvements in instrumentation and procedure have been made. Over one hundred and fifty research papers and some twenty reviews have now been published on the subject.

1.2 THEORY

1.2.1 Scope

In the remainder of this chapter it is proposed to discuss the various atomic fluorescence processes which can occur and may be made use of in analytical atomic fluorescence spectroscopy, and to consider the factors which affect the intensity of atomic fluorescence and the shape of atomic fluorescence calibration curves.

1.2.2 Atomic fluorescence processes

1.2.2.1 Basic considerations

The simplest description of the process of atomic fluorescence is as follows. A ground state atom absorbs a quantum of electromagnetic radiation, which raises it to an excited electronic energy state. The atom subsequently re-emits the absorbed energy as a photon, on returning to the ground state. Atomic fluorescence spectroscopy is concerned with the measurement of the re-emitted radiation from an atomic population, normally in a flame cell.

All atoms have a large number of excited energy states, and these energy states are characteristic of the element. The energy states all have

known energy values, and so a specific quantum of radiation is required to raise a particular atom to an excited energy state. When excitation occurs from the ground state to an excited energy state, due to the absorption of radiation, the amount of energy absorbed E_a, is related to the wavelength of the absorbed radiation λ , by the expression,

$$E_a = h\nu = \frac{hc}{\lambda}$$

where h is Planck's constant, v is the frequency of the absorbed radiation and c is the velocity of light. Therefore, to cause the excitation of an atom to a higher energy state, by the absorption of radiation, that radiation must be of a specific wavelength.

Similarly, when deactivation occurs from an excited energy state to a lower energy state by the emission of fluorescent radiation, a corresponding relationship applies, and the fluorescent radiation will also be of a specific wavelength.

Since each atom possesses a large number of excited energy states, there are several different mechanisms by which atomic fluorescence processes can occur, and these are illustrated diagrammatically in Figure 1.1 and explained below.

1.2.2.2 Resonance fluorescence

Resonance fluorescence occurs when atoms are excited from their ground state to an excited energy state by the absorption of radiation, and then undergo radiational deactivation back to the ground state, emitting fluorescent radiation of the same wavelength as that of the absorbed radiation. The most intense resonance fluorescence occurs from the first excited state of the atom to the ground state. An example of resonance fluorescence is the atomic fluorescence of zinc at 213.9 nm., after irradiation with light of that wavelength (26).

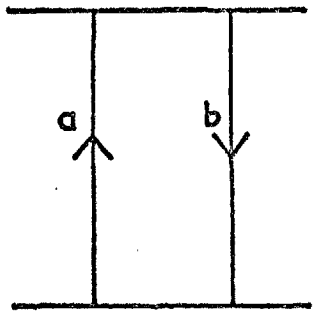
1.2.2.3 Direct-line fluorescence

Direct-line fluorescence occurs when an atom is raised to an excited energy state, considerably higher than the ground state, by the absorption

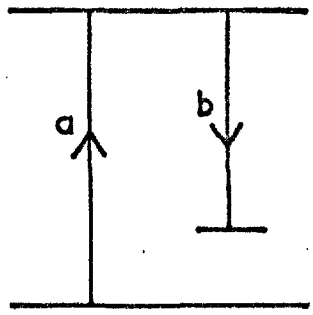
FIGURE 1.1

TYPES OF ATOMIC FLUORESCENCE

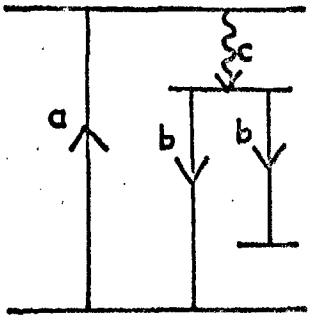
Resonance



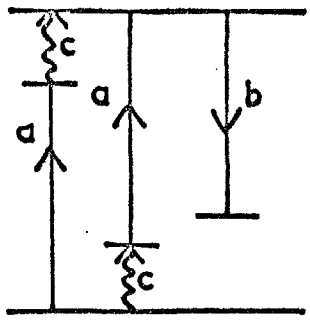
Direct-line



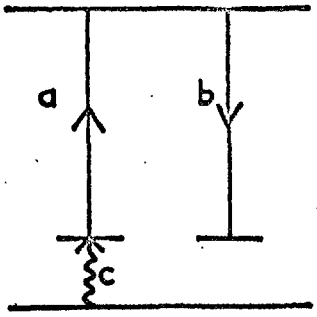
Stepwise



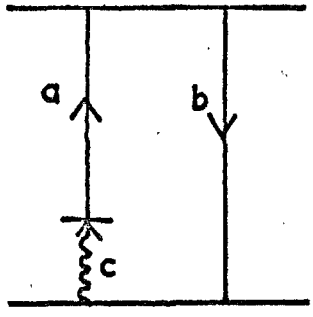
Thermally-assisted direct-line



Thermally-assisted resonance



Thermally-assisted anti-Stokes



Sensitised

$A + h\nu \longrightarrow A^{*}$

$A^{*} + M \longrightarrow M^{*} + A$

$M^{*} \longrightarrow M + h\nu$

a absorption

b fluorescence

c thermal

of radiation, and then undergoes radiational deactivation to a metastable lower excited state, before returning to the ground state by a non-radiative process. Therefore, the emitted radiation is of a higher wavelength than that of the absorbed radiation. An example of direct-line fluorescence is the atomic fluorescence of thallium at 535.0 nm., after excitation with radiation at 377.6 nm. (27).

1.2.2.4 Stepwise fluorescence

In stepwise fluorescence, the atom, after excitation to a high excited energy state by the absorption of radiation, returns to the ground state via a lower excited state. The radiational deactivation occurs from the lower excited state, and hence the fluorescent radiation emitted is of a higher wavelength than that of the absorbed radiation. The atomic fluorescence of the sodium 589.0 nm. doublet, after excitation with radiation of the 330.3 nm. doublet (28) is an example of stepwise fluorescence.

1.2.2.5 Thermally-assisted resonance fluorescence

Thermally-assisted resonance fluorescence occurs when an atom is initially raised to an excited state by the absorption of thermal energy from the flame (c.f. atomic emission spectroscopy) and then absorbs radiation to raise it to a higher energy state. Radiational deactivation occurs as the atom returns to the lower energy state. Thus the fluorescent radiation is of the same wavelength as that of the absorbed radiation. An example of thermally-assisted resonance fluorescence is the atomic fluorescence of indium at 410.2 nm., after excitation with radiation of that wavelength (29).

1.2.2.6 Thermally-assisted direct-line fluorescence

In thermally-assisted direct-line fluorescence the atom is raised to a slightly higher energy state than in normal direct-line fluorescence due to the absorption of thermal energy from the flame. Radiational deactivation then occurs to a lower excited energy state. The atomic fluorescence of antimony at 259.8 nm., after excitation with light at 206.8 nm. has been

attributed to thermally-assisted direct-line fluorescence (30).

1.2.2.7 Thermally-assisted anti-Stokes fluorescence

Thermally-assisted anti-Stokes fluorescence is similar to thermally-assisted resonance fluorescence, except that the radiational deactivation is back to the ground state, rather than to a lower excited state. Hence, the fluorescent radiation emitted is of a shorter wavelength than that of the absorbed radiation. An example of thermally-assisted anti-Stokes fluorescence is the atomic fluorescence of gallium at 403.3 nm., after excitation with radiation at 417.2 nm. (29).

1.2.2.8 Sensitised fluorescence

Sensitised fluorescence occurs when donor atoms or molecules are excited by the absorption of radiation to an excited energy state, and then collide with ground state sample atoms, transferring energy to them, and thus raising them to an excited energy state. The excited sample atoms then undergo radiational deactivation to a lower energy state, emitting fluorescent radiation. For example, if a gas containing a high pressure of mercury vapour and a low pressure of thallium vapour is excited with mercury radiation at 253.7 nm., some thallium atomic fluorescence at 377.6 nm. and 535.0 nm. will be observed (28).

1.2.2.9 Use of the different types of fluorescence in analytical atomic fluorescence spectroscopy

Resonance fluorescence is the most commonly used of the above processes in analytical atomic fluorescence spectroscopy. The probabilities for the transitions causing resonance fluorescence are much greater than those for the other types of fluorescence. However, the main advantage of resonance fluorescence in analysis is that the fluorescent radiation intensities are significantly greater than those with the other types of fluorescence.

However, an important disadvantage of resonance fluorescence is that scatter of the incident radiation by particles in the flame can cause errors, since the scattered radiation will be of the same wavelength as that of the fluorescent radiation. This interference does not affect the other types of atomic fluorescence, when the incident radiation and the fluorescent radiation are of different wavelengths.

Sensitised fluorescence is not observed in flames under normal conditions, since it is impossible to obtain a large enough concentration of donor atoms in a flame cell to stimulate the atomic fluorescence.

1.2.3 The intensity of atomic fluorescence and the theoretical derivation of analytical atomic fluorescence spectroscopy curves

1.2.3.1 Introduction

The intensity of the fluorescent radiation produced by an atomic population in atomic fluorescence spectroscopy is proportional to:-

1. The intensity of the incident radiation directed on to the atomic population from the source of excitation.

2. The fraction of the incident radiation absorbed by the atoms. This is a function of the concentration of absorbing atoms.

3. The efficiency of the conversion of absorbed radiation into fluorescent radiation.

4. The fraction of the fluorescent radiation self-absorbed by ground state atoms. This is a function of the atomic concentration, and at high concentrations is a cause of quenching.

The first attempt to explain the shape of atomic fluorescence and atomic concentration curves, in relation to the above factors, was made by Winefordner and Vickers (24). Their theoretical calculations may be simplified, for the case of resonance fluorescence with a low atomic concentration, to give the following expression for the intensity of the observed fluorescent radiation E_f,

$$E_f = CI_\nu N_o$$

where C is a constant for the particular element and experimental conditions, I_v is the intensity of the incident radiation and N_o is the number of absorbing atoms present. Therefore, at low atomic concentrations, the intensity of the fluorescent radiation is proportional only to the intensity of the incident radiation and to the number of atoms present, which can absorb that incident radiation.

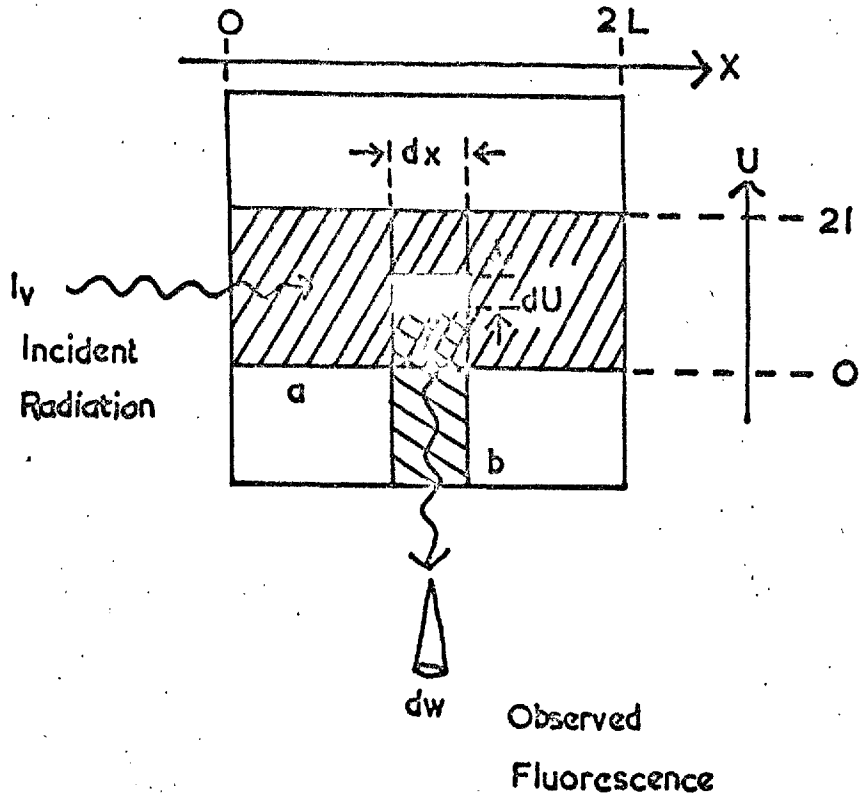
This elementary equation, although correct in principle, is somewhat restricted in its application, since the effect of certain absorption parameters is not fully considered. Several other attempts have been made to explain the shape of analytical atomic fluorescence spectroscopy curves (31 - 35), both for resonance fluorescence and for some of the other types of atomic fluorescence. The most exhaustive of these calculations are those made by Hooymayers (34), and his approach to resonance fluorescence curves will be considered below. Equations for the other types of atomic fluorescence, which are considerably more complex, will not be considered here, but may be found in the relevant literature (31 - 34).

1.2.3.2 General expression for resonance fluorescence

A discussion of the theory of analytical atomic fluorescence curves necessitates a preliminary consideration of an ideal flame cell. This is illustrated in Figure 1.2. It is possible to construct such a flame cell in practice (35), provided it is surrounded by a mantle flame of the same gas composition, in order to achieve a uniform temperature throughout the flame. A homogenous parallel beam of incident radiation of rectangular cross-section σ = 21 x 21' traverses the flame, intersecting the flame axis at right angles. The dimension 21 lies in the plane of the diagram, whilst 21' is perpendicular to the plane of the diagram. A uniform distribution of ground state atoms throughout the flame is assumed. The fluorescent radiation considered is that emitted through a small solid angle $d\omega$, perpendicular to the direction of the incident radiation and to the flame cell.

FIGURE 1.2

CROSS-SECTION OF IDEAL FLAME CELL



The integrated energy absorbed per second E_a, by the absorbing atoms in the volume element of the flame cell 21'dudx (the black shaded area in Figure 1.2) is given by,

$$E_a = 21' du\, dx \int_0^\infty I_\nu K_\nu e^{-K_\nu x} d\nu \qquad \ldots (1)$$

where I_ν is the radiation flux of the incident light beam, expressed as energy per unit time per unit area at frequency v and per unit frequency interval, K_ν is the absorption coefficient (in $cm.^{-1}$) at frequency v, and $K_\nu dx$ is the fraction of energy of frequency v which is absorbed as the incident beam travels over a distance dx in the flame, and is given by,

$$K_\nu dx = B_\nu N_0 dx \qquad \ldots (2)$$

where B_ν is the self-absorption factor, and N_0 is the concentration of ground state atoms in $cm.^3$.

Therefore, the intensity of the observed fluorescent radiation dE_f, emitted by the excited atoms in this volume of the flame cell, and observed through the small solid angle $d\omega$, is given by,

$$dE_f = \frac{d\omega}{4\pi} \left[21' du dx \int_0^\infty I_\nu d\nu K_\nu e^{-K_\nu x}\right] \left[\int_0^\infty p\, \alpha_{\nu'} e^{-K_{\nu'}(L-1+u)}\right] d\nu' \qquad \ldots (3)$$

where $e^{-K_{\nu'}(L-1+u)}$ allows for the loss in the fluorescent intensity due to self-absorption in the flame cell, p is the fluorescence yield factor (i.e. the fractional probability that an excited atom will lose its energy by the radiation of a photon before it suffers a quenching collision), $\alpha_{\nu'} d\nu'$ is the probability of an emitted photon having a frequency between v' and v' + dv', and L is the flame thickness.

$\alpha_{\nu'}$ represents the normalised shape of the fluorescent spectral line when not distorted by self-absorption. It is derived from classical theory and is given by

$$\alpha_{\nu'} = 8\pi \frac{1}{\lambda_0^2} \frac{g_0}{g_1} \frac{1}{A N_0} K_{\nu'} \qquad \ldots (4)$$

where g_0 and g_1 are respectively the statistical weights of the ground and excited energy states involved in the transition, A is the transition probability in S^{-1} and λ_0 is the centre of the wavelength of the fluorescent radiation.

By substituting equation (4) in equation (3) and integrating x and u between 0 and 2L and 0 and 2l respectively, the following expression for the total fluorescent radiation flux E_f, may be obtained,

$$E_f = \frac{\partial\omega}{4\pi} 2l' P \frac{8\pi}{N_0 A \lambda_0^2} \frac{g_0}{g_1} \int^{\infty} I_\nu \left(1 - e^{(-k_\nu 2l)}\right) d\nu_0 \int^{\infty} e^{-k_{\nu'}(L-1)} - e^{-k_{\nu'}(L+1)} d\nu' \quad \ldots (5)$$

Introducing the dimensionless variable $J = K_0 L$ = constant $N_0 L$, where K_0 is the maximum value of the absorption coefficient Kv, when the only broadening effect is Doppler broadening at the specific flame temperature, the following equation is obtained,

$$E_f = \frac{\partial\omega}{4\pi} \sigma P \Delta\nu_D (\pi \ln 2)^{-\frac{1}{2}} \frac{L}{l} \frac{1}{J_0} \int^{\infty} I_y \left(1 - e^{-2JQ_y}\right) dy_0 \int^{\infty} \left[1 - e^{-Q_{y'} J\left(1+\frac{l}{L}\right)} - \left(1 - e^{-Q_{y'} J\left(1-\frac{l}{L}\right)}\right)\right] dy' \quad \ldots (6$$

where y is the dimensionless frequency difference $\frac{2\nu - \nu_0}{\Delta\nu_D} (\ln 2)^{\frac{1}{2}}$, ν_0 being the central frequency of the spectral line. $\Delta\nu_D$ is the Doppler half-intensity width of the spectral line, and is given by,

$$\Delta\nu_D = \frac{1}{\lambda_0} \left(\frac{8\pi K_0 t}{m} \ln 2\right)^{\frac{1}{2}} \quad \ldots (7)$$

where t is the temperature of the flame, and m is the mass of the absorbing atoms in the flame.

The value of K_0 is given by,

$$K_0 = \frac{2(\ln 2)^{\frac{1}{2}} \lambda_0^2}{\Delta\nu_D \pi^{\frac{1}{2}} 8\pi} A N_0 \frac{g_1}{g_0} \quad \ldots (8)$$

Qy is given by the expression,

$$Q_y = \frac{K\nu}{K_0} = \frac{a}{\pi^{\frac{1}{2}}} \int^{\infty} \frac{e^{-t^2} dt}{a^2 + (y-t)^2} \quad \ldots (9)$$

The parameter a in equation (9) is the damping constant for the particular sample atoms and flame gases, and is given by,

$$a = \frac{\Delta\nu_L}{\Delta\nu_D} (\ln 2)^{\frac{1}{2}}$$

where $\Delta\nu_L$ is the Lorentz half-intensity width of the spectral line. Thus Qy describes the normal spectral shape of an isolated resonance line due to both Doppler and Lorentz broadening.

E_f may be evaluated from equation (6) in the case of a very narrow line source and a continuum source. However, if the width of the absorption line and the width of the incident line are comparable, information on the frequency distribution of the incident line will also be required. The deriv-

ation of analytical atomic fluorescence spectroscopy curves for these two limiting cases will now be considered.

1.2.3.3 Analytical curve for a continuum source

In the case of a continuum source of excitation Iy is virtually constant over the frequency range of interest, and may be replaced by I_o, where Iy = Io for the central frequency of the absorption line of the atoms in the flame cell. By this substitution and the rearrangement of equation (6), the following expression is obtained,

$$E_f / \frac{\partial \omega}{4\pi} I_o \sigma \Delta\nu_D \left(\frac{\pi}{\ln 2}\right)^{1/2} P = \frac{1}{\pi} \frac{1}{L} \frac{1}{J_o} \int_0^{\infty} \left(1 - e^{-2JQ_y}\right) dy_o \int_0^{\infty} 1 - e^{-Q_y' J\left(1+\frac{1}{L}\right)} - \left(1 - e^{-Q_y' J\left(1-\frac{1}{L}\right)}\right) dy' \quad \ldots (10)$$

Hence the double logarithmic plot of $E_f / \frac{\partial \omega}{4\pi} I_o \sigma \Delta\nu_D \left(\frac{\pi}{\ln 2}\right)^{1/2} P$ and J (=constant $N_o L$) represents the theoretical analytical atomic fluorescence curve. Some analytical curves, for various values of the damping constant, derived from the above theory for a single spectral line with a continuum source are shown in Figure 1.3. These curves show that at high atomic concnetrations the intensity of the fluorescent radiation is no longer dependent on the atomic concentration, and the curves tend towards horizontal asymptotes. The point of intersection of the high and low concentration asymptotes is dependent on the value of the damping constant.

1.2.3.4 Analytical curve for a narrow line source

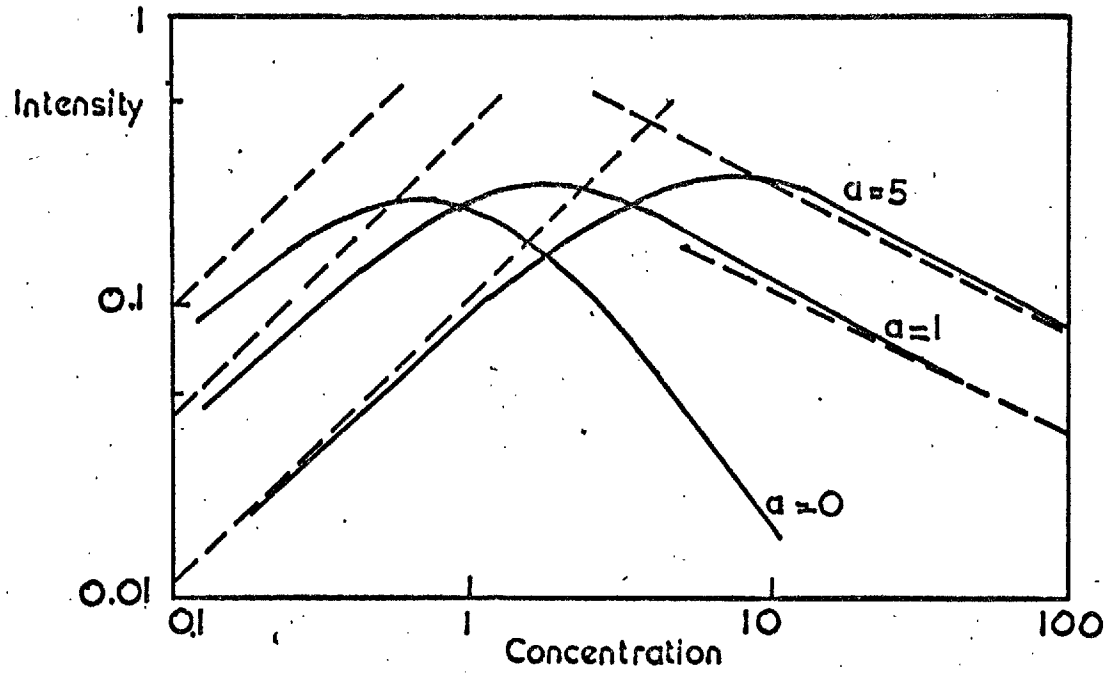
When the half-intensity width of the incident radiation is small compared with the absorption line half-intensity width, the integral function $\int_0^{\infty} I_\nu \left(1 - e^{-k\nu 2L}\right) d\nu$ in equation (6) may be replaced by the expression $I\left(1 - e^{-Q_o 2J}\right)$, where I = Ivdv, being the integrated radiation flux of the incident beam per unit time per unit area. By this substitution and the rearrangement of equation (6), the following expression is obtained

$$E_f / \frac{\partial \omega}{4\pi} \sigma P 2I = \tfrac{1}{2} (\pi)^{-1/2} \frac{1}{J} \frac{1}{L} \left(1 - e^{-Q_o 2J}\right) \int_0^{\infty} \left[1 - e^{-Q_y J\left(1+\frac{1}{L}\right)} - \left(1 - e^{-Q_y J\left(1-\frac{1}{L}\right)}\right)\right] dy \quad \ldots (11)$$

Hence the double logarithmic plot of $E_f / \frac{\partial \omega}{4\pi} \sigma P 2I$ and J (=constant $N_o L$) represents the theoretical analytical atomic fluorescence curve. Some analytical curves for various values of the damping constant, derived from the above

FIGURE 1.3

SOME THEORETICAL ANALYTICAL CURVES FOR A SINGLE SPECTRAL LINE IN THE CASE OF A CONTINUUM SOURCE.



theory for a single spectral line with a narrow line source are shown in Figure 1.4. As with the continuum source, at high atomic concentrations the intensity of the fluorescent radiation is not dependent on the atomic concentration, but in this case tends towards sloping asymptotes.

1.2.3.5 Comparison with experimental curves

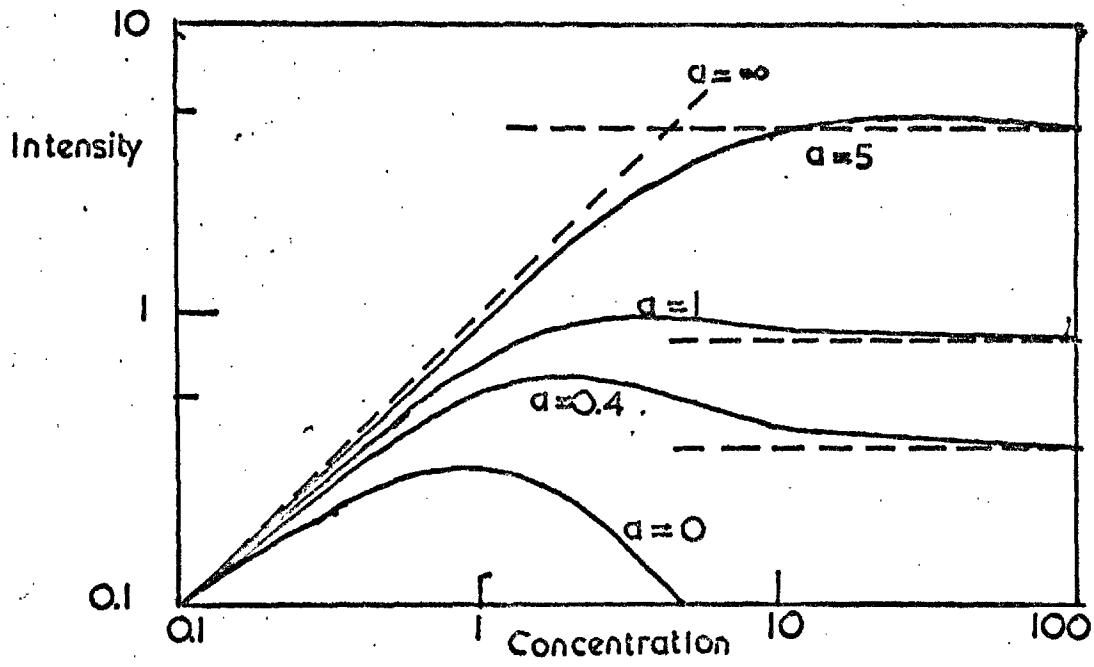
Zeegers and Winefordner (35) have compared theoretical analytical atomic fluorescence curves derived from Hooymayers theory, as outlined above, with experimental analytical curves for the resonance fluorescence of magnesium at 285.2 nm. In the case of a continuum source (xenon arc lamp) the shapes of the theoretical and experimental curves were identical, although the values of $E_f/\frac{\partial\omega}{4\pi} I_o \sigma \Delta\nu_D \left(\frac{\pi}{\ln 2}\right)^{1/2} P$ in the experimental curves are less than those in the theoretical curves. This was attributed to systematic errors in the geometrical factors in the experimental arrangement. Similarly, good correlation between the two sets of curves was also found with a narrow line source (electrodeless discharge lamp).

1.2.3.6 Conclusion

Hooymayers theoretical treatment (34) confirms that, at low concentrations, the intensity of the fluorescent radiation is proportional to the intensity of the incident radiation and the concentration of ground state atoms. However, at high concentrations self-absorption factors and the nature of the incident radiation significantly affect the intensity of the fluorescent radiation. This theoretical treatment provides an adequate explanation of quantitative atomic fluorescence spectroscopy.

FIGURE 1.4

SOME THEORETICAL ANALYTICAL CURVES FOR A SINGLE SPECTRAL LINE IN THE CASE OF A NARROW LINE SOURCE.



CHAPTER 2

REVIEW OF ANALYTICAL ATOMIC FLUORESCENCE SPECTROSCOPY

2.1 INSTRUMENTATION FOR ATOMIC FLUORESCENCE SPECTROSCOPY

2.1.1 General requirements

Nearly all of the reported studies of atomic fluorescence spectroscopy have been carried out using either conversions of existing commercial atomic emission or atomic absorption spectrometers, or home-constructed instrumentation. The lack of a commercially available atomic fluorescence spectrometer is one reason for the surprisingly small number of applications of atomic fluorescence spectroscopy to the analysis of technical materials. This topic is discussed in more detail in Chapter 7.

The instrumental requirements for atomic fluorescence spectroscopy are not as stringent as those for atomic emission and atomic absorption. The normal basic components for an atomic fluorescence spectrometer comprise, an intense spectral source, atom reservoir, lenses and/or mirrors, form of monochromation, detector, amplifier and read-out. The general arrangement of such instrumentation for atomic fluorescence spectroscopy is shown in Figure 2.1. These components are discussed individually in more detail below.

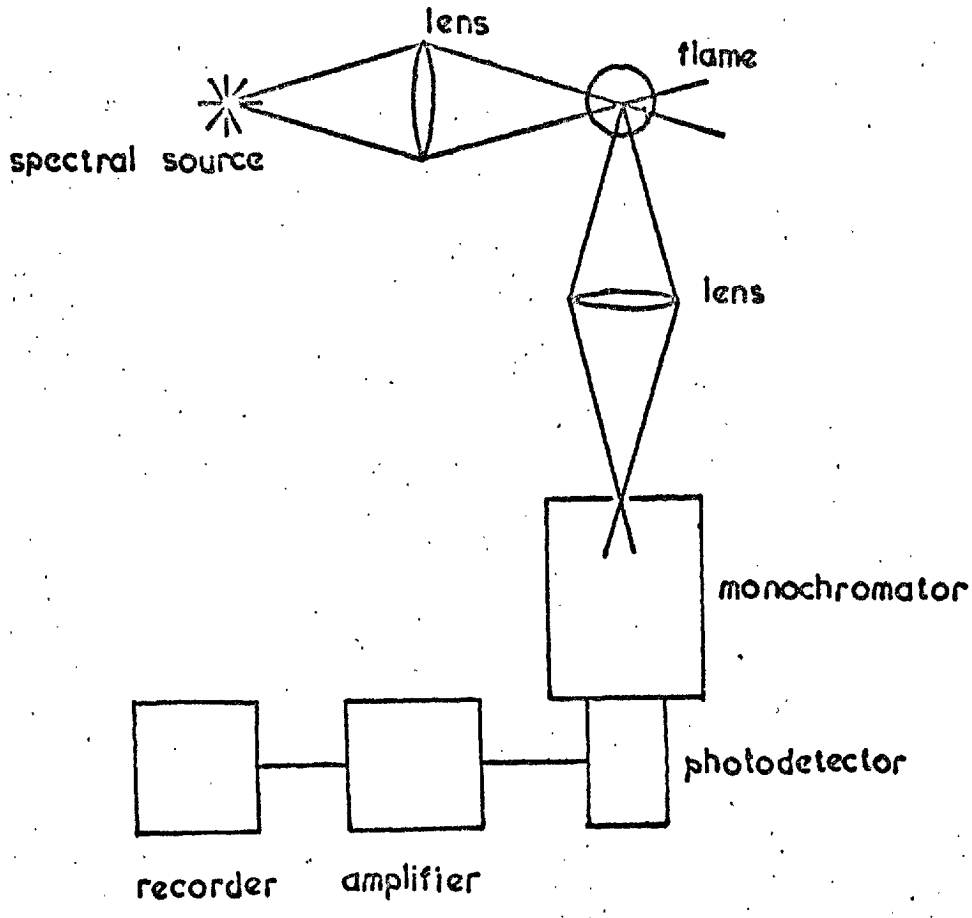
2.1.2 Spectral sources

Since the intensity of the fluorescent radiation produced in atomic fluorescence spectroscopy is proportional to the intensity of the incident radiation, as well as to the concentration of the absorbing atoms present in the atom reservoir, suitable spectral sources should produce the emission of an intense resonance line of the element concerned. Ideal sources should also be free from self-reversal and self-absorption, have the maximum reproducibility and stability, and have the minimum fluctuational noise. The sources should also have a short warm-up time and a long life. They should be available cheaply for a wide range of elements, and should require the minimum amount of material in their construction.

In the first studies of analytical atomic fluorescence spectroscopy, metal vapour discharge lamps, which were the most intense line sources available at that time, were employed as spectral sources (25,29, 36-47). Whilst

FIGURE 2.1

GENERAL ARRANGEMENT OF INSTRUMENTATION FOR ATOMIC FLUORESCENCE SPECTROSCOPY.



these sources have proved adequate for the excitation of the atomic fluorescence of a few elements, they are not readily available for a large number of elements. Ordinary hollow cathode lamps (48-53), being the conventional source for atomic absorption spectroscopy, and demountable water-cooled hollow cathode lamps (54-56) have also been used. More recently, however, much better results have been obtained with high-intensity hollow cathode lamps (57-80) of the types proposed by Sullivan and Walsh (81) and Lowe (82). Microwave-excited electrodeless discharge lamps, operated from a variety of antennae and microwave cavities, have also been extensively used as spectral sources in atomic fluorescence spectroscopy (27,30,39,46,50-53,57,59,61,64,83-119) and these have been prepared for at least fifty-seven elements (120). This application and their use as spectral sources in atomic absorption spectroscopy has lead to considerable interest in improvements in the construction and operation of electrodeless discharge lamps (115,116,121-130). High-intensity hollow cathode lamps and electrodeless discharge lamps now provide the most intense spectral sources available for atomic fluorescence spectroscopy.

Although narrow line sources have normally been used for atomic fluorescence spectroscopy, they are not essential, and 150 watt (26,49,131-133), 450 watt (134-136), 500 watt (137) and 900 watt (138) xenon arc lamp continua have all been employed. However, these sources are not usually as intense as the corresponding line sources.

In addition to the above types of spectral source, a mercury pen light (105,139-141), a radio-frequency plasma (142) and a pulsed laser (143) have also been successfully used to obtain the atomic fluorescence of certain elements.

2.1.3. Atom reservoirs

The limiting factor in the sensitivity of atomic fluorescence spectroscopy is the shot noise produced in the photomultiplier (144). The signal received by the photomultiplier from a flame contains, in addition to

the atomic fluorescence component, other components due to thermal and chemiluminescence emissions from atoms and molecules present in the flame. When the atomic fluorescence component is small, these other components become significant. Therefore, the replacement of the flame by another type of atom reservoir, in which these other components do not occur or are negligible, would be expected to be advantageous for improving the sensitivity of atomic fluorescence spectroscopy. Other major disadvantages in the use of flames as atom reservoirs are, the inefficiency of the atomisation process, requiring comparatively large amounts of sample, and uneven distribution of the atoms throughout the flame.

Despite the above disadvantages, flames are versatile and relatively cheap and convenient to use, and so have been employed as atom reservoirs in the majority of atomic fluorescence studies. Most of the early atomic fluorescence investigations were carried out using hydrogen-based and propane-based flames, with both premixed and total consumption burners (25-27,30,37-39, 41,46,49,55,56,64,67-71,73-77,87-89,91,95-98,100,105,109,110,117,131-133, 139,145). Although the relatively low temperature of these flames prevented the production of large atomic populations, enhanced interferences by refractory materials, and placed a limitation on the variety of elements which could be determined, these disadvantages were countered by their low flame background in comparison with acetylene-based flames. The development of separating burners for use in analytical atomic spectroscopy (106,149-159) has led to the almost exclusive use of inert gas-separated acetylene-based flames in atomic fluorescence spectroscopy (40,63,64,65,66,68,74-76,92-94,102,106-108, 111-113,160).

Several types of non-flame atom reservoir have been used in atomic fluorescence spectroscopy. The Massmann furnace (80), a modification of this involving continuous nebulisation into a platinum furnace (105), the carbon filament atom reservoir (57-61, 79,83) and a platinum wire loop (84,85) have all been employed for the atomic fluorescence determination of

a number of elements. A method for the pulsed atomisation of solid samples has been developed (50-53). A variety of quartz cells have been employed in the atomic fluorescence determination of mercury (40,141,142) and iodine (86), although their use is restricted to those elements. An induction coupled radio frequency plasma torch (161) has also been used to produce an atomic vapour for atomic fluorescence spectroscopy. Several other types of non-flame atom reservoir (162), although of use in atomic absorption spectroscopy, are not readily adaptable for atomic fluorescence work.

2.1.4. Optical arrangement

The purpose of the various optical systems which have been employed in atomic fluorescence spectrometers is to direct the greatest possible amount of the incident radiation on to the atomic population, and the greatest amount of the fluorescent radiation on to the entrance slit of the monochromator.

Silica lenses have been employed extensively for both of these purposes. The advantages of their use in the latter application are obvious. However, in the former case, particularly when an electrodeless discharge lamp is used as the spectral source, more radiation can frequently be directed on to the flame cell by placing the source as close as possible to the flame.

Mirrors have been used (48,72, 75,88) both to obtain a double pass of the incident radiation through the flame, and to reflect additional radiation on to the monochromator. It has been shown (163) that the first of these applications does produce an effective doubling of atomic fluorescence signals, whilst the latter is of little advantage in improving the sensitivity, since the flame noise is increased in proportion with the atomic fluorescence signal. A system using three mirrors, the third surrounding the entrance slit of the monochromator, has also been proposed (164).

The use of an aluminium ellipse, with the spectral source (an electrodeless discharge lamp operated in an A-antenna) and the flame at the

two focal points of the ellipse, enabled a greater amount of incident radiation to be directed on to the flame and has resulted in ten-fold improvements in detection limits (114).

An unsuccessful attempt has also been made to use polarisers between the spectral source and the flame, and the flame and the entrance slits of the monochromator, in order to reduce the scatter of the incident radiation (165). However, it was found that the atomic fluorescence signal was reduced in proportion with the scatter signal.

2.1.5 Monochromation

Since the spectral source is not viewed directly by the detector, and the absorbing atoms themselves act as their own monochromating, or more accurately polychromating, system (a phenomenon which has been made use of in the development of resonance monochromators (166-170)), the use of a narrow band-pass monochromator for atomic fluorescence spectroscopy is not necessary, when used in conjunction with a narrow line source. However, monochromators have normally been used in atomic fluorescence studies, mainly because they were a part of the atomic emission or atomic absorption spectrometer employed, for which they are essential. When monochromators have been employed the band-passes used for atomic fluorescence were frequently far greater than those which would be tolerable in the other two techniques of atomic spectroscopy.

Optical interference filters (44,45,62,63,70,71,103) and some completely non-dispersive systems (43,65,66,171,172) have been used, with excellent results. These systems enable the fluorescent radiation from a large solid angle to be directed on to the detector. When a non-dispersive system was compared with an optical system incorporating a monochromator, using identical instrumentation and operating conditions, a ten-fold increase in atomic fluorescence detection limits was reported (65).

2.1.6 Detectors

Normal photomultiplier tubes are generally used in atomic fluorescence spectrometers. Solar-blind photomultipliers have proved suitable, particularly with non-dispersive and optical filter systems (43-45,62,63,65,66,70,71,103,171,172). Photon counting, which is particularly advantageous for measuring small signals, has been applied to atomic fluorescence spectroscopy (173-175), and presents a viable alternative to the use of conventional photomultipliers, especially when used in conjunction with non-flame atom reservoirs.

2.1.7 Amplification

Both a.c. and d.c. amplification systems have been used in atomic fluorescence spectroscopy instrumentation. The optimum system for use with a flame cell is a.c. with a synchronously modulated spectral source, since this minimises the effects of thermal and chemiluminescence emissions from the flame. The modulation of hollow cathode lamps is simple and facilities for this are available with almost all atomic absorption spectrometers. However, the modulation of other types of spectral source is more difficult, and choppers are frequently used, although various forms of electronic modulation have been used for electrodeless discharge lamps (124,126,129, 130).

With some non-flame atom reservoirs, such as the carbon filament, when the atomic fluorescence signal is transient and the background signal is low, d.c. amplification systems must be used, since a.c. amplification would require modulation at a higher frequency than is at present practicable.

2.1.8 Read-out

Any conventional signal recording devices are suitable, although with non-flame atom reservoirs which produce transient signals, fast response recorders, such as oscillographs, are necessary (59).

2.2 THE ROLE OF ATOMIC FLUORESCENCE SPECTROSCOPY IN ANALYTICAL CHEMISTRY

2.2.1 Introduction

Atomic fluorescence spectroscopy has now been applied to the analytical determination of nearly forty elements. The range of elements which have been determined has been restricted to the metals; the only non-metal for which atomic fluorescence has been observed is iodine (86), and since this occurs at a wavelength well below 200 nm., the instrumentation necessary for the determination is not particularly suitable for operation in routine chemical analysis.

It seems to be most probable that the future role of atomic fluorescence spectroscopy in chemical analysis will be as a complementary technique to the two well-established methods of atomic emission and atomic absorption spectroscopy for trace metal analysis. Therefore, in the following discussion of atomic fluorescence spectroscopy as an analytical technique, it will be compared with these other two methods. The three techniques of atomic emission, atomic absorption and atomic fluorescence have recently been critically compared on a mainly theoretical basis by Winefordner et al (176).

2.2.2 Detection limits

A comparison of the signal strengths obtainable in atomic absorption and atomic fluorescence (177), has shown that with a flame cell and a monochromator the atomic absorption signal may be up to 1000 times greater than the atomic fluorescence signal. However, the detection limits obtainable in all three techniques depend primarily on the signal to noise ratio. Atomic fluorescence detection limits are dependent on a larger number of experimental parameters than are those in the other two methods, and therefore, there is far greater scope for improving atomic fluorescence detection limits. The most influential parameter in atomic fluorescence is the intensity of the spectral source. Other parameters include, the

optimisation of the optical system, the wavelength used for both the incident radiation and the fluorescent radiation, the composition of the flame, the flame gas flow rates, and the type of burner used. A major limitation on the sensitivity obtainable in atomic absorption is the direct viewing of the spectral source by the monochromator. This does not apply in atomic fluorescence. In order to obtain some degree of selectivity in atomic emission a narrow band-pass (ca.0.002 nm. (120)) monochromator must be used, which restricts the amount of radiation, which can be observed. As discussed earlier, this restriction also does not apply to atomic fluorescence. Therefore, it is possible to obtain superior detection limits in atomic fluorescence, particularly if the fluorescent radiation over a large solid angle can be observed.

The best reported detection limits for atomic fluorescence, atomic absorption and atomic emission spectroscopy, obtained using flame cells and monochromation, are given in Table 2.1. It seems probable that in nearly all cases the optimal operating conditions were used, and so this table should give a fairly good comparison between the three techniques. However, it should be borne in mind when considering the data presented in this table, that several alternative definitions of detection limits have been quoted by different groups of workers, and that whilst detection limits for atomic absorption are given here, the sensitivity is usually of more significance in that method.

Thirty-seven of the sixty-nine elements listed in Table 2.1 have been determined by atomic fluorescence spectroscopy. Atomic fluorescence provides the lowest detection limit for thirteen of these elements (viz: antimony, cadmium, copper, germanium, gold, manganese, mercury, nickel, silicon, silver, tellurium, thallium and zinc) and detection limits equal to those obtained by the next best method for three others (viz: bismuth, cobalt and lead).

TABLE 2.1

COMPARATIVE DETECTION LIMITS FOR ATOMIC FLUORESCENCE, ATOMIC ABSORPTION AND ATOMIC EMISSION SPECTROSCOPY.

ELEMENT	ATOMIC FLUORESCENCE				ATOMIC ABSORPTION				ATOMIC EMISSION			
	1	2	3	4	1	2	3	4	1	2	3	4
Aluminium	396.2	SAN	1-1	93	309.3	AN	3-2	186	396.2	AN	5-3	180
Antimony	217.6	PA	5-2	30	217.6	AA	1-1	184	259.8	AO	2+1	181
Arsenic	193.7	HA	1-1	96	193.7	HA	5-2	185	235.0	AO	5+1	181
Barium		---			553.6	AN	1-2	188	553.6	AN	1-3	179
Beryllium	234.9	SAN	3-2	106	234.9	AN	1-3	186	234.9	SAN	1-1	106
Bismuth	306.8	SAA	4-2	107	223.1	AA	4-2	186	306.8	SAA	2-0	151
Boron		---			249.8	AN	2-0	188	249.8	AO	3+1	181
Cadmium	228.8	HA	1-6	118	228.8	AA	6-4	188	326.1	AN	2-0	178
Caesium		---			852.1	PA	2-2	188	852.1	AO	8-3	181
Calcium	422.7	HA	2-2	118	422.7	AN	5-4	188	422.7	AN	1-4	179
Cerium		---			520.0	AN	3+2	188	569.7	AO	1+1	181
Chromium	359.3	SAA	5-3	112	357.9	AA	3-3	186	425.4	AN	5-3	178
Cobalt	240.7	HA	5-3	64	240.7	AA	5-3	184	352.6	SAA	4-2	151
Copper	324.7	HA	1-3	67	324.7	AA	2-3	186	425.4	AN	1-2	178
Dysprosium		---			421.2	AN	3-2	188	404.6	AN	7-2	183
Erbium		---			400.8	AN	5-2	188	400.8	AN	4-2	183
Europium		---			459.4	AN	2-2	188	459.4	AN	6-4	183
Gadolinium		---			368.4	AN	4-0	184	452.2	AO	2-0	181
Gallium	417.2	HA	3-1	96	287.4	AA	7-2	184	417.2	AN	1-2	180
Germanium	265.1	SAN	1-1	94	265.2	AN	2-1	188	265.2	AN	5-1	180
Gold	242.8	HA	5-3	68	242.8	AA	1-2	188	267.6	AN	5-1	178
Hafnium		---			307.3	AN	2-0	188	368.2	AO	8+1	181
Holmium		---			410.4	AN	1-1	184	405.4	AN	2-2	183
Indium	451.1	HA	1-1	118	303.9	AA	5-2	184	451.1	AN	2-3	180

TABLE 2.1 (Continued)

ELEMENT	ATOMIC FLUORESCENCE				ATOMIC ABSORPTION				ATOMIC EMISSION			
	1	2	3	4	1	2	3	4	1	2	3	4
Iodine	---				183.0 SAN	4+1	187		---			
Iridium	254.4 HA	1+2	49		208.9 AA	4-1	188		380.0 AO	1+2	181	
Iron	248.3 HA	8-3	96		248.3 AA	5-3	184		372.0 SAN	3-2	151	
Lanthanum	---				670.8 AA	5-3	184		441.7 AN	1-1	178	
Lead	405.8 HA	1-2	88		283.3 AA	1-2	184		405.8 AN	2-1	178	
Lithium	---				550.1 AN	6-4	186		579.1 AN	3-5	178	
Lutetium	---				336.0 AN	1-0	188		331.2 AO	2-1	181	
Magnesium	285.2 SAA	2-4	65		285.2 AA	1-4	186		285.2 AN	5-3	179	
Manganese	279.5 SAA	1-3	102		279.5 AN	2-3	184		403.1 AN	5-3	178	
Mercury	253.7 HA	2-2	139		253.7 AA	2-1	188		253.7 AO	4+1	181	
Molybdenum	313.3 SAN	5-1	93		313.3 AA	3-2	184		379.8 AO	3-2	181	
Neodymium	---				463.4 AN	2-0	184		488.3 AN	6-2	183	
Nickel	232.0 AA	3-3	69		232.0 AA	5-3	184		341.5 AN	3-2	178	
Niobium	---				334.4 AN	1-0	186		405.9 SAN	6-2	154	
Osmium	---				290.9 AN	1-1	188		442.0 AO	1-2	181	
Palladium	244.8 SAA	3-2	76		247.6 AA	2-2	186		363.5 AN	5-2	178	
Platinum	265.9 HA	5+1	49		265.9 AA	1-1	184		265.9 AN	2-0	178	
Potassium	---				766.5 AA	3-3	188		766.5 AO	3-3	181	
Praseodymium	---				495.1 AN	1+1	184		495.1 AN	1-0	183	
Rhenium	---				346.0 AN	9-1	188		346.0 AN	2-1	178	
Rhodium	369.2 HA	3-0	49		343.5 AA	6-3	188		369.2 SAA	2-1	182	
Rubidium	---				780.0 AA	3-3	188		780.0 AO	2-3	181	
Ruthenium	372.8 HA	1+2	49		349.9 AA	2-1	188		372.8 AO	3-1	181	
Samarium	---				429.7 AN	2-0	184		476.0 AN	2-1	183	
Scandium	390.7 HA	1+1	118		391.2 AN	5-2	188		391.2 AN	3-2	178	

TABLE 2.1 (Continued)

ELEMENT	ATOMIC FLUORESCENCE				ATOMIC ABSORPTION				ATOMIC EMISSION			
	1	2	3	4	1	2	3	4	1	2	3	4
Selenium	204.0	PA	1-1	98	196.0	HA	5-2	185	---			
Silicon	251.6	SAN	7-2	108	251.6	AN	8-2	186	251.6	AO	5-0	181
Silver	328.1	HA	1-4	118	328.1	AA	5-4	184	328.1	AN	2-2	178
Sodium	---				589.0	AA	3-4	188	589.0	AO	1-4	181
Strontium	460.7	HA	3-2	118	460.7	AA	4-3	188	460.7	AN	1-4	179
Tantalum	---				271.5	AN	2-0	186	481.3	AO	2+1	181
Tellurium	214.3	PA	5-2	98	214.3	AA	9-2	186	283.3	AO	2+2	181
Terbium	---				432.7	AN	5-1	188	431.9	AN	4-1	183
Thallium	377.6	HA	8-3	118	276.8	AA	2-2	188	377.6	AN	2-2	180
Thorium	---				371.9	AN	2+2	188	576.1	AO	2+2	181
Thulium	---				371.8	AN	2-2	188	371.8	AN	2-2	183
Tin	303.4	HA	1-1	87	224.6	HA	1-2	185	284.0	AN	3-1	178
Titanium	319.9	SAN	4-0	66	364.3	SAN	3-2	93	399.9	SAN	2-1	93
Tungsten	---				255.1	AN	1-0	188	400.9	SAN	4-1	154
Uranium	---				351.5	AN	3+1	184	351.5	AO	1+1	181
Vanadium	318.4	SAN	7-2	93	318.4	AN	2-2	184	437.9	AN	1-2	178
Ytterbium	---				398.8	AN	4-2	184	398.8	AN	2-3	183
Yttrium	---				407.7	AN	3-1	184	362.1	AN	4-2	183
Zinc	213.9	HA	4-5	118	213.9	HA	2-3	185	213.9	AO	5+1	181
Zirconium	---				360.1	AN	3-1	93	477.2	SAN	1-0	93

Notes

1. Wavelength (nm.).

2. Flame. AN = nitrous oxide - acetylene, SAN = inert gas - separated nitrous oxide - acetylene, AA = air - acetylene, SAA = inert gas - separated air - acetylene, AO = oxy - acetylene, HA = air - hydrogen (or inert gas - entrained air - hydrogen) and PA = air - propane.

3. Detection limit (ppm.) in aqueous solution. (i.e. 3-1 = 3×10^{-1} = 0.3 ppm., 1 - 0 = 1×10^{0} = 1 ppm. and 5 + 1 = 5×10^{1} = 50 ppm.).

4. Reference.

Atomic fluorescence detection limits in a flame cell obtained with a line source and a monochromator, with a continuous source and a monochromator, and with a line source and a non-dispersive system are given in Table 2.2. Absolute detection limits by atomic fluorescence and atomic absorption obtainable with the carbon filament atom reservoir have been given elsewhere (57-61, 79,83).

Thus, although atomic fluorescence detection limits, and also ranges of determination, are comparable with and in some cases very much better than those obtained by atomic emission and atomic absorption, they are not as good as those which were originally, somewhat extravagantly, predicted for the method (24,28).

2.2.3 Selectivity

Atomic fluorescence spectroscopy using a line source and monochromation appears to be as free from interferences due to other species as is atomic absorption. The only additional interference effects which can occur in atomic fluorescence are quenching, which is due to the flame gases rather than to other species present in the sample solution, and the scatter of the incident radiation by small particles in the flame. Quenching is discussed more thoroughly in Chapter 3 and scatter in Chapter 8. Those interferences which have been reported are normally small and may be overcome by the same methods as those which are used in atomic absorption (e.g. solvent extraction, suppressing agents, standard additions etc.). When a continuous source is used spectral interferences may occur as a result of the close proximity of the spectral lines of different elements (137), giving a situation similar to, although not quite as serious as, that found in atomic emission. Little is known of interference effects with non-dispersive systems, although if a.c. amplification and a narrow line source are used, there is little reason to suppose that there would be any increase in interferences over systems employing monochromation.

TABLE 2.2

COMPARATIVE DETECTION LIMITS FOR ATOMIC FLUORESCENCE SPECTROSCOPY WITH A LINE SOURCE, A CONTINUOUS SOURCE, AND A NON-DISPERSIVE SYSTEM

ELEMENT	LINE SOURCE				CONTINUOUS SOURCE				NON-DISPERSIVE				
	1	2	3	4	1	2	3	4	1	2	3	4	
Aluminium	396.2	SAN	1-1	93		---				SAN	4+1	66	
Antimony	217.6	PA	5-2	30	231.1	HA	1+2	131		SAA	4-2	65	
Arsenic	193.7	HA	1-1	96		---				SAA	6-0	65	
Beryllium	234.9	SAN	1-2	106		---				SAN	3-2	66	
Bismuth	306.8	SAA	4-2	107	306.8	HO	2-0	133		SAA	2-1	65	
Cadmium	228.8	HA	1-6	118	228.8	HO	8-2	133		SAA	2-4	65	
Calcium	422.7	HA	2-2	118	422.7	HA	1-1	136		---			
Chromium	359.3	SAA	5-3	112	359.3	AA	3-0	137	F	SAA	2-3	65	
Cobalt	240.7	HA	5-3	64	240.7	HA	5-1	136		SAA	1-3	65	
Copper	324.7	HA	1-3	67	324.7	HA	2-2	135	F	SAA	1-3	65	
Gallium	417.2	HA	3-1	96	417.2	HA	5-0	49		SAA	6-0	65	
Germanium	265.1	SAN	1-1	94		---				SAN	4-1	66	
Gold	242.8	HA	5-3	68	267.6	HO	4-0	133		SAA	5-3	65	
Indium	451.1	HA	1-1	118	410.5	HA	2-0	49		SAA	1-0	65	
Iridium	254.4	SAA	2+2	65	254.4	HA	1+2	49		SAA	4-0	65	
Iron	248.3	HA	8-3	96	248.3	HA	1-0	49		SAA	3-3	65	
Lead	405.8	HA	1-2	88	283.3	HA	3-0	49		SAA	1-0	65	
Magnesium	285.2	SAA	2-4	65	285.2	HA	1-2	136		SAA	2-4	65	
Manganese	279.5	SAA	1-3	102	279.5	HA	2-1	131		SAA	1-2	65	
Mercury	253.7	HA	2-2	139	253.7	HA	1+2	131		SAA	7-2	65	
Molybdenum	313.3	SAN	5-1	93		---				---			
Nickel	232.0	AA	3-3	69	232.0	HA	1-0	135		SAA	2-3	65	

TABLE 2.2 (Continued)

ELEMENT	LINE SOURCE				CONTINUOUS SOURCE				NON-DISPERSIVE			
	1	2	3	4	1	2	3	4	1	2	3	4
Palladium	244.8	SAA	3-2	76	340.5	HA	5+1	49		SAA	1+1	65
Platinum	265.9	HA	5+1	49	265.9	HA	5+2	49		SAA	3-1	65
Rhodium	369.2	HA	3-0	49	369.2	HA	1+2	49		SAA	3+1	65
Ruthenium	372.8	HA	2+2	49	372.8	HA	1+2	49		SAA	8+1	65
Scandium	390.7	HA	1+1	118		---				---		
Selenium	204.0	PA	1-1	98	196.0	HA	1+4	131		SAA	6-0	65
Silicon	251.6	SAN	7-2	108		---				---		
Silver	328.1	HA	1-4	118	328.1	HA	1-3	135	F	SAA	2-4	65
Strontium	460.7	HA	3-2	118		---				---		
Tellurium	214.3	PA	5-2	98	214.3	HA	5+1	131		SAA	3-0	65
Thallium	377.6	HA	8-3	118	377.6	HA	7-2	135		SAA	3-1	65
Tin	303.4	HA	1-1	87	303.4	HA	5-0	131		SAA	3-0	65
Titanium	319.9	SAN	4-0	66		---				SAN	8+1	66
Vanadium	318.4	SAN	7-2	93		---				---		
Zinc	213.9	HA	4-5	118	213.9	HA	3-2	136		SAA	3-4	65

Notes.

1. Wavelength (nm.). F = optical filter.
2. Flame. See notes to Table 2.1. Additionally HO = oxy-drogen.
3. Detection limit (ppm.) in aqueous solution.
4. Reference.

2.2.4 Other considerations

Atomic fluorescence calibration curves are normally linear over several orders of magnitude, which is a considerable improvement on atomic absorption. This is particularly useful since it is possible to alter the range of determination by controlling the intensity of the spectral source.

The relative simplicity and low cost of atomic fluorescence instrumentation, when compared with that necessary for similar determinations by atomic emission and atomic absorption will be appreciated from the discussion earlier in this chapter.

The other main advantage of atomic fluorescence is that it is potentially more suitable for simultaneous multi-element determinations than are atomic emission or atomic absorption. The whole field of multi-element atomic spectroscopy is discussed in more detail in Chapter 8.

CHAPTER 3

THE ATOMIC FLUORESCENCE CHARACTERISTICS AND ANALYTICAL DETERMINATION OF CHROMIUM IN AN ARGON-SEPARATED AIR-ACETYLENE FLAME USING A CHROMIUM CHLORIDE ELECTRODELESS DISCHARGE LAMP

3.1 INTRODUCTION

There are numerous references in the literature to the determination of chromium by atomic absorption spectroscopy, including the analysis of a wide range of technical materials. The majority of these determinations were carried out in air-acetylene flames, although air-hydrogen and nitrous oxide-acetylene flames have also been used. Atomic absorption detection limits appear generally to be of the order of 0.01 ppm.; the best to have been reported being 0.003 ppm. (186) in an air-acetylene flame. Approximately fifteen interferences by other ions have been reported, probably the most serious being that due to iron (189). Although it has been shown that the majority of these interferences may be reduced by the use of a fuel-lean flame (189-191), the sensitivity of the determination is also significantly reduced (192-194). In some cases complexation and solvent extraction or suppressing agents have been used to overcome these interferences.

Chromium is not normally determined by atomic emission spectroscopy, and until the application of narrow band-pass monochromation to atomic emission analysis was reported (195), any determinations of chromium by this method were accompanied by preliminary complexation and solvent extraction procedures (196). Atomic emission detection limits for chromium are also normally of the order of 0.01 ppm.; the best to have been reported being 0.005 ppm. (178) in a nitrous oxide-acetylene flame.

In spite of the above limitations of atomic emission and atomic absorption for the determination of chromium, no full investigation of its atomic fluorescence characteristics and analytical determination has yet been undertaken. However, atomic fluorescence detection limits at 357.9 nm. and 359.3 nm. have been reported by several groups of workers. Cresser and West (137) obtained detection limits of 3 ppm. for the combined fluorescence of the 357.9 nm., 359.3 nm. and 360.5 nm. lines and 20 ppm. for the combined fluorescence of the 425.4 nm., 427.5 nm. and 428.9 nm. lines, using a 500 watt xenon arc lamp continuum and a slightly fuel-rich premixed air-acetylene flame.

These workers (89) also reported detection limits of 20 ppm. with some concentric two-chamber type dual-element electrodeless discharge lamps, containing chromium chloride, and a slightly fuel-rich turbulent oxy-hydrogen flame, at 359.3 nm. Dagnall, Taylor and West (96) obtained a detection limit of 0.05 ppm. at 357.9 nm., using a chromium chloride electrodeless discharge lamp and a premixed air-hydrogen flame. Dinnin (55) reported a detection limit of 100 ppm. at 357.9 nm. with a demountable water-cooled hollow cathode lamp and a turbulent air-hydrogen flame. Manning and Heneage (49) obtained a detection limit of 10 ppm. with a 150 watt xenon arc lamp continuum, and 20 ppm. with a hollow cathode lamp, in an air-hydrogen flame at 357.9 nm. Omnetto and Rossi (56) reported a detection limit of 1 ppm. with a demountable water-cooled hollow cathode lamp and an air-hydrogen flame at 357.9 nm., and (41) 5 ppm. by spectral overlap at 359.3 nm. using a mercury vapour discharge lamp and a turbulent air-hydrogen flame. Zacha et al (118) obtained a detection limit of 10 ppm. with a chromium/chromium iodide electrodeless discharge lamp and a turbulent air-hydrogen flame, at 359.3 nm. It is apparent, however, from the monochromator slit-widths reported to have been used in some of the above studies, that the combined atomic fluorescence of the 357.9 nm., 359.3 nm. and 360.5 nm. lines was observed, rather than that of the particular wavelength specified. Omnetto and Rossi (197) calculated the theoretical relative atomic fluorescence intensities of these three resonance lines. However, when compared with experimental values, obtained using a demountable water-cooled hollow cathode lamp as the spectral source, little correlation was found. This difference was attributed to the occurrence of thermally-assisted processes in addition to resonance fluorescence.

In this chapter the preparation and operation of a chromium chloride electrodeless discharge lamp, and its use in an investigation of the atomic fluorescence characteristics and analytical determination of chromium in an argon-separated air-acetylene flame, is described.

3.2 EXPERIMENTAL

3.2.1 Apparatus

The spectrometer used was a Southern Analytical A1740 grating flame spectrometer. This atomic emission spectrometer had previously been modified to make it more suitable for atomic fluorescence determinations (137,198). The original monochromator, a grating blazed at 500 nm., with a fixed slit-width of 0.1 mm., corresponding to a spectral band-pass of 0.6 nm., had been replaced by a grating blazed at 300 nm. and a Southern Analytical A3000 type variable slit mechanism. This provided a choice of six slit-widths of up to 1 mm., corresponding to nominal spectral band-passes of 0.18, 0.35, 0.6, 1.5, 3 and 6 nm. The EMI 9663B photomultiplier tube, which was most sensitive to the higher wavelengths normally associated with atomic emission spectroscopy, had been replaced by a u.v.-sensitive Hamamatsu type R213 photomultiplier tube. These modifications to the monochromator and detector meant that the automatic background correction facility originally available with this instrument could no longer be used, although the d.c. background correction and integration facilities remained. The integrator gave a choice of 2, 5, 10, 15 and 20 second periods of integration of the photomultiplier signal at a fixed wavelength. The spectrometer was equipped for wavelength scanning at a speed of 75 nm. $min.^{-1}$.

The amplification system of this instrument was d.c., and therefore, any thermal emission signals observed, due to either flame background or atomic emissions, had to be subtracted from the total signal recorded, in order to obtain the atomic fluorescence signal by difference. To facilitate this procedure, and to enable the full scale of the recording potentiometer to be used for the atomic fluorescence signals, the d.c. background correction was employed to minimise the thermal emission signals.

The above limitation on the operation of this instrument for atomic fluorescence determinations made low background flames desirable. Attempts had previously been made to modify the large (ca. 40 mm. diameter) Southern

Analytical burner for use with separated flames, although the best result which could be achieved was a form of inert gas shielding (198), which, however, proved adequate for some subsequent atomic fluorescence studies which had been carried out with this instrument (91,137). This burner was not considered to be suitable for the determination of chromium and similar elements, and therefore, the burner and burner housing were completely removed. A Unicam SP900 air-acetylene burner head and stem were adapted for use with a separated flame, in a similar fashion to that described elsewhere (150), using glass beads and alternate rows of corrugated and plain chrome-nickel strip, to provide a laminar flow of the inert gas. Several unsuccessful attempts were made to use this burner in conjunction with the Southern Analytical nebuliser, but eventually a Unicam SP900 nebuliser unit was also used. This nebuliser is of the cyclone type and so is particularly effective for removing large droplets, so that only a fine homogenous mist reaches the burner. The resultant burner assembly gave excellent results when used with both separated and unseparated air-hydrogen and air-acetylene flames.

The output from the amplifier was fed to a Servoscribe chart recorder, as well as to the recording potentiometer on the spectrometer. The chart recorder was used on the 20 millivolt range and could be operated at six speeds, ranging from 0.5 mm. $min.^{-1}$. to 600 mm. $min.^{-1}$. This was particularly useful for examining the spectra and operating characteristics of electrodeless discharge lamps. However, when integration was used for atomic fluorescence measurements, it was found to be more convenient to note down the readings directly from the recording potentiometer on the instrument.

The electrodeless discharge lamps were operated at 2450 $\pm$25 MHz. with a Microtron 200 microwave generator and a three-quarter wave (Broida type) resonant cavity. A quarter wave (Evenson type) resonant cavity was also available, but this was found to be less suitable for the operation of the electrodeless discharge lamps examined in this work. The discharge of the lamps was initiated using a Tesla high-frequency vacuum tester.

The general arrangement of the instrumental components for atomic fluorescence determinations was illustrated in Figure 2.1. The electrodeless discharge lamp was placed as close as possible to the flame (ca. 35 mm. from the centre of the flame). An asbestos screen with a slit 30 x 15 mm. was placed between the resonant cavity and the flame. It was so arranged that this screen could be moved backwards and forwards to act as a shutter to eliminate the irradiation of the flame by the spectral source. The centre of the flame was situated ca. 50 mm. from the entrance slit of the monochromator.

3.2.2. Preparation of electrodeless discharge lamps

The general procedure for the preparation of electrodeless discharge lamps and the equipment required have been described previously (99,127). The chromium electrodeless discharge lamps used in this work were prepared by the following method. A blank tube ca. 40 mm. long was prepared from 8 mm. internal bore quartz tubing and degassed in the usual manner. Chromium chloride hexahydrate (ca. 1 mg. A.R. grade) was introduced. The tube was reconnected to the vacuum line, evacuated to ca. 0.1 torr, and heated gently for five minutes, flushing several times with argon, to dehydrate the metal chloride. The dehydrated metal chloride was sublimed ca. 20 mm. up the walls of the tube. The tube was then pressurised with argon at 3-4 torr and sealed. The freshly prepared lamps were conditioned in the microwave cavity for ca. 1 hour before use.

3.2.3 Reagents

1000 ppm. chromium stock solution. 5.1233 g. of A.R. grade chromium chloride hexahydrate was dissolved in distilled water and diluted to 1 $dm.^3$. This solution was diluted as required immediately before use.

Diverse ions. Solutions were prepared from A.R. grade metals, salts and acids, and distilled water.

3.3 RESULTS AND DISCUSSION

3.3.1 Operation of electrodeless discharge lamps

The optimal incident power for the operation of the chromium chloride electrodeless discharge lamps was found to be 50 watts. After the initial running-in period the lamps required a warm-up time of ca. 10 minutes when the discharge was initiated from the cold. Under these conditions the lamps were an intense blue in colour and exhibited the main lines of the chromium (I) spectrum. The relative intensities of those lines which had an intensity of greater than 5% of that of the 357.9 nm. and 359.3 nm. lines are listed in Table 3.1. The line to background ratios of the 357.9 nm. and 359.3 nm. lines were greater than 100:1, and the stability of the lamps at these wavelengths was within $\pm$3% over a period of 1 hour.

3.3.2 Atomic fluorescence measurements

The wavelengths at which atomic fluorescence signals were observed when a 10 ppm. solution of chromium was nebulised into the argon-separated air-acetylene flame, and the relative intensities of this fluorescence are given in Table 3.1. The most intense atomic fluorescence observed was the resonance fluorescence at 357.9 nm., 359.3 nm. and 360.5 nm., arising from transitions between the $y^7P^o_4$, $y^7P^o_3$ and $y^7P^o_2$ excited states and the ground state a^7S_3 (199,200). The wavelength at which atomic emission signals were observed when a 10 ppm. solution of chromium was nebulised under the same conditions and the relative intensities of this emission are also given in Table 3.1. The most intense atomic emission was observed at 425.4 nm., 427.5 nm. and 428.9 nm., arising from transitions between the $z^7P^o_4$, $z^7P^o_3$ and $z^7P^o_2$ excited energy states and the ground state (199,200).

By the use of the maximum monochromator slit-width of 1 mm., corresponding to a spectral band-pass of 6 nm., the atomic fluorescence signals observed at 357.9 nm., 359.3 nm. and 360.5 nm. could be combined to give a considerable increase in the total atomic fluorescence signal observed by the photomultiplier. For this purpose the wavelength control of the spectrometer was set at 359 nm.

TABLE 3.1

RELATIVE SOURCE, ATOMIC FLUORESCENCE AND ATOMIC EMISSION INTENSITIES FOR CHROMIUM

WAVELENGTH (nm.).	TRANSITION b	RELATIVE INTENSITY OF SOURCE a	RELATIVE ATOMIC FLUORESCENCE INTENSITY a	RELATIVE ATOMIC EMISSION INTENSITY a
299.88 c	$a^5S_2 - x^5P^o_1$	8	-	-
300.09 c	$a^5D_3 - y^5D^o_2$			
300.51	$a^5D_4 - y^5D^o_3$	19	-	-
302.91 c	$a^5D_2 - x^5P^o_1$	10	-	-
303.02 c	$a^5D_3 - y^5D^o_2$			
303.13 c	$a^5D_1 - y^5F^o_1$			
357.87	$a^7S_3 - y^7P^o_4$	100	100	14
359.35	$a^7S_3 - y^7P^o_3$	100	77	29
360.53	$a^7S_3 - y^7P^o_2$	94	33	27
390.88	$a^5D_3 - z^5D^o_3$	12	-	-
391.92	$a^5D_3 - z^5D^o_4$	7	-	-
396.37	$a^7S_3 - y^5H^o_7$	22	-	0.5
425.43	$a^7S_3 - z^7P^o_4$	62	10	47
427.48	$a^7S_3 - z^7P^o_3$	57	20	81
428.97	$a^7S_3 - z^7P^o_2$	55	18	100
434.45	$a^5D_3 - z^5F^o_4$	20	-	4
435.18	$a^5D_4 - z^5F^o_5$	20	-	3
520.45 c	$a^5S_2 - a^5P^o_3$	44	1.5	7.5
520.60 c	$a^5S_2 - z^5P^o_2$			
520.84 c	$a^5S_2 - z^5P^o_1$			

Notes.

a - The values of relative intensity are uncorrected for detector response and the three scales of relative intensity are not directly comparable with each other.

b - References 199 and 200. The ground state of Cr(I) is a^7S_3.

c - Lines unresolved by the monochromator.

3.3.3 Choice of flame

Atomic fluorescence detection limits at 359 nm. with an air-hydrogen and an air-acetylene flame, both argon-separated and unseparated, are given in Table 3.2. The lowest detection limit was obtained in the argon-separated air-acetylene flame.

Argon was chosen as the separating gas in preference to nitrogen, since it was found that the atomic fluorescence signals were considerably reduced when nitrogen was used. The effect of these two separating gases on the atomic fluorescence signals of a number of elements including chromium is shown in Table 3.3. This shows that in most cases the atomic fluorescence signal is approximately halved when nitrogen is used, compared with the argon-separated flame. In some cases the actual signal may be smaller with the nitrogen-separated flame than with the unseparated flame, although at the same time the detection limit is improved by separation, due to the tremendous reduction in the flame background. These observations may be attributed to the greater quenching and cooling effects of nitrogen. The large diatomic nitrogen molecules, with their large quenching cross-section, are likely to have considerably more collisions with, and hence deactivate, more excited chromium atoms, than are the smaller monatomic argon molecules. The higher thermal capacity and higher conductivity of nitrogen lower the temperature, and hence the efficiency, of the flame. This latter effect is of more significance in atomic emission spectroscopy than in atomic fluorescence or atomic absorption. The only advantage to be found in the use of nitrogen as a separating gas for atomic fluorescence spectroscopy is that it is only about one tenth of the cost of argon.

A slightly fuel-lean flame was used, and the optimal gas flow rates were found to be 1.1 $dm.^3 min.^{-1}$ acetylene, 7 $dm.^3 min.^{-1}$ air and 10 $dm.^3 min.^{-1}$ argon. The atomic fluorescence signals were slightly greater, although not significantly so, in a more fuel-rich flame, but it was found that interferences from other ions were also greater. This is similar to the situation

TABLE 3.2

ATOMIC FLUORESCENCE DETECTION LIMITS FOR CHROMIUM AT 359 NM. IN A VARIETY OF ANALYTICALLY USEFUL FLAMES.

FLAME	DETECTION LIMIT (ppm.)
Air-hydrogen	0.5
Argon-separated air-hydrogen	0.1
Air-acetylene	0.05
Argon-separated air-acetylene	0.005

TABLE 3.3

COMPARISON OF ATOMIC FLUORESCENCE SIGNALS IN ARGON-SEPARATED AND NITROGEN-SEPARATED AIR-ACETYLENE FLAMES

ELEMENT	WAVELENGTH nm.	ARGON-SEPARATED FLAME (arbitrarily 100)	NITROGEN-SEPARATED FLAME
Chromium	359	100	51
Cobalt	240.7	100	46
Iron	248.3	100	58
Manganese	279.8	100	70
Mercury	253.7	100	67
Silver	328.0	100	50
Zinc	213.8	100	35

reported for the atomic absorption determination of chromium (189,191), although in atomic absorption the reduction in signal in the fuel-lean flame appeared to be more significant (192-194) than was experienced in atomic fluorescence. This is partly because in atomic fluorescence, any reduction in the number of chromium atoms produced in the flame caused by altering the stoichiometry of the flame, is also accompanied by a considerable decrease in the flame background, which enables higher instrumental gains to be used.

The optimal flame height for atomic fluorescence measurements was between 15 and 35 mm. above the burner head.

3.3.4 Detection limits and calibration data

A comparison of atomic fluorescence and atomic emission detection limits at the main wavelengths for chromium, the three lines near 359 nm., the three lines near 427 nm., and the three lines at 520 nm., in the argon-separated air-acetylene flame is given in Table 3.4. Due to the use of integration the detection limit was defined as the concentration of chromium in aqueous solution which produced a signal equivalent to twice the standard deviation in signal near the lower limit of the calibration curve. The best atomic fluorescence detection limit was 0.005 ppm. at 359 nm. and the best atomic emission detection limit was 0.02 ppm. at 427 nm.

A calibration curve for the atomic fluorescence determination of chromium under the optimal conditions established is given in Figure 3.1. This shows a linear working range of over three orders of magnitude.

3.3.5 Interference

The effect on the atomic fluorescence signal produced at 359 nm. by a 2 ppm. solution of chromium of a 250-fold weight excess of thirty-eight elements (viz: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cu, F, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, S, Sb, Si, Sn, Sr, Ta, Ti, Tl, V, W, Zn and Zr) was investigated in a fuel-lean flame. The only significant interference (i.e. greater than twice the standard deviation in signal at this concentration) were due to cerium (+6%), silicon (+5%) and titanium (+4%).

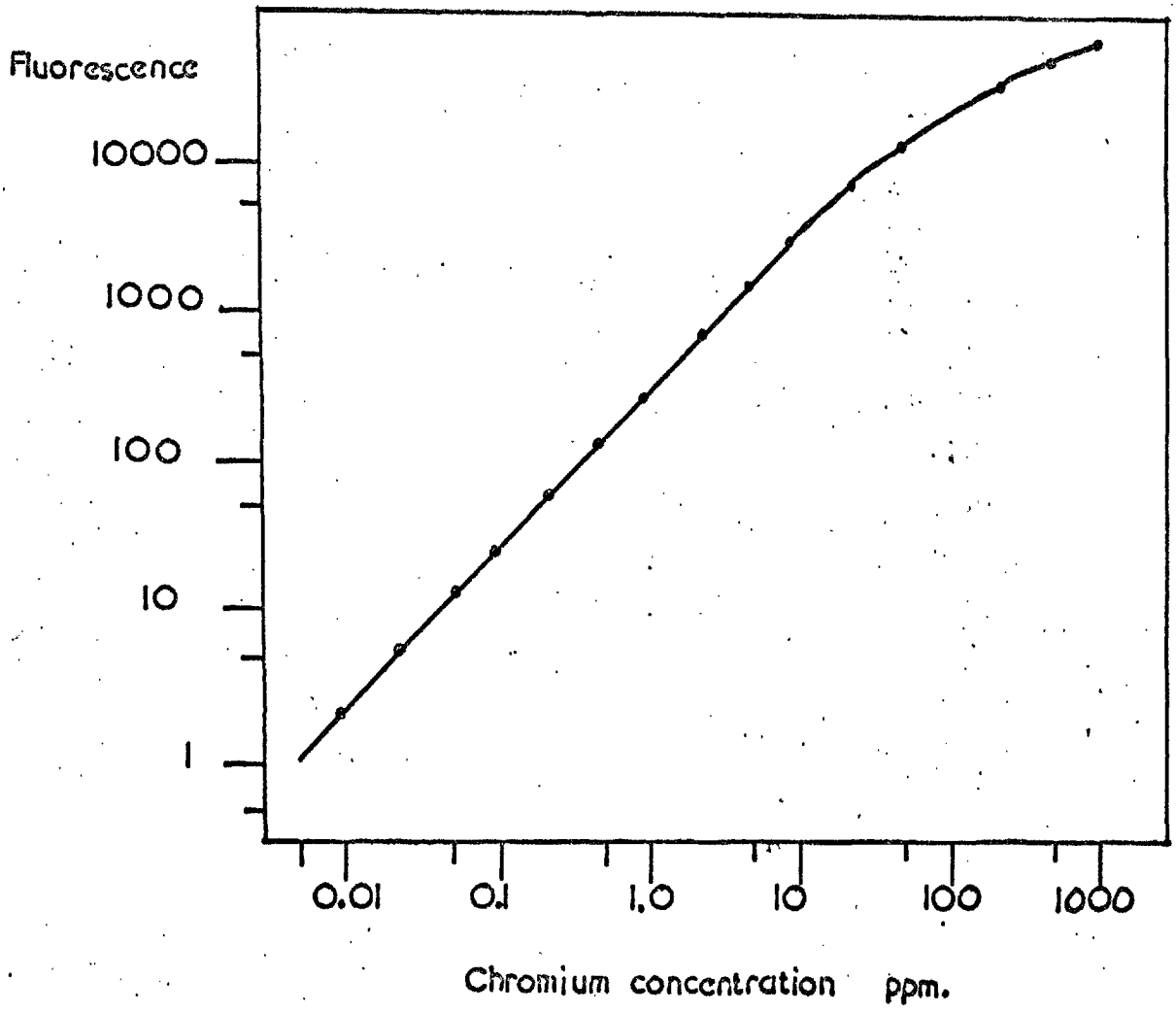
TABLE 3.4

ATOMIC FLUORESCENCE AND ATOMIC EMISSION DETECTION LIMITS FOR CHROMIUM IN AN ARGON-SEPARATED AIR-ACETYLENE FLAME

WAVELENGTH (nm.).	ATOMIC FLUORESCENCE DETECTION LIMIT (ppm.).	ATOMIC EMISSION DETECTION LIMIT (ppm.).
357.9 359.3 360.5	0.005	0.1
425.4 427.5 428.9	0.1	0.02
520.4 520.6 520.8	2.0	0.2

FIGURE 3.1

ATOMIC FLUORESCENCE CALIBRATION CURVE FOR CHROMIUM AT 359 NM



These interferences may all be attributed to the refractory nature of these elements, and none of them are particularly serious.

The effect of the same excess of eighteen of the above elements on the atomic fluorescence signal produced by a 2 ppm. solution of chromium in a fuel-rich argon-separated air-acetylene flame was also examined. The following interferences were observed, Ce (+20%), Mo (+15%), V, Si (+10%), Be (+6%), Hg (+5%), Mg, Li (-4%), Bi (-6%), Ag, As, Au, K, P, Pb, S, Sb and Zn no interference.

A brief investigation of the effect of the same excesses of some of the elements considered above on the atomic emission of chromium showed that the majority of these elements interfered, in both a fuel-rich and a fuel-lean flame, at both 359.3 nm. and 427.5 nm., even when a narrower monochromator slit-width, corresponding to a spectral band-pass of 0.6 nm., was used.

3.4 CONCLUSION

The detection limit obtained for the atomic fluorescence determination of chromium compares favourably with those reported in the literature for atomic absorption and atomic emission. As in the case of atomic absorption spectroscopy (189-191), interferences are reduced by the use of a fuel-lean flame, but in atomic fluorescence this is not accompanied by such a significant loss in sensitivity. Unless an extremely narrow monochromator slit-width were used, atomic fluorescence appears to be far freer from interferences than is atomic emission for the determination of chromium.

Since the work described above was completed, atomic fluorescence detection limits for chromium of 0.0015 ppm. (65) and 0.002 ppm. (201) have been reported using inert gas-separated air-acetylene flames, high-intensity hollow cathode lamps and atomic fluorescence spectrometers incorporating filters. These results confirm the observations made in the above work that chromium atomic fluorescence signals are enhanced by the use of a wide spectral band-pass, enabling the observation of the atomic fluorescence of the 357.9 nm.,

359.3 nm. and 360.5 nm. lines. The close proximity of these three resonance lines greatly enhances the potential of atomic fluorescence for the determination of chromium, when compared with atomic emission and atomic absorption, particularly with non-dispersive systems.

CHAPTER 4

SOME ANALYTICAL APPLICATIONS OF THE SPECTRAL OVERLAP OF THE NEON 359.352 NM. AND THE CHROMIUM 359.349 NM. SPECTRAL LINES IN ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE SPECTROSCOPY

4.1 INTRODUCTION

The overlap of the spectral lines of several pairs of elements has been observed in both atomic absorption (202-206) and atomic fluorescence (41,83,100,104, 106). In atomic absorption an emission line of an element emitted by the spectral source overlaps sufficiently with an absorption line of a second element present in the flame, so that the atomic population of the second element absorbs some of the incident radiation. In atomic fluorescence this absorption of radiation induces the atomic fluorescence of the element in the flame. Although this phenomenon occurs as a spectral interference in atomic absorption, it may be used to advantage in atomic fluorescence, since the atomic fluorescence produced need not necessarily be resonance fluorescence.

Spectral overlap occurs because atomic emission and absorption lines become broadened. The factors affecting the broadening of atomic spectral lines in flames have been discussed by Winefordner et al (207), who calculated the theoretical half-intensity widths of the main emission and absorption lines of sixty elements. The broadening of the spectral lines emitted by electrodeless discharge lamps has been discussed by Cooke (123), although self-reversal and self-absorption make the calculation of half-intensity widths impractical. However, it may be concluded from the theoretical values obtained in the above work, that spectral overlap could occur with pairs of spectral lines nominally less than 0.010 nm. apart.

The first reported use of spectral overlap in atomic fluorescence spectroscopy was the determination of bismuth using an iodine electrodeless discharge lamp (100,106). The iodine 206.163 nm. non-resonance line overlaps with the bismuth 206.170 nm. absorption line, to stimulate the direct-line atomic fluorescence of bismuth at 302.464 nm. An atomic fluorescence detection limit of 0.09 ppm. was reported at this wavelength with an iodine lamp, compared with 0.04 ppm. for the direct-line atomic fluorescence of bismuth at 306.772 nm., after excitation with a bismuth electrodeless discharge lamp (106).

Corresponding atomic absorption detection limits were 10 ppm. at 206.2 nm. with the iodine source, and 1 ppm. at 223.1 nm. with the bismuth source (100).

Similarly, an arsenic electrodeless discharge lamp has been used to stimulate the atomic fluorescence of cadmium (83,104). The arsenic 228.812 nm. resonance line overlaps with the cadmium 228.802 nm. resonance line, resulting in the resonance atomic fluorescence of cadmium at 228.802 nm. (83,104), and the atomic phosphorescence of cadmium at 326.106 nm. (83). Detection limits by atomic fluorescence of 10 ppm. with the arsenic source and 0.0017 ppm. with a cadmium electrodeless discharge lamp, and by atomic absorption of 45 ppm. with the arsenic source and 0.3 ppm. with the cadmium source, were obtained at 228.8 nm. (104).

Mercury and cadmium metal vapour discharge lamps have been used to excite the atomic fluorescence of some other elements (viz: chromium, iron, magnesium, palladium and thallium). However, it is not certain how much of this atomic fluorescence occurs as a result of spectral overlap and how much is induced by the continua of the lamps.

Spectral overlap has been reported as an interference in atomic absorption for several pairs of elements (e.g. europium and copper (202), platinum and iron (202), vanadium and aluminium (202), vanadium and silicon (202), cobalt and mercury (203), gallium and manganese (204) and antimony and lead (205)).

The spectral overlap of the neon 359.352 nm. and the chromium 359.349 nm. spectral lines has also been reported (206), although this is not a spectral interference in the same sense as the examples given above. Neon is frequently used as the fill gas in hollow cathode lamps, and a calibration curve was obtained between 10 and 300 ppm. for the atomic absorption of chromium, using a neon-filled aluminium hollow cathode lamp (206). Omnetto and Rossi (197) attempted to stimulate the atomic fluorescence of chromium using a neon-filled hollow cathode lamp, but the intensity of the neon 359.352 nm. line was not sufficient for this.

In this chapter the construction and operation of a neon electrodeless discharge lamp, and its use as a spectral source for the atomic absorption and atomic fluorescence determination of chromium, is described. Neon-filled chromium chloride electrodeless discharge lamps are also examined as potential sources for the atomic fluorescence determination of chromium.

4.2 EXPERIMENTAL

4.2.1 Apparatus

Atomic fluorescence spectroscopy. The instrumentation and its application to atomic fluorescence determinations, and the optimal operating parameters for the determination of chromium, were described in Chapter 3.

Atomic absorption spectroscopy. Measurements were made using a Techtron AA4 atomic absorption spectrometer. An unseparated air-acetylene flame, with an acetylene flow rate of 1.0 $dm.^3 min.^{-1}$ and an air flow rate of 8 $dm.^3 min.^{-1}$, was burnt on a 100 mm. long path burner. The part of the flame viewed by the monochromator was 4-8 mm. above the burner head. The electrodeless discharge lamps were modulated in phase with the spectrometer amplifier at 285 Hz., using a Microtron 200 modulator unit. A monochromator slit-width of 0.1 mm., corresponding to a spectral band-pass of 0.3 nm. was used.

4.2.2 Reagents

The chromium solutions were freshly prepared from a stock solution, as described in Chapter 3.

4.2.3 Construction of electrodeless discharge lamps

The equipment and general procedure adopted have been described previously (99,127). The lamps used in this work were prepared in the following way.

Neon electrodeless discharge lamps. A blank tube ca.40 mm. long was prepared from 8 mm. nominal internal bore quartz tubing, in the usual manner. The blank tube was connected to the vacuum line and evacuated. It was flushed

with neon (ordinary grade) and reevacuated, several times. The tube was heated under vacuum to red heat for 3-4 minutes, and flushed several times with neon to remove any occluded gases. The tube was cooled to room temperature, pressurised with neon at the required pressure, and sealed. Freshly prepared lamps were conditioned in the microwave cavity for ca. 20 minutes before use.

Neon-filled chromium chloride electrodeless discharge lamps. These lamps were prepared in the same fashion and at the same fill gas pressure as the argon-filled chromium chloride lamps described in Chapter 3, except that neon was used in place of argon.

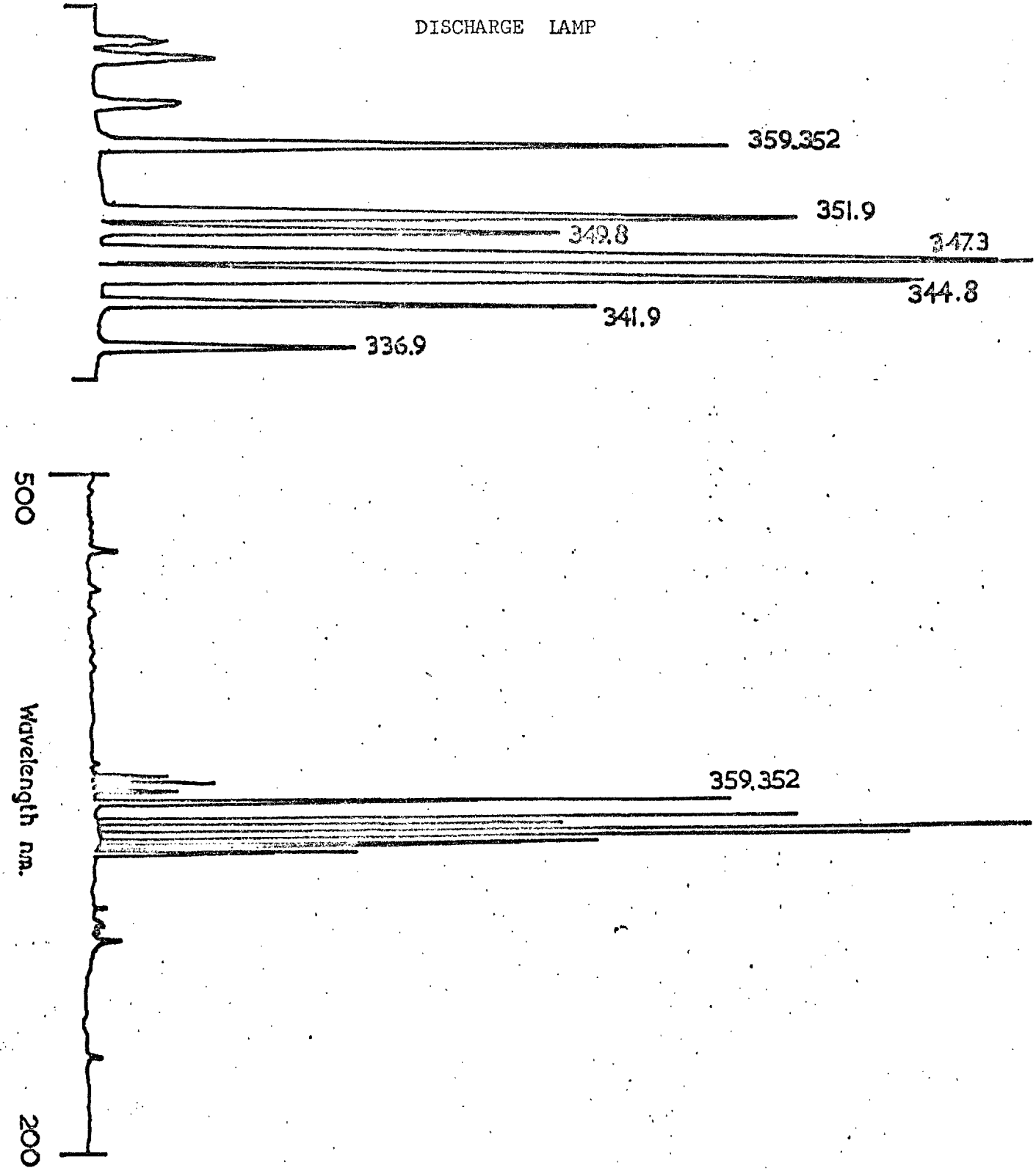
4.3 RESULTS AND DISCUSSION

4.3.1 Spectrum of neon electrodeless discharge lamps

The neon electrodeless discharge lamps were an intense red in colour; a colour similar to that which is characteristic of neon-filled hollow cathode lamps. The spectrum of a neon electrodeless discharge lamp, between 200 nm. and 500 nm., is shown in Figure 4.1. All of the most intense emission lines in this part of the spectrum, including that at 359.352 nm., are identifiable as those of the neon (1) spectrum (208), although it is probable that some of the less intense lines observed may be attributable to the neon (II)-(V) spectra, or to the spectra of impurities present in the ordinary grade neon gas. The most intense neon emission lines appeared above 550 nm., and these accounted for the predominant red colour in the discharge. However, the wavelengths of these lines are too high for them to be of use in the excitation of atomic fluorescence. These lines at higher wavelengths are more intense since these are resonance lines, whereas those in the 330 nm. to 370 nm. wavelength range are non-resonance lines (e.g. the 359.352 nm. line is attributable to the transition between the $4p'(\frac{1}{2})_1$ excited energy state and the $3s'(\frac{1}{2})_1$ excited energy state, whilst the ground state for neon is $2p^6 {}^1S_o$ (201)).

FIGURE 4.1

EMISSION SPECTRUM BETWEEN 200 AND 500 NM FOR A NEON ELECTRODELESS DISCHARGE LAMP



4.3.2 Operation of electrodeless discharge lamps

Incident power and emission intensity plots for neon electrodeless discharge lamps pressurised at 1, 5 and 10 torr, at 359.352 nm., are given in Figure 4.2. The lamps containing 5 torr of neon were slightly more intense than those prepared at the other pressure. It is apparent, from these plots, that at powers above ca. 30 watts the emission intensity ceases to increase significantly with the incident power. Therefore, in order not to overrun the lamps, they were normally operated at 25-30 watts incident power.

When operated at this power the electrodeless discharge lamps required virtually no warming-up time, and exhibited the maximum emission intensity immediately upon initiation of the discharge. The stability of these lamps at 359.352 nm. over a period of 1 hour was within $\pm$1.5%. The line to background ratio at this wavelength was greater than 100:1. The lamps appear to have a reasonably long life-time, being as bright after over 100 hours operation as when first prepared.

4.3.3 Atomic fluorescence determination of chromium

Atomic fluorescence measurements were made in an argon-separated air-acetylene flame, using the optimal operating parameters previously established for chromium (Chapter 3). An incident power and atomic fluorescence plot obtained with a neon electrodeless discharge lamp pressurised at 5 torr, whilst nebulising a 20 ppm. solution of chromium is given in Figure 4.3, together with the comparative incident power and source intensity plot. At powers above ca. 30 watts the atomic fluorescence signal decreases as the incident power increases.

A detection limit of 2.5 ppm. was obtained for chromium atomic fluorescence at 359 nm., using a monochromator band-pass of 6 nm. Due to the use of integration the detection limit was defined as the concentration of chromium in aqueous solution which produced a signal equivalent to twice the standard deviation in signal near the lower limit of the calibration curve. The calibration

FIGURE . 4.2

POWER AND INTENSITY PLOTS FOR SOME NEON ELECTRODELESS DISCHARGE LAMPS

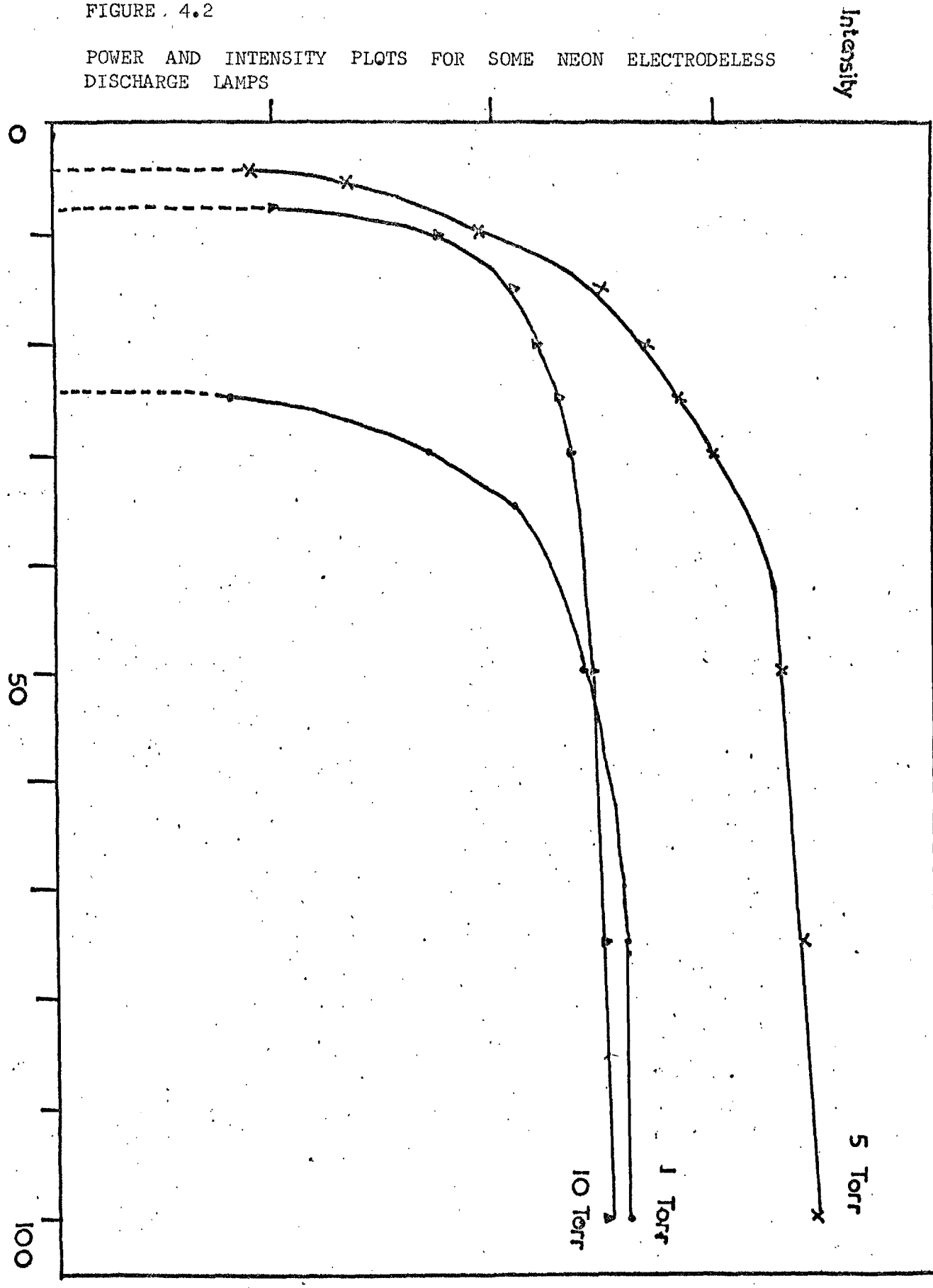
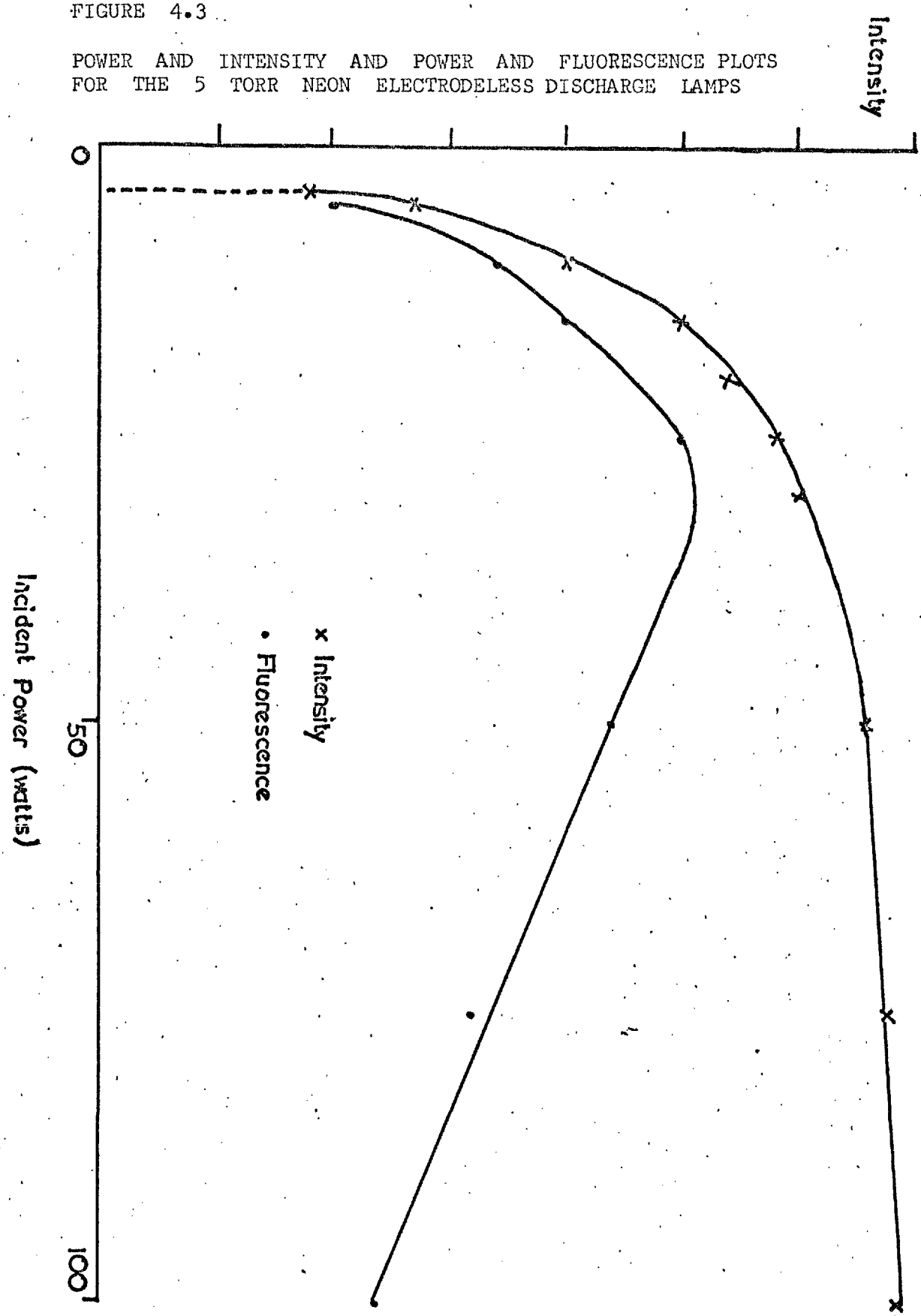


FIGURE 4.3

POWER AND INTENSITY AND POWER AND FLUORESCENCE PLOTS FOR THE 5 TORR NEON ELECTRODELESS DISCHARGE LAMPS



curve was linear up to ca. 50 ppm. and passed through the origin. Above 50 ppm. it curved towards the concentration axis. This compares with a detection limit of 0.005 ppm. and a linear calibration curve up to 50 ppm. obtained with an argon-filled chromium chloride electrodeless discharge lamp (112, Chapter 3).

The atomic fluorescence detection limit obtained with the neon electrodeless discharge lamp would be expected to be much worse than that obtained with the chromium chloride lamp, since in addition to the reduction in sensitivity due to the use of spectral overlap, only the atomic fluorescence at 359.3 nm. is stimulated, whilst with the chromium chloride lamp that at 357.9 nm. and 360.5 nm. is also stimulated.

4.3.4 Atomic absorption determination of chromium

For atomic absorption measurements the electrodeless discharge lamps were modulated at 285 Hz. Under these conditions the lamps had to be operated at 35-40 watts incident power, since below these powers they went out, unless a low percentage modulation was used. A detection limit of 0.1 ppm. was obtained in the air-acetylene flame. In this case the detection limit was defined as the concentration of chromium in aqueous solution which produced a signal equivalent to twice the noise near the lower limit of the calibration curve. The calibration curve was slightly curved towards the concentration axis, and passed through the origin. This is comparable with a detection limit of 0.003 ppm. obtained with a chromium hollow cathode lamp in an air-acetylene flame (186).

4.3.5 Atomic fluorescence determination of chromium with a neon-filled chromium chloride electrodeless discharge lamp.

The optimal incident power for these lamps was found to be 50 watts. They required a warm-up time of ca. 10 minutes on initiation of the discharge from the cold, after which they displayed the main spectral lines of chromium, the most intense being 357.9 nm., 359.3 nm. and 360.5 nm. These lamps were as intense as the corresponding argon-filled lamps. An atomic fluorescence detection limit of 0.005 ppm. was obtained with a neon-filled chromium chloride lamp, which is the same as that previously obtained with an argon-filled lamp (112, Chapter 3).

4.4 CONCLUSION

A neon electrodeless discharge lamp may be used as the spectral source for the atomic fluorescence and atomic absorption determination of chromium. As would be expected, the detection limits are ca. 100 fold poorer than with chromium sources. However, neon sources could be useful for chromium determinations when chromium is present in samples at reasonable concentrations. Neon-filled chromium lamps showed no advantages when compared with argon-filled chromium lamps.

CHAPTER 5

THE ATOMIC FLUORESCENCE DETERMINATION OF ANTIMONY IN COPPER-BASE ALLOYS USING AN ARGON-HYDROGEN DIFFUSION FLAME AND AN ELECTRODELESS DISCHARGE LAMP.

5.1 INTRODUCTION

As shown in Table 2.1, antimony is one of those elements with better reported detection limits by atomic fluorescence than by atomic absorption or atomic emission. Dagnall, Thompson and West (30) first excited the atomic fluorescence of antimony, obtaining a detection limit of 0.05 ppm at 217.6 nm in an air-propane flame with an electrodeless discharge lamp. Several other groups of workers have also reported detection limits for the atomic fluorescence determination of antimony, using a variety of flames and spectral sources (65,89,104,118,129). Recently, Kolihova and Sychra (209) have examined the atomic fluorescence of antimony in various premixed flames, and obtained a detection limit of 0.03 ppm in an argon-hydrogen diffusion flame at 217.6 nm with a high-intensity hollow cathode lamp.

Although both argon-hydrogen and nitrogen-hydrogen diffusion flames provide good detection limits for the analysis of several elements by atomic spectroscopy, interference effects would be expected to be significant due to the low temperature (ca. 300^{o}C) of these flames. A recent publication (210) has reported the effects of interferences by other species on the atomic absorption determination of tin in an argon-hydrogen diffusion flame. Most of the nineteen elements examined caused enhancements of the tin absorption. This was attributed to the transfer of heat from particles of these metals to the tin, increasing the rate of volatilisation of the tin, and to absorption by non-atomised particles. However, it is probable that these flames may well be of use for the determination of technical materials, provided that the sample matrix is not too variable.

The atomic absorption determination of antimony in metallurgical products frequently involves a solvent extraction procedure (211,212). This should provide a relatively constant sample matrix. This chapter describes the application of such a solvent extraction procedure to the determination of

antimony in copper-base alloys by atomic fluorescence spectroscopy, using an argon-hydrogen diffusion flame and an electrodeless discharge lamp.

5.2 EXPERIMENTAL

5.2.1 Apparatus

The Southern Analytical A1740 grating flame spectrometer and ancillary equipment, as described in Chapter 3, were used to obtain the atomic fluorescence measurements. The preparation and operation of antimony electrodeless discharge lamps has been described previously (30). The argon-hydrogen diffusion flame was burnt on the Unicam SP900 air-acetylene burner head, although these flames are probably best supported on a piece of ca. 10 mm diameter quartz tubing. A flow rate of 2 dm^3 min^{-1} hydrogen and 8 dm^3 min^{-1} argon was used. The part of the flame viewed by the monochromator was between 20 mm and 40 mm above the burner head.

5.2.2 Reagents

100 ppm antimony stock solution. 0.2668 g of A.R. grade potassium antimony tartrate were dissolved in distilled water and diluted to 1 dm^3. This solution was diluted as required immediately before use.

5% sodium nitrite solution. 5 g of sodium nitrite were dissolved in distilled water and diluted to 100 dm^3.

Iso-butyl acetate.

Hydrochloric acid and nitric acid. A.R. grade.

5.2.3 Procedure for calibration curve

10 cm^3 of the 100 ppm antimony stock solution were transferred to a 100 cm^3 volumetric flask and diluted to volume with distilled water. 0, 1, 2, 5 and 10 cm^3 aliquots of this solution were transferred to a series of 100 cm^3 volumetric flasks, 60 cm^3 of A.R. grade hydrochloric acid were added to each flask, and the solutions diluted to volume with distilled water. 20 cm^3 aliquots of each solution were transferred to a series of 100 cm^3 separating funnels. 0.5 cm^3 of the 5% sodium nitrite solution were added and the separating funnels shaken vigorously for 1 minute to oxidise the Sb (III)

to $SbCl_6^-$. 5 cm^3 of iso-butyl acetate were added and the separating funnels shaken vigorously for 2 minutes to extract the $SbCl_6^-$. The aqueous layers were discarded and the organic layers nebulised into the argon-hydrogen diffusion flame. Atomic fluorescence signals were obtained for each solution using 10 second integration, and these results were plotted against the antimony concentration to obtain a calibration curve between 0.1 and 1 ppm.

5.2.4 Procedure for the analysis of copper-base alloys

0.1-0.2 g of the copper-base alloy was weighed into a 100 cm^3 beaker. 6 cm^3 of A.R. grade hydrochloric acid and 2 cm^3 of A.R. grade nitric acid were added. The beaker was covered with a watch glass and heated gently to dissolve the copper-base alloy. When the copper-base alloy was completely dissolved, the solution was evaporated to a volume of 2-3 cm^3 to remove the nitric acid. The solution was transferred to a 100 cm^3 volumetric flask and diluted to volume. A 10 cm^3 aliquot of this solution was pipetted into a 100 cm^3 volumetric flask. 60 cm^3 of A.R. grade hydrochloric acid were added, and the solution diluted to volume with distilled water. A 20 cm^3 aliquot of this solution was transferred to a 100 cm^3 separating funnel. 0.5 cm^3 of 5% sodium nitrite solution were added and the separating funnel shaken vigorously for 1 minute. 5 cm^3 of iso-butyl acetate were added and the separating funnel shaken vigorously for 2 minutes. The aqueous layer was discarded and the organic layer nebulised into the argon-hydrogen diffusion flame. The atomic fluorescence signal obtained was compared with those obtained with the standard solutions.

5.3 RESULTS AND DISCUSSION

5.3.1 Calibration curve

The atomic fluorescence calibration curve for antimony in iso-butyl acetate, for concentrations between 0.1 and 1 ppm in the aqueous solution before solvent extraction, was linear and passed through the origin.

5.3.2 Interference and matrix effects

The effects of the matrix element, copper, and the other major constituents in the copper-base alloys on the atomic fluorescence determination of antimony was investigated. The effects of a 1000-fold (weight) excess of copper and 100-fold (weight) excesses of arsenic, bismuth, iron, lead, nickel, tin and zinc, on the atomic fluorescence signal produced by an 0.5 ppm solution of antimony were examined. No interference (i.e. less than $\pm$5% deviation in signal) was observed with any of these elements.

Yanagisawa et al (211) found that of the elements investigated above, arsenic, iron and tins were the only ones which were either completely or partially extracted into iso-butyl acetate with the antimony. Therefore, these are the only elements from which an interference in the flame could be expected. Since these elements are relatively easily atomised in argon-hydrogen diffusion flames, the lack of interferences is not unexpected.

5.3.3 Analysis of copper-base alloys

The results obtained for the determination of antimony in three copper-base alloys from the B.C.S. range (Bureau of Analysed Samples Ltd., Middlesborough) are given in Table 5.1, together with the certificate values. Two samples of each alloy were weighed, dissolved and extracted, and three atomic fluorescence readings were taken for each solution and averaged to obtain these results. The standard deviations for these analyses are also given in Table 5.1.

5.4 CONCLUSION

The above results demonstrate that the use of an argon-hydrogen diffusion flame, together with a solvent extraction procedure is a practical method for the determination of antimony in copper-base alloys by atomic fluorescence spectroscopy.

TABLE 5.1

ATOMIC FLUORESCENCE DETERMINATION OF ANTIMONY IN COPPER-BASE ALLOYS

SAMPLE		CERTIFICATE VALUE (%)	ATOMIC FLUORESCENCE	% STANDARD DEVIATION
B.C.S. 183/3	Leaded gunmetal	0.25	0.26	2.8
B.C.S. 207/1	Bronze	0.084	0.090	3.8
B.C.S. 364	Leaded bronze	0.18	0.18	3.0

CHAPTER 6

THE CONSTRUCTION OF MULTI-ELEMENT ELECTRODELESS DISCHARGE LAMPS AND THEIR APPLICATION TO ATOMIC FLUORESCENCE SPECTROSCOPY

6.1 INTRODUCTION

6.1.1. Types of multi-element source for atomic fluorescence spectroscopy.

The advantages to be found in the use of a single spectral source for the determination of a number of elements by atomic absorption or atomic fluorescence are mainly economic ones of reduced warm-up times and storage space, leading to greater availability of instrumentation and hence a reduction in costs. To achieve this both continuum sources and multi-element line sources have been used.

High pressure xenon arc lamps have been used in atomic fluorescence spectroscopy for the determination of twenty-seven elements (26,49, 131-138). The best detection limits reported with these sources are compared with those obtainable with line sources in Table 2.2. The major disadvantage in the use of xenon arc lamps is that their peak emission intensities are normally in the region of 400-500 nm., and they are not particularly intense in the 200-285 nm., wavelength range, where atomic fluorescence is frequently the most sensitive method of analysis in flames. A study of interference effects has shown that spectral interferences are greater with a continuum source than with a line source (137). Continuum sources are not generally practical for atomic absorption, unless extremely narrow spectral band-passes are used.

A pulsed dye laser has also been used (143) to stimulate the atomic fluorescence of nine elements (viz: aluminium, calcium, chromium, gallium, indium, iron, manganese, strontium and titanium). The detection limits obtained with this source are of the same order as those obtainable with line sources.

Multi-element hollow cathode lamps have been manufactured for use in atomic spectroscopy by several groups of workers (213-219). Although these sources are sometimes suitable for atomic absorption spectroscopy, selective sputtering of the most volatile element frequently causes the emission lines of that element to predominate in the spectral emission of the lamp. Thus the radiation of only one element will be of a sufficient intensity to stimulate

atomic fluorescence. Demountable hollow cathode lamps have also been used for atomic fluorescence spectroscopy (54-56), and although these have some merit in solving some of the problems associated with multi-element sources, they are not suitable for simultaneous or rapid sequential multi-element determinations.

The development of electrodeless discharge lamps as spectral sources for atomic absorption and atomic fluorescence spectroscopy (99,118,127) has led to some investigations into their possible use as multi-element sources.

6.1.2 Multi-element electrodeless discharge lamps

Electrodeless discharge lamps are normally prepared from either the metal, the metal chloride, the metal iodide, the metal plus iodine, or a mercury-metal amalgam, depending upon the volatility of the element. Those lamps which contain the metal together with iodine or mercury may be considered to be potential multi-element sources.

Lamps containing iodine have been recommended for several elements (e.g. antimony (30), arsenic (97) and selenium (98)). Whilst it has been found impossible to excite iodine atomic fluorescence with the 206.162 nm. line radiation, since this is a non-resonance line (220), spectral overlap with the bismuth 206.170 nm. line may be used to stimulate the direct-line atomic fluorescence of bismuth (100,106).

Mercury amalgam lamps have been successfully prepared for copper, indium, lead, silver and thallium (109), although it should be noted that mercury is probably present in the majority of electrodeless discharge lamps due to diffusion from the vacuum gauge during preparation. The mercury radiation emitted from these lamps may be utilised to obtain the resonance fluorescence of mercury at 253.7 nm.

The first multi-element electrodeless discharge lamps specifically constructed for use in atomic spectroscopy were reported by Marshall and West (110), who prepared cadmium-zinc, gallium-indium and bismuth-mercury-selenium-tellurium sources. Fulton, Thompson and West (104) have constructed an antimony-

arsenic source, which was also used for the determination of bismuth by iodine spectral overlap, and cadmium by the spectral overlap of the arsenic 228.812 nm. and the cadmium 228.802 nm. lines. These two investigations of the construction and operation of multi-element electrodeless discharge lamps have shown that the combination of two or more elements, or their halides, in the same lamp, does not give rise to more interferences than are found with the corresponding single-element lamps, and that there is no decrease in the line intensity of the source or in the intensity of the atomic fluorescence produced upon irradiation of an atomic population of the appropriate species in a flame. Five or six-element sources of this type have been suggested (221), although there would be limitations on the choice of elements which could be used together, due to difficulties in obtaining elements or their compounds of compatible vapour pressures.

This restriction led Cresser and West (89) to propose a concentric two-chamber arrangement, consisting of a 2 mm. internal bore tube inside an 8 mm. internal bore tube. This followed observations that the stability of electrodeless discharge lamps could be improved by the use of a vacuum jacket surrounding the lamp (118,222). Since the inner tube will become much hotter than the outer during operation, the less volatile material should be placed there, and the more volatile material in the outer tube. It is possible to seal the inner and outer tubes at different inert gas pressures. Electrodeless discharge lamps of this type have been reported for eleven pairs of elements (viz: tellurium-selenium, arsenic-selenium, silver-zinc, silver-cadmium, silver-mercury, zinc-mercury, lead-cadmium, chromium-cadmium, nickel-chromium, manganese-chromium and antimony-bismuth). Some of these pairs of elements are of widely different volatilities.

The operation of clusters of two or four 2 mm. internal bore lamps in one resonant cavity has also been investigated (223, 224). Combinations of lamps used in this manner were selenium-tellurium, cadmium-zinc and cadmium-zinc-gallium-thallium.

The three types of multi-element electrodeless discharge lamp which have been proposed for use in atomic fluorescence spectroscopy are illustrated in Figure 6.1. Comparisons of the operating characteristics of these three types of lamp have been carried out for selenium-tellurium (233) and cadmium-zinc (224) dual-element combinations. When more than one tube was operated in the same resonant cavity, either in a cluster or in a concentric two-chamber arrangement, the discharge of one element tended to predominate in the spectral emission, and it became difficult to initiate the discharge of all of the tubes, or relaxation oscillations occurred, which in extreme cases led to two tubes alternately switching on and off. The small 2 mm. diameter lamps had a much shorter life than the larger lamps. The glass-blowing associated with the preparation of the concentric two chamber type lamps was much more difficult than that for the other types. The conclusion from both sets of observations (223,224) was that the combination of several elements or compounds in a single tube was the simplest and best means of providing stable, intense multi-element electrodeless discharge lamps for atomic fluorescence spectroscopy.

In this chapter the construction and operation of a number of multi-element electrodeless discharge lamps of the type proposed by Marshall and West (110), and their use as spectral sources for atomic fluorescence spectroscopy, is described.

6.2 EXPERIMENTAL

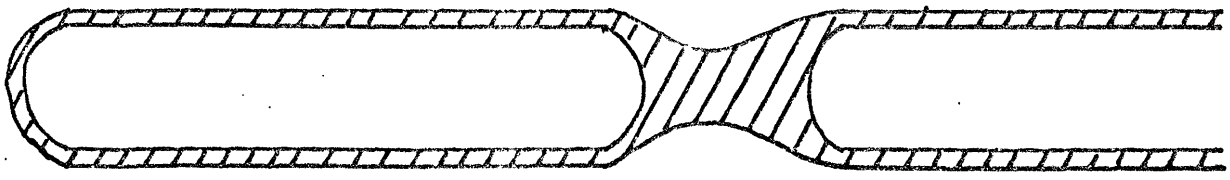
6.2.1 Preparation of multi-element electrodeless discharge lamps

The equipment and general procedure used were as described previously (99,127). However, since there are some minor differences in the construction of multi-element electrodeless discharge lamps, the procedure adopted will be outlined. A blank tube ca. 40 mm. long was prepared from 8 mm. internal bore quartz tubing, and degassed in the usual manner. The least volatile fill material was introduced. The tube was reconnected to the vacuum line and

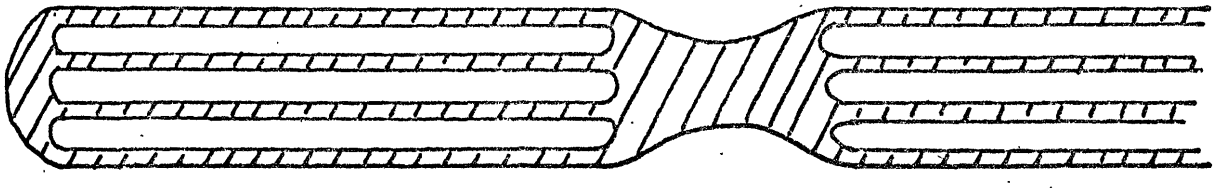
FIGURE 6.1

TYPES OF MULTI-ELEMENT ELECTRODELESS DISCHARGE LAMP

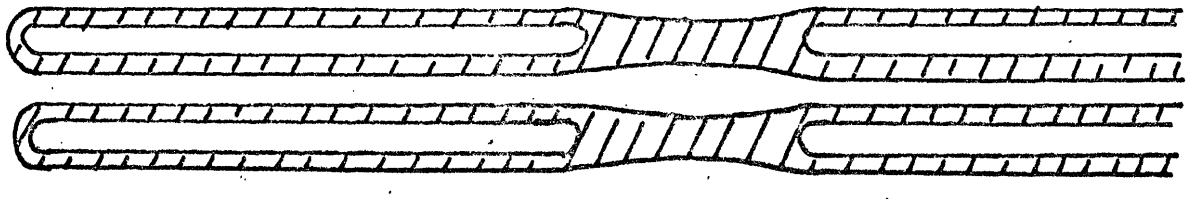
1. SINGLE TUBE



2. CONCENTRIC TWO-CHAMBER ARRANGEMENT



3. CLUSTER OF SMALL TUBES



evacuated to ca. 0.1 torr. The fill material was sublimed ca. 20 mm. up the walls of the tube. The more volatile fill material was then introduced, the tube reconnected to the vacuum line and evacuated to ca. 0.1 torr, and the fill material sublimed ca. 20 mm. up the walls of the tube. If more than two fill materials are used, this procedure should be repeated until all have been introduced. If the fill materials are of similar volatility they may be introduced and sublimed together. When hydrated metal chlorides were used, the compound was dehydrated in situ, by heating the tube gently under vacuum for 5-10 minutes, with several flushings of argon, before sublimation on the walls of the tube. The freshly prepared lamps were finally conditioned in the resonant cavity for ca. 1 hour before use.

The fill materials used were A.R. grade metals or salts, when these were available. The type of fill material used (e.g. metal, metal chloride, metal iodide or metal plus iodine) was normally that previously reported to be the most suitable for use in the preparation of the corresponding single-element lamps (222), although the relative volatilities of the materials had to be taken into consideration. Argon was used throughout as the fill gas.

The amounts and type of fill material and argon pressures used for the electrodeless discharge lamps prepared in this work, together with those previously reported (104,110), are listed in Table 6.1 for dual-element lamps and Table 6.2 for multi-element lamps.

6.2.2 Apparatus

The multi-element electrodeless discharge lamps were operated at 2450±25 MHz with a Microtron 200 microwave generator and a three-quarter wave (Broida type) resonant cavity. The discharge of the lamps was initiated with a high-frequency Tesla vacuum tester. The spectral emission produced by the lamps was monitored with the modified Southern Analytical A1740 grating flame spectrometer, described in Chapter 3.

TABLE 6.1

CONSTRUCTION AND OPERATING PARAMETERS AND ATOMIC FLUORESCENCE DETECTION LIMITS FOR SOME DUAL-ELEMENT ELECTRODELESS DISCHARGE LAMPS.

EDL	Contents	Operating Power watts	Wavelength nm.	AFS detection limit[a] ppm
Zinc-cadmium (110)	1 mg zinc, 1 mg cadmium, 3 torr argon.	60	213.8	0.001
			228.8	0.001
Gallium-Indium (110)	5 mg gallium, 5 mg indium, 3 torr argon.	60	417.2	1.0[b]
			451.1	0.2[b]
Selenium-Tellurium (110)	5 mg selenium, 5 mg tellurium, 5 mg iodine, 1 torr argon.	40-50	204.0	10[b]
			238.3	1.5[b]
Arsenic-Antimony (104)	4 mg arsenic, 4 mg antimony, 27 mg iodine, 3 torr argon.	40-45	235.0	25[c]
			217.6	0.9[c]
Cobalt-Nickel	1 mg cobalt chloride, 1 mg nickel chloride, 4-5 torr argon.	60	240.7	0.01
			232.0	0.02
Manganese-Chromium	1 mg manganese chloride, 1 mg chromium chloride, 4 torr argon.	60	279.8	0.005
			359.3[d]	0.005
Nickel-Chromium	1 mg nickel chloride, 1 mg chromium chloride, 4 torr argon.	60	232.0	0.01
			359.3[d]	0.008
Copper-Nickel	1 mg copper chloride, 1 mg nickel chloride, 4 torr argon.	50	324.7	0.01
			232.0	0.07
Cobalt-Iron	1 mg cobalt chloride, 1 mg ferrous chloride, 4 torr argon.	60	240.7	0.01
			248.3	0.1
Lead-Manganese	1 mg lead chloride, 1 mg manganese chloride, 3 torr argon.	50	405.8	0.01
			279.8	0.01
Cadmium-Lead	1 mg cadmium chloride, 1 mg lead chloride, 3 torr argon	45	228.8	0.008
			405.8	0.3
Iron-Manganese	1 mg ferrous chloride, 1 mg manganese chloride, 4 torr argon.	60	248.3	0.01
			279.8	0.005

a. In argon-separated air-acetylene flame using modified Southern A1740 with 10 or 20-second integration.
b. In air-propane flame, using unmodified Southern A1740 with 20-second integration. (110)
c. In unseparated air-acetylene flame using Techtron AA4. (104)
d. Combined fluorescence at 357.9 nm, 359.3 nm, and 360.5 nm.

TABLE 6.2

CONSTRUCTION AND OPERATING PARAMETERS FOR SOME MULTI-ELEMENT ELECTRODELESS DISCHARGE LAMPS.

Lamp	Contents	Operating Power watts	Wavelength nm.	AF detection limit ppm.
Selenium-Tellurium-Bismuth-Mercury (110)	5 mg selenium, 5 mg tellurium, 5 mg bismuth, 5mg iodine, mercury diffused from gauge, 0.5 torr argon	40-50	204.0	10[a]
			238.3	1.5[a]
			302.5	0.5[a]
			253.7	0.6[a]
Arsenic-Antimony-Bismuth-Cadmium (109)	4mg arsenic, 4 mg antimony, 27 mg iodine, 3 torr argon	40-45	235.0	25[b]
			217.6	0.9[b]
			302.5	2.5[b]
Zinc-Cadmium-Thallium-Mercury-Bismuth	1 mg zinc, 4 mg cadmium, chloride, 5 mg thallous iodide, mercury diffused from gauge, 4 torr argon	70	228.8	10[c]
			213.8	0.004[d]
			228.8	0.002[d]
			253.7	1[d]
			377.6	0.4[d]
			302.5	10[d]

a. In air-propane flame using unmodified Southern A1740 with 20-second integration. (110)
b. In unseparated air-acetylene flame using Techtron AA4 (104)
c. In unseparated air-acetylene flame using unmodified Southern A1740 with 20-second integration. (104)
d. In argon-separated air-acetylene flame using modified Southern A1740 with 10-second integration.

6.3 RESULTS AND DISCUSSION

6.3.1 Operation of multi-element electrodeless discharge lamps

All of the dual-element electrodeless discharge lamps were an intense blue in colour. The main spectral lines of both elements (e.g. cobalt 240.7 nm. and nickel 232.0 nm.) were of approximately equal intensity, in all cases. The line to background ratios of the main resonance lines were all greater than 100:1. To give an example of the type of spectrum obtained, the spectrum of a cadmium-lead dual-element electrodeless discharge lamp, between 300 nm. and 600 nm., is shown in Figure 6.2. In some of the lamps OH bands between 305 nm. and 315 nm. were observed. Their presence was attributed to failure to obtain complete dehydration of the hydrated metal chlorides used in the preparation of the lamps. The presence of the OH bands did not appear to interfere with the efficiency of these lamps.

The five element bismuth-cadmium-mercury-thallium-zinc lamp was an intense green in colour, due to the predominant emission of the thallium 535.0 nm. line. The main resonance lines of each element in this lamp were not of such comparable intensities as those of the dual-element lamps. The main lines observed in the spectral emission of this lamp, between 200 nm. and 400 nm., and their relative intensities, are listed in Table 6.3.

The optimal incident powers for the operation of the multi-element lamps are given in Tables 6.1 and 6.2. The optimal incident power was that which resulted in the maximum atomic fluorescence intensity being produced upon irradiation of an atomic population of the appropriate element in a flame, for the element in the combination giving the lowest atomic fluorescence signal, consistent with a stability of $\pm 3\%$ over a period of 1 hour at the main resonance line of each element. After the initial running-in period, a warm-up time of ca. 10 minutes was required when the discharge was initiated from the cold.

Atomic fluorescence detection limits obtained with the multi-element electrodeless discharge lamps, mostly in an argon-separated air-acetylene flame, are given in Tables 6.1 and 6.2.

FIGURE 6.2

EMISSION SPECTRUM BETWEEN 200 AND 600 NM FOR A LEAD-CADMIUM DUAL-ELEMENT ELECTRODELESS DISCHARGE LAMP (Major lines of each element only identified).

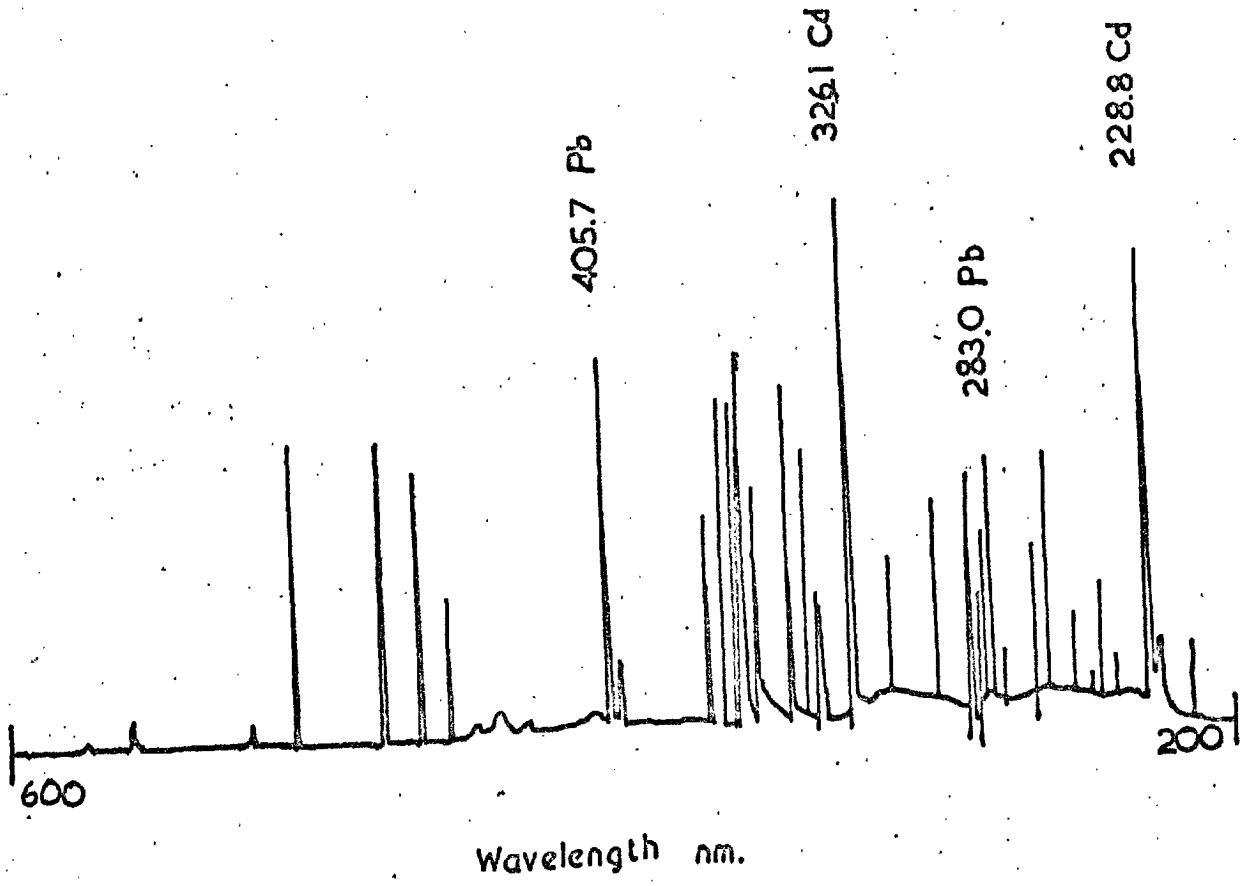


TABLE 6.3

MOST INTENSE EMISSION LINES DISPLAYED BY ZINC-CADMIUM-THALLIUM-MERCURY-BISMUTH FIVE-ELEMENT ELECTRODELESS DISCHARGE LAMP.

Line (nm)	Element	Intensity
206.2	I_2	18.5
213.8	Zn (1)	39.0
226.4	Cd (11)	12.0
228.8	Cd (1)	56.0
237.9	Tl (1)	4.0
253.7	Hg (1)	49.0
258.0	Tl (1)	4.0
270.9	Tl (1)	4.5
276.8	Tl (1)	25.5
279.4	--	3.0
287.5	--	5.5
291.8	Tl (1)	19.5
297.5	--	10.0
306.4	--	4.5
312.5	Hg (1)	4.0
322.9	Tl (1)	6.5
326.1	Cd (1)	65.0
328.3	Zn (1)	4.0
330.3	Zn (1)	18.5
334.5	Zn (1)	27.0
340.3	Cd (1)	19.5
346.6	Cd (1)	37.5
351.9	Tl (1)	53.5
361.0	Cd (1)	45.5
365.0	Hg (1)	4.0
377.6	Tl (1)	55.5

The operating characteristics (incident power and intensity plots, incident power and atomic fluorescence plots, stabilities and detection limits) for the cobalt-nickel, chromium-nickel and chromium-manganese dual-element electrodeless discharge lamps were compared with those for single-element chromium, cobalt, manganese and nickel lamps, prepared in a similar manner from the hydrated metal chlorides. No significant differences were observed in the operation of the dual-element and single-element lamps. This confirmed previous observations (104,110).

6.3.2 Attempts to prepare multi-element electrodeless discharge lamps for other combinations of elements

Attempts were made to prepare electrodeless discharge lamps for combinations of elements other than those listed in Tables 6.1 and 6.2. Some combinations of elements used include manganese-nickel, mercury-tin, cadmium-tin, lead-tin, lead-thallium, chromium-manganese-nickel, cobalt-iron-nickel and cadmium-mercury-selenium-tellurium-thallium-zinc. These lamps were all unsuitable for analytical use, either due to lack of stability and short life, or to the predominance of the spectral emission of one of the elements in the discharge. It should also be noted that for several of those multi-element electrodeless discharge lamps which were found to be satisfactory, the particular combination of the metals and/or their halides used, was often the only such combination which resulted in the construction of a successful lamp.

6.3.3 Discussion

Generally dual-element electrodeless discharge lamps were found to be as easy to construct as the corresponding single-element lamps, provided that the two elements combined in the lamp were of reasonably compatible vapour pressures. Although these dual-element lamps have proved successful in various applications, as discussed in Chapters 7 and 8, it would obviously be more advantageous to be able to construct lamps combining a greater number of elements. However, it was only found possible to prepare one five-element lamp in this work.

The main difficulty experienced in the preparation of lamps containing several elements was in the control of the amounts of the fill materials used. Firstly, the relative amounts of each fill material must be carefully controlled, and secondly, the total amount of fill material must not be too great. Separate sublimation of each fill material, commencing with the least volatile, helps to overcome these difficulties. However, this is tedious when a large number of fill materials are involved.

It is probable that most of these constructional problems could be solved by introducing the fill materials in solution, and evaporating and drying in situ under vacuum. It would then be simple to control the relative amounts of each element or compound present, as well as the total amount of fill material used. This technique has already been adopted for the preparation of single-element cadmium and zinc electrodeless discharge lamps (122,123). Some preliminary investigations (225) suggest that this method will be advantageous in the construction of multi-element lamps, and a four-element cadmium-gallium-indium-zinc lamp has been prepared in this manner, as well as dual-element cadmium-zinc and gallium-indium lamps.

6.4 CONCLUSION

There are a considerable number of parameters involved in the preparation and operation of electrodeless discharge lamps. The investigation of these parameters has been the subject of much work (115,116,121-123), which has done much to explain their effects. However, it is apparent that there is still a lot not known about the preparation and operation of these lamps. Until a better procedure is evolved for their reproducible construction, the production of multi-element electrodeless discharge lamps will remain, to some extent, a matter of trial and error.

CHAPTER 7

THE ATOMIC FLUORESCENCE DETERMINATION OF CHROMIUM, COBALT, MANGANESE AND NICKEL IN STEELS USING AN ARGON-SEPARATED AIR-ACETYLENE FLAME AND SOME DUAL-ELEMENT ELECTRODELESS DISCHARGE LAMPS

7.1 INTRODUCTION

Despite its inherent advantages of high sensitivity, high selectivity and simplicity, atomic fluorescence spectroscopy has been somewhat neglected as a method for the determination of minor constituents in technical materials. This may partially be attributed to the omission of an atomic fluorescence spectrometer in the range of commercially available instrumentation.

Klaus (47) has determined zinc and cadmium in biological materials, using metal vapour discharge lamps and an air-hydrogen flame. Vickers and Merrick (139) have determined mercury in urine, after solvent extraction, using a pen-light source and an oxy-hydrogen flame. Matousek and Sychra (68) have analysed gold in mine waters, in an argon-oxy-hydrogen flame with a high-intensity hollow cathode lamp. These workers (74) have also determined nickel in gas oils and petroleum distillation residues, using a high-intensity hollow cathode lamp and a nitrogen-separated air-acetylene flame. Cotton and Jenkins (134) have analysed copper, iron and lead in hydrocarbon fuels, burning the fuels with nitrogen on a specially constructed burner, and using a 450 watt xenon arc lamp. Marshall and Smith (226) have determined zinc in high-pressure boiler feed waters, using an electrodeless discharge lamp and an air-hydrogen flame. Winefordner and co-workers have determined wear metals in jet engine oils: copper, iron, lead, magnesium, nickel and silver were determined using a hydrogen-argon-entrained air flame or an air-hydrogen flame and electrodeless discharge lamps (117), and copper, iron, magnesium and silver were determined by a combined atomic emission-atomic fluorescence procedure, using a 150 watt xenon arc lamp and a hydrogen-argon-entrained air flame (132). Hobbs, Kirkbright and West (107) have determined bismuth in aluminium alloys, using an iodine electrodeless discharge lamp and a nitrogen-separated air-acetylene flame. Dagnall, Taylor and West (95) have analysed lead in steels, using an electrodeless discharge lamp and an air-propane flame. Kirkbright, Rao and West (108) have determined

silicon in low alloy steels, using an electrodeless discharge lamp and a nitrogen-separated nitrous oxide-acetylene flame.

The Technicon AFS6 multi-channel atomic fluorescence spectrometer has been used for the atomic fluorescence determination of calcium, copper, magnesium, manganese and zinc in soil extracts (63), and copper, iron, magnesium, manganese, nickel and zinc in aluminium alloys (64), using high-intensity hollow cathode lamps and a nitrogen-separated air-acetylene flame.

Non-flame techniques have also been used. Amos et al (60) have utilised the carbon filament atom reservoir for the atomic fluorescence determination of lead in blood, using a high-intensity hollow cathode lamp. Belyaev et al (50-53) have used a pulsed atomisation technique for solid samples to determine cadmium in graphite.

This chapter reports the application of two of the dual-element electrodeless discharge lamps, the preparation of which was described in Chapter 6, to the determination of chromium, cobalt, manganese and nickel in a variety of different types of steel.

The atomic fluorescence determination of all four of these elements has been described previously. Fleet, Liberty and West (64) studied cobalt using both a high-intensity hollow cathode lamp and an electrodeless discharge lamp as spectral sources. Armentrout (48) has examined nickel using a hollow cathode lamp, and Matousek and Sychra (69) have examined both elements using high-intensity hollow cathode lamps. Ebdon, Kirkbright and West (102) have investigated the atomic fluorescence of manganese using a manganese chloride electrodeless discharge lamp, whilst the atomic fluorescence of chromium with a chromium chloride electrodeless discharge lamp was described in Chapter 3.

7.2 EXPERIMENTAL

7.2.1 Apparatus

The instrumentation used and its application to atomic fluorescence determinations was discussed in Chapter 3. A monochromator slit-width of

0.5 mm., corresponding to a spectral band-pass of 3 nm., was used, except for chromium determination, when the maximum slit-width was used. The facilities for 20 second integration were employed. The flame used was slightly fuel-lean argon-separated air-acetylene. The construction and operation of the electrodeless discharge lamps was discussed in Chapter 6.

7.2.2 Reagents

100 ppm. stock solutions of each element were prepared respectively by dissolving 0.4037 g. of A.R. grade cobalt chloride hexahydrate, 0.4049 g. of A.R. grade nickel chloride hexadrate, 0.5123 g. of A.R. grade chromium chloride hexahydrate and 0.3566 g. of A.R. grade hydrated manganese chloride, in distilled water, and diluting each to 1 $dm.^3$.

The hydrochloric acid, nitric acid and amyl acetate used were all A.R. grade.

7.2.3 Procedure for the analysis of steel samples

An appropriate amount of the steel (1.0-1.5 g. for steels containing ca. 0.01% of the element, 0.02 g. for steels containing ca. 0.5% of the element etc.) was weighed out into a 100 cm^3.beaker. 15 $cm.^3$ of concentrated hydrochloric acid and 7.5$cm.^3$ of concentrated nitric acid were added. The beaker was covered with a watch glass and heated gently to dissolve the steel. When all of the steel had dissolved, the solution was diluted to 50 $cm.^3$ and filtered through a filter paper, the filtrate being collected in a 100 $cm.^3$ volumetric flask. The beaker and filter paper were washed thoroughly and the filtrate and washings diluted to volume with distilled water. For steels of widely different concentrations of the four elements, dilutions were carried out, so that the final solution contained ca. 1 ppm. of the element concerned. In some cases, different amounts of acid were required to dissolve the steel, depending on the major constituents.

Due to the depressing matrix effect of iron on the atomic fluorescence determination of chromium, it was found necessary to remove most of the

iron from sample solutions, when the steel contained less than 0.5% chromium. This was achieved by extracting the iron from the hydrochloric acid/nitric acid solution after dissolution, with an equal phase volume of amyl acetate. One extraction in this way was sufficient to remove 60% of the iron present. Pre-equilibration of the aqueous solution to 8M with respect to hydrochloric acid increased the efficiency of the iron extraction to ca. 95%.

Calibration solutions in the range of 0-2 ppm. were prepared by transferring 10 $cm.^3$ of the relevant stock solution to a 100 $cm.^3$ volumetric flask and diluting to volume with distilled water. 0, 5, 10, 15 and 20 $cm.^3$ aliquots of this solution were transferred to a series of 100 $cm.^3$ volumetric flasks. 15 $cm.^3$ of hydrochloric acid and 7.5 $cm.^3$ of nitric acid were added to each flask. The solutions were diluted to volume with distilled water. If the quantities of acid used to dissolve the steel sample are different to those stated, the standard solutions should be prepared to contain corresponding amounts of acid.

The discharge of the electrodeless discharge lamp was initiated and the lamp allowed to stabilise at its operating power for ca. 10 minutes. The standard and sample solutions were nebulised into the argon-separated air-acetylene flame as required. The d.c. background correction facility was used to minimise the thermal emission signal, and the background reading subtracted from the total signal to obtain the atomic fluorescence signal.

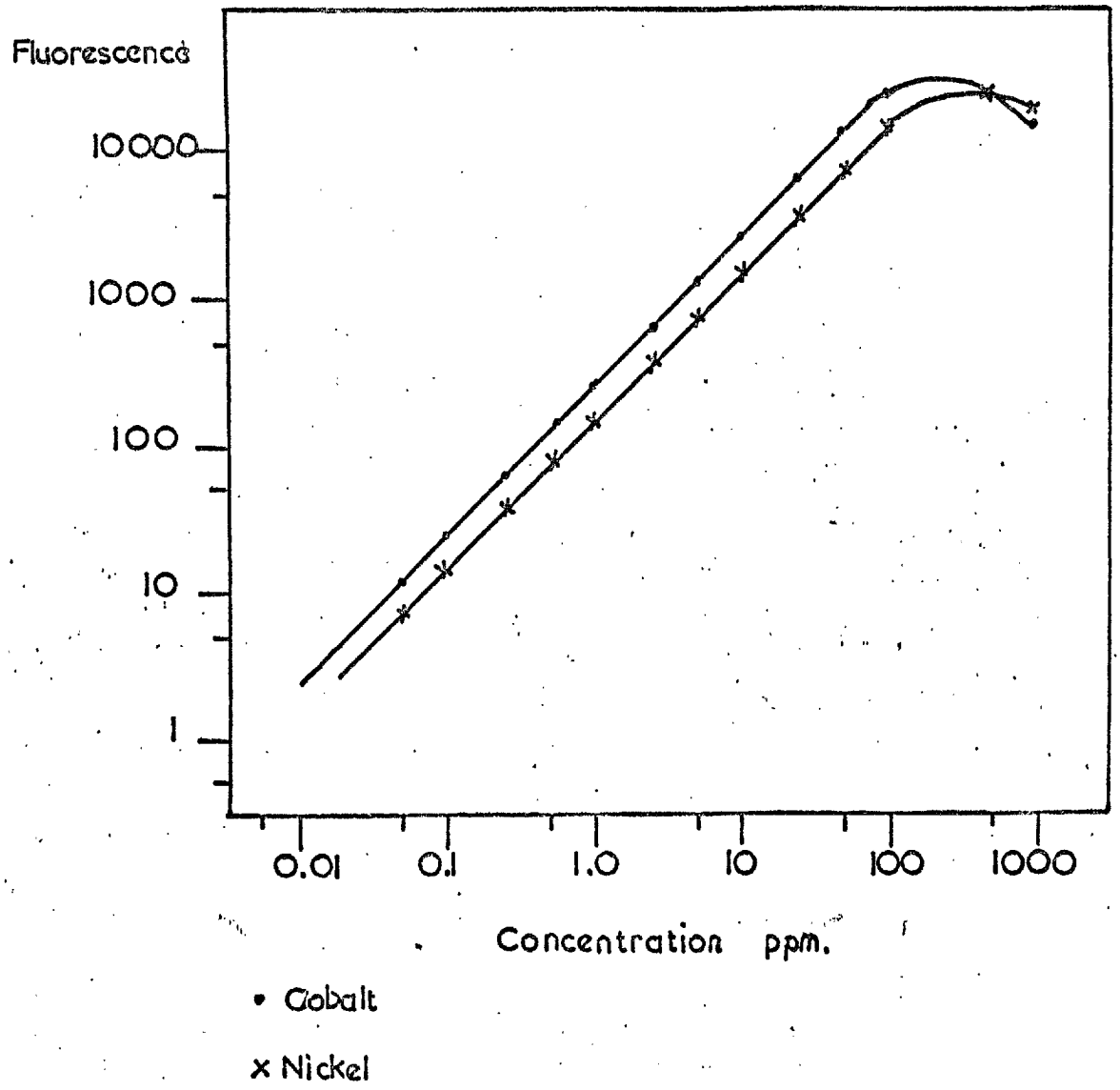
7.3 RESULTS AND DISCUSSION

7.3.1 Calibration data

Complete atomic fluorescence calibration curves for cobalt and nickel in acidic solution are given in Figure 7.1. A calibration curve for chromium in aqueous solution was given in Figure 3.1, and the shape of the manganese atomic fluorescence curve has been described elsewhere (102). All of these curves are of the same general shape as that discussed in Chapter 1. Detection limits obtainable in aqueous solution are given in Table 6.1.

FIGURE 7.1

ATOMIC FLUORESCENCE CALIBRATION CURVES FOR COBALT AT 240.7 NM AND NICKEL AT 232.0 NM



The calibration curves used for the steel determinations, obtained using acidic solutions between 0 and 2 ppm. were linear and passed through the origin.

7.3.2 Interference and matrix effects

The effects of 250-fold weight excesses of thirty-eight ions on the atomic fluorescence of a 2 ppm. solution of chromium were discussed in Chapter 3. The effects of 1000-fold weight excesses of twenty-six ions on the atomic fluorescence of an 0.5 ppm. solution of manganese has also been discussed recently (102). Both studies were carried out in inert gas-separated air-acetylene flames, and the only interferences observed were due to refractory metals, which were present at insignificant levels in the steels under investigation.

The effects on the atomic fluorescence of a 5 ppm. solution of cobalt and a 5 ppm. solution of nickel of a 100-fold excess of twenty-five elements commonly found in steels (viz: Al, As, B, Bi, Ca, Cd, Co, Cr, Cu, Mg, Mn, Mo, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ta, Ti, V, W, Zn and Zr) were examined. No interference (i.e. greater than $\pm$3% deviation in signal) was observed with any of these elements.

The effects of a 10,000-fold weight excess of the matrix element (iron) on the atomic fluorescence of a 2 ppm. solution of chromium, cobalt, manganese and nickel were investigated. In the case of cobalt, manganese and nickel there was a decrease in the atomic fluorescence signal of less than 2%. This was not considered sufficiently significant to warrant further investigation of the effect of iron on the atomic fluorescence of these elements. However, a significant reduction in signal (ca. 20%) was observed for chromium, and, therefore, a preliminary solvent extraction procedure with amyl acetate was used to remove most of the iron before chromium determination.

The effect of the acids used in the dissolution of the steel samples was also examined. Chromium, cobalt, manganese and nickel standards

(5 ppm. of each element) were prepared in 10% (v/v) nitric acid and 20% (v/v) hydrochloric acid solution. (This was the highest acid concentration necessary to dissolve any of the steel samples used in this work). The atomic fluorescence signals obtained from these solutions were compared with those of aqueous solutions. The atomic fluorescence signals of the acid solutions were ca. 5% less than those of the aqueous solutions for each element. This effect was attributed to the higher surface tension and viscosity of the acid solutions reducing the efficiency of nebulisation compared with aqueous solutions. This showed the need for preparing standard solutions with approximately the same acid concentrations as the sample solutions.

7.3.3 Analysis of steel samples

The results obtained for the determination of chromium, cobalt, manganese and nickel in a variety of different types of standard steel, mostly from the B.C.S. range (Bureau of Analysed Samples Ltd., Middlesborough), are given in Table 7.1, together with the certificate values. One sample of each steel was weighed and dissolved, and four atomic fluorescence readings were taken and averaged to obtain these results.

The precision of the method was also investigated using one of the standard steels (B.C.S. 277 Mild steel for cobalt and nickel and B.C.S. 406 alloy steel for chromium and manganese). Seven samples of the steel were weighed and dissolved. Four atomic fluorescence readings were taken and averaged for each solution, to obtain the results from which the ranges and standard deviations were calculated. These data are given in Table 7.2.

7.4 CONCLUSION

The above results show that atomic fluorescence spectroscopy, with a dual-element source, has considerable merit as a method for the determination of minor constituents in steels.

TABLE 7.1

ATOMIC FLUORESCENCE DETERMINATION OF CHROMIUM, COBALT, MANGANESE AND NICKEL IN STEELS

SAMPLE		CHROMIUM		COBALT		MANGANESE		NICKEL	
		Standard analysis[a]	Atomic fluorescence	Standard analysis[a]	Atomic fluorescence	Standard analysis[a]	Atomic fluorescence	Standard analysis[a]	Atomic fluorescence
B.C.S. 277	Mild steel	0.075	0.07	0.125	0.127	0.49	0.49	0.233	0.233
B.C.S. 273	Mild steel	0.03	0.04	0.021	0.020	0.50	0.50	0.031	0.030
B.C.S. 271	Mild steel	--	--	0.012	0.010	--	--	0.013	0.014
B.C.S. 225	Ni-Cr-Mo steel	1.04	1.05	0.01	0.010	0.595	0.60	1.67	1.64
B.C.S. 225/2	Ni-Cr-Mo steel	1.08	1.08	--	--	0.56	0.56	1.43	1.43
B.C.S. 406	Low alloy steel	2.12	2.11	--	--	0.53	0.53	1.69	1.67
B.C.S. 407	Low alloy steel	3.00	3.00	--	--	0.13	0.13	0.61	0.60
B.C.S. 328	Mild steel	--	--	0.17	0.168	0.43	0.44	--	--
B.C.S. 260/3	High-purity iron	--	--	0.010	0.011	--	--	0.004	0.005
B.C.S. 334	Austenitic stainless steel	25.6	25.5	0.052	0.052	0.85	0.84	20.6	20.5
B.C.S. 341	Ferritic stainless steel	24.0	23.7	--	--	0.43	0.42	0.56	0.56
B.C.S. 483	High-speed steel	3.21	3.18	1.94	1.93	0.29	0.29	--	--
3857y	Stainless steel	--	--	0.66	0.67	--	--	2.07	2.08
3924y	Stainless steel	--	--	0.36	0.38	--	--	0.82	0.84
7120(08891)	Stainless steel	--	--	0.027	0.027	--	--	0.24	0.237

a. B.C.S. certificate values for B.C.S. samples. The remaining three samples had been analysed by 'Quantovac' emission spectrography

TABLE 7.2

RANGES AND STANDARD DEVIATIONS FOR THE ATOMIC FLUORESCENCE DETERMINATION OF CHROMIUM, COBALT, MANGANESE AND NICKEL IN STEELS

B.C.S. 277

	Cobalt	Nickel
Certificate value	0.12(5)	0.23(3)
Mean value of atomic fluorescence analysis	0.127	0.233
Range in certificate values	0.119 - 0.137	0.227 - 0.242
Range by atomic fluorescence	0.120 - 0.133	0.225 - 0.237
Standard deviation (%) by atomic fluorescence	3.5	2.0

B.C.S 406

	Chromium	Manganese
Certificate value	2.12	0.53
Mean value of atomic fluorescence analysis	2.11	0.531
Range in certificate values	2.08 - 2.15	0.53 - 0.54
Range by atomic fluorescence	2.04 - 2.18	0.525- 0.538
Standard deviation (%) by atomic fluorescence	2.5	1.8

CHAPTER 8

A SCANNING TECHNIQUE FOR MULTI-ELEMENT DETERMINATIONS BY ATOMIC FLUORESCENCE SPECTROSCOPY

8.1 INTRODUCTION

8.1.1 Multi-element atomic spectroscopy

One of the major limitations of atomic spectroscopy as a method of chemical analysis is that no entirely satisfactory system for simultaneous or rapid sequential multi-element determinations has yet been developed. This aspect of atomic spectroscopy has been the subject of a considerable amount of research work over the last few years (170, 227), resulting in a number of possible multi-element instrumental systems for atomic emission, atomic absorption and atomic fluorescence.

The general reasons for the difficulties in the design of suitable instrumentation for multi-element atomic spectroscopy are summarised below.

1. A single set of instrumental operating parameters may normally only be used over a concentration range of one order of magnitude for maximum sensitivity.

2. For certain elements, the number of emission, absorption or fluorescence wavelengths which are available for measurement is small, and the different wavelengths may give sensitivities which differ by several orders of magnitude. Therefore, sample dilutions will be necessary if the analysis is required over a wide concentration range, which may result in the determination of several solutions for the multi-element analysis of one sample.

3. The optimum operating parameters (e.g. flame type, gas flow rates and height above the burner) vary from element to element, if the maximum sensitivity and selectivity are to be attained.

The various instrumental systems which have been developed to overcome these and other difficulties will now be considered.

8.1.2 Multi-element atomic emission spectroscopy

Although simultaneous multi-element analysis for many elements may be readily accomplished for solid samples by atomic emission spectroscopy, using arc and spark excitation and multi-channel spectrographs, the simultaneous

multi-element determination of liquid samples in flame cells is complicated by the large number of emission lines displayed by some elements, band emissions and other interference effects.

An automatic high-speed scanning multi-channel spectrometer, based on an oscillating diffraction grating and using a scanning speed of 1800 nm sec^{-1} has been constructed (228). This spectrometer was used for the rapid sequential determination of calcium, magnesium, potassium and sodium in clinical samples. The adaption of this spectrometer for multi-element atomic absorption and atomic fluorescence has also been suggested.

Recently, a rapid (450 nm min^{-1}) scanning technique, employing a commercially-available single-channel atomic absorption spectrometer with a fast response operational amplifier and a u.v. recorder, and a nitrogen-separated nitrous oxide-acetylene flame has been reported (229). This technique was successfully applied to the rapid sequential determination of copper, magnesium, manganese and strontium in milk solutions.

8.1.3 Multi-element atomic absorption spectroscopy

A major limitation on the construction of multi-element spectrometers for atomic absorption is the rigidity of the optical arrangement (i.e. source, atom reservoir and monochromator in a straight line). However, a number of systems have been adopted to obtain a single light path through the atom reservoir and on to the monochromator, for the radiation of several elements.

Mavrodineau and Hughes (230) angled the radiation from a number of hollow cathode lamps on to a diffraction grating. The hollow cathode lamps were so aligned that a single beam was produced. This passed through the flame and on to a second diffraction grating, which split the beam into its spectral components which were directed on to a series of photomultipliers. Strasheim and co-workers (215,231) have used multi-element hollow cathode lamps, tandem-mounted hollow cathode lamps, semi-transparent mirrors or a time-resolved spark, to produce a single beam which was passed through the

flame cell and on to a four - or six-channel quartz spectrograph, fitted with a direct-reading attachment. Brech (232,233) has reported a similar system, incorporating two six-element hollow cathode lamps and a twelve-channel spectrograph. Walsh (170) has suggested the isolation of the resonance lines of different elements by the selective modulation of hollow cathode lamps (81,234-236).

Walsh (170) has also reported the operation of a six-channel atomic absorption spectrometer, using resonance detectors (166-169,171), which greatly reduce the bulk of the monochromation-detection system. This differs from the systems previously described in that no attempt is made to obtain a single light path through the flame cell. Six high-intensity hollow cathode lamps are arranged on one side of the flame cell and six resonance monochromator-detectors on the other side. Since there are six light paths through the flame, the burner is star-shaped and may only be used with an air-propane flame. This instrument has been used for the simultaneous determination of copper, lead, nickel and silver in mineral ores.

8.1.4 Multi-element atomic fluorescence spectroscopy

Atomic fluorescence is far more suitable for simultaneous or rapid sequential multi-element analysis than is atomic absorption. Since the incident radiation is not measured by the detector, it is easy to direct the light from several spectral sources on to the flame cell. It is also possible to simplify the detection system by the use of optical filters in place of a monochromator.

A spectrometer designed specifically for multi-element atomic fluorescence was initially reported by Mitchell and Johansson (70,71), who used it for the simultaneous determination of copper, iron, magnesium and silver. Dagnall, Kirkbright, West and Wood (62,63) have described the application of a similar atomic fluorescence spectrometer, capable of the

simultaneous determination of up to six elements, to the analysis of calcium, copper, magnesium, manganese, potassium and zinc in soil extracts (62), and copper, iron, magnesium, manganese, nickel and zinc in aluminium alloys (63). These instruments are complex, requiring individual single-element hollow cathode lamps, a rotating wheel with an optical filter for each element, which is synchronised with the lamp power supply, and a sophisticated signal-processing system. Walsh (170) has reported the use of a simpler non-dispersive seven-channel atomic fluorescence spectrometer, incorporating a solar-blind photomultiplier. More recently, Malmstadt and Codos (237) have proposed a twelve-channel atomic fluorescence instrument.

The potential use of a scanning technique for multi-element atomic fluorescence, employing commercially-available atomic emission/atomic absorption instrumentation, has been discussed elsewhere (110,120). This chapter describes the application of some of the dual-element electrodeless discharge lamps, the preparation and operation of which was discussed in Chapter 6, to multi-element atomic fluorescence determinations by a scanning technique.

8.2 EXPERIMENTAL

8.2.1 Apparatus

The modified Southern Analytical A1740 grating flame spectrometer and ancillary equipment for atomic fluorescence determinations, as described in Chapter 3, was used in conjunction with an air-hydrogen flame for some preliminary studies of the scanning technique. The spectrometer was equipped for scanning at 75 nm min^{-1}. This instrument has a d.c. amplification system, and with the scanning technique there is no means of backing off the flame background emission. Although this instrumental system was not particularly suitable for the scanning technique, satisfactory results were obtained for the rapid sequential determination of zinc and cadmium.

The following experimental arrangement was therefore finally selected for the scanning technique:-

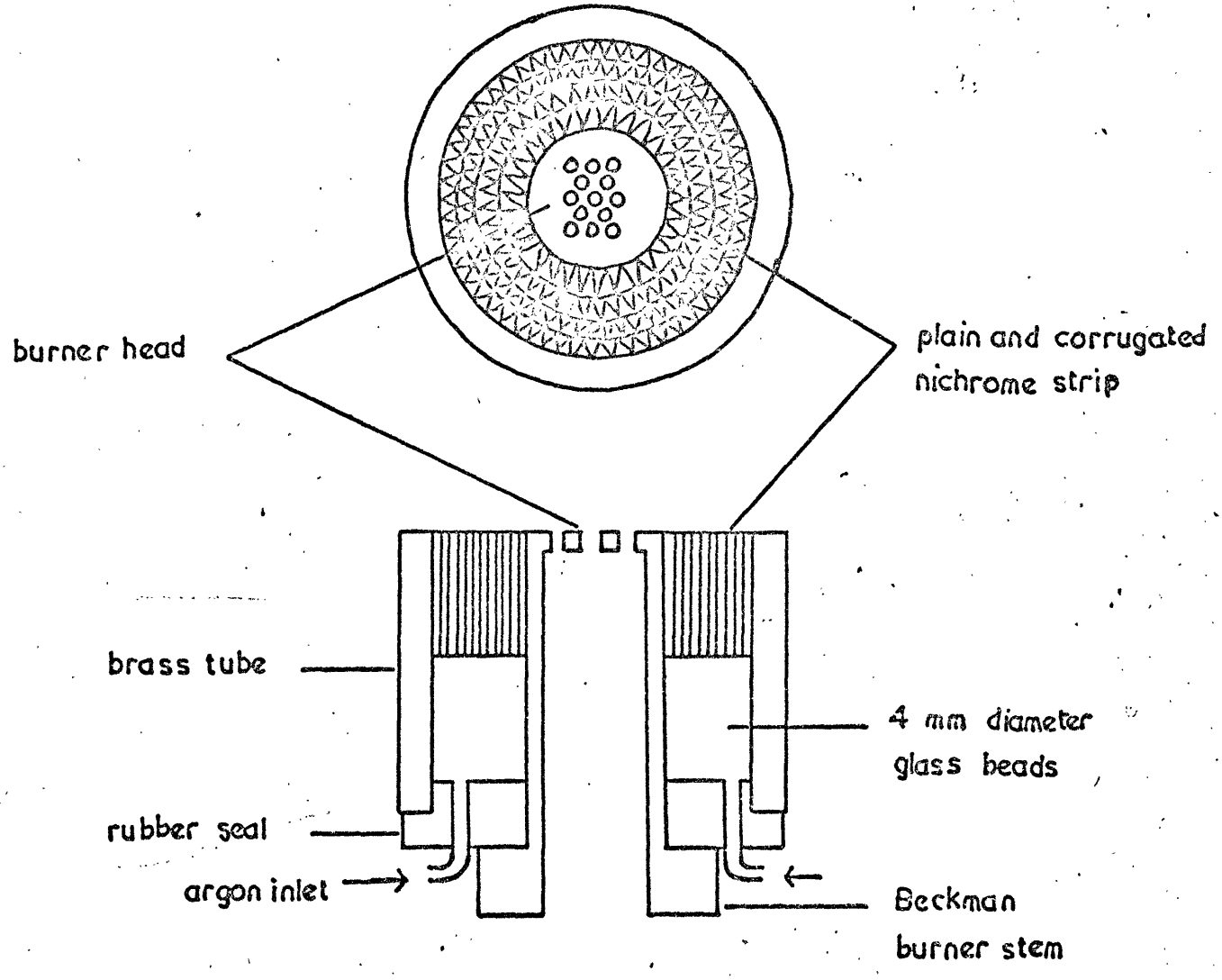
Spectral sources. The dual-element electrodeless discharge lamps were operated at 2450±25 MHz with a Microtron 200 Mark II microwave generator (Electro-medical Supplies Ltd., Wantage. U.K., Model 2000L) and two three-quarter wave (Broida type resonant cavities (EMS Model 210L). In order to operate the two resonant cavities from one microwave generator, a two-port power divider (EMS Model 4000L) was used. The power divider was connected to the microwave generator by an 18 in. length of coaxial cable (EMS Model 2009L), and to the two resonant cavities by two 54 in. lengths of coaxial cable (EMS Model 2010L). The use of the two-port power divider enabled the output from the microwave generator to be divided equally between the two resonant cavities. This meant that the lamps in both cavities had to be operated at the same incident power. However, the majority of the dual-element electrodeless discharge lamps have optimal operating powers of ca. 60 watts, so that the choice of lamps which could be operated together from one microwave generator was not greatly restricted. The output from the microwave generator was modulated at 285 Hz, using a Microtron Mark II modulator unit (EMS Model 3005L). The discharge of the lamps was initiated using a Tesla high-frequency vacuum tester.

Burner. An air-acetylene flame was supported on a Meker type circular burner head (Beckman-RIIC Ltd., London. U.K.). This flame was separated with argon. Initially a commercial emission burner shield (Beckman-RIIC) was used, but this did not prove very successful. A separator, similar to that used with the Unicam SP900 burner described in Chapter 3, was constructed around the short (height 4.5 cm.) Beckman burner. Although this burner required four argon inlets, the separation achieved was as good as that obtained with the separator previously built around the Unicam burner. A diagram of this burner is shown in Figure 8.1.

Spectrometer. The spectrometer used was a Techtron AA4 atomic absorption spectrometer (Varian-Techtron Pty. Ltd., Melbourne, Australia.), fitted with a Hamamatsu type R213 uv-sensitive photomultiplier. This spectro-

FIGURE 8.1

SEPARATING BURNER BASED ON THE BECKMAN EMISSION BURNER

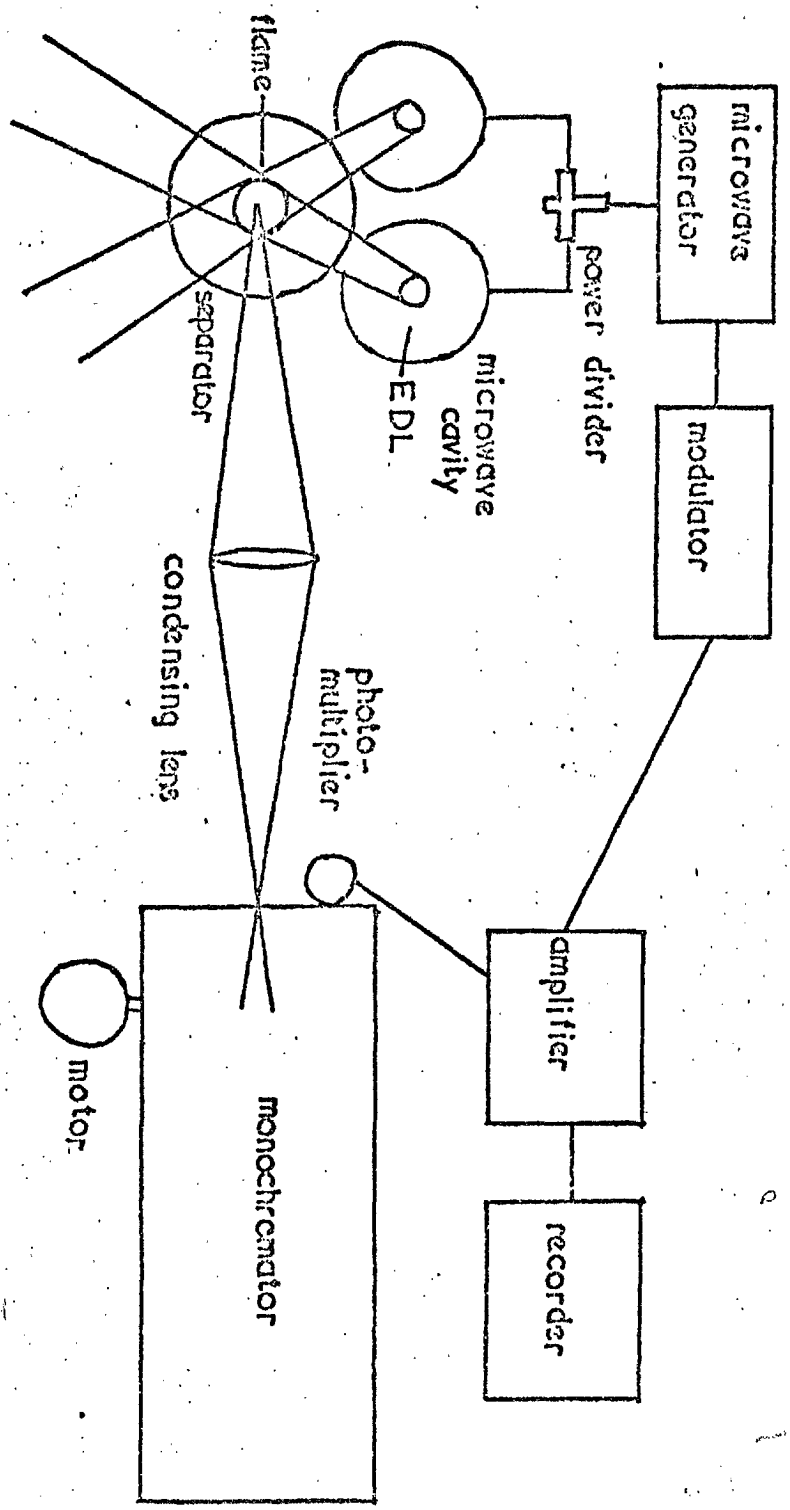


meter has a range of monochromator slit-widths up to 0.3 mm, corresponding to a spectral band-pass of 1 nm. The only wavelength scanning facilities available with this instrument are at 450 nm min^{-1}, which is too fast for use with conventional chart recorders. Therefore, a variable speed stirrer motor (Citenco Ltd., Borehamwood, U.K., Model KQPS 24) was connected to the monochromator 'wavelength set' control by means of a brass sleeve. This made available a choice of scanning speeds between 10 and 50 nm min^{-1}. This motor could be engaged or disengaged using the arrangement for the operation of the 'wavelength set' control, so that when disengaged the scanning motor on the monochromator could be used for resetting the wavelength after a scan. The amplifier, which is modulated at 285 Hz, was synchronised with the Microtron modulator unit via the connector normally used to synchronise a chopper. The output signal from the amplifier was connected to a Servoscribe potentiometric chart recorder (Smiths Industries Ltd., London. U.K., Model RE 511).

Optical arrangement. The optical arrangement is shown in the block diagram in Figure 8.2. The dual-element electrodeless discharge lamps were placed as close as possible to the flame (ca. 60 mm from the centre of the flame). The resonant cavities were ca. 10 mm apart, and it was not found necessary to use any screening arrangement between them. The only difficulty caused by placing the resonant cavities so close together was experienced in initiating the discharge of both lamps. However, once alight, the close proximity of the two resonant cavities did not appear to affect the operation of the lamps. It was found necessary to cover one of the side holes of the cavity nearer to the monochromator to prevent any stray radiation from the lamp falling on to the entrance slits of the monochromator, either directly or through the condensing lens. The atomic fluorescence from the flame was focussed on to the entrance slits of the monochromator with a Techtron condensing lens (focal length 62.5 mm.).

FIGURE 8.2

INSTRUMENTAL ARRANGEMENT FOR SCANNING ATOMIC FLUORESCENCE



8.2.2 Reagents

All stock solutions (1000 ppm) were prepared from A.R. grade reagents and distilled water. The stock solutions were diluted as required immediately before use.

8.2.3 Procedure

The discharge of both electrodeless discharge lamps was initiated and they were allowed to stabilise at their normal operating power for ca. 10 minutes. The wavelength control was set so that a wavelength ca. 5 nm below that of the lowest resonance line required was indicated. The scanning motor was engaged, the solution was nebulised into the flame, and the chart recorder and then the scanning motor were switched on. After scanning to ca. 5 nm. above the wavelength of the highest resonance line required, the scanning motor was switched off and disengaged, and the chart recorder switched off. The monochromator was returned to the original wavelength by means of the spectrometer scanning motor. The procedure was then repeated with the next solution. As usual in atomic fluorescence determinations it is desirable to nebulise a standard solution between each unknown solution. The peak heights were measured, and those of the unknown solutions compared with those of the standard solutions.

8.3. RESULTS AND DISCUSSION

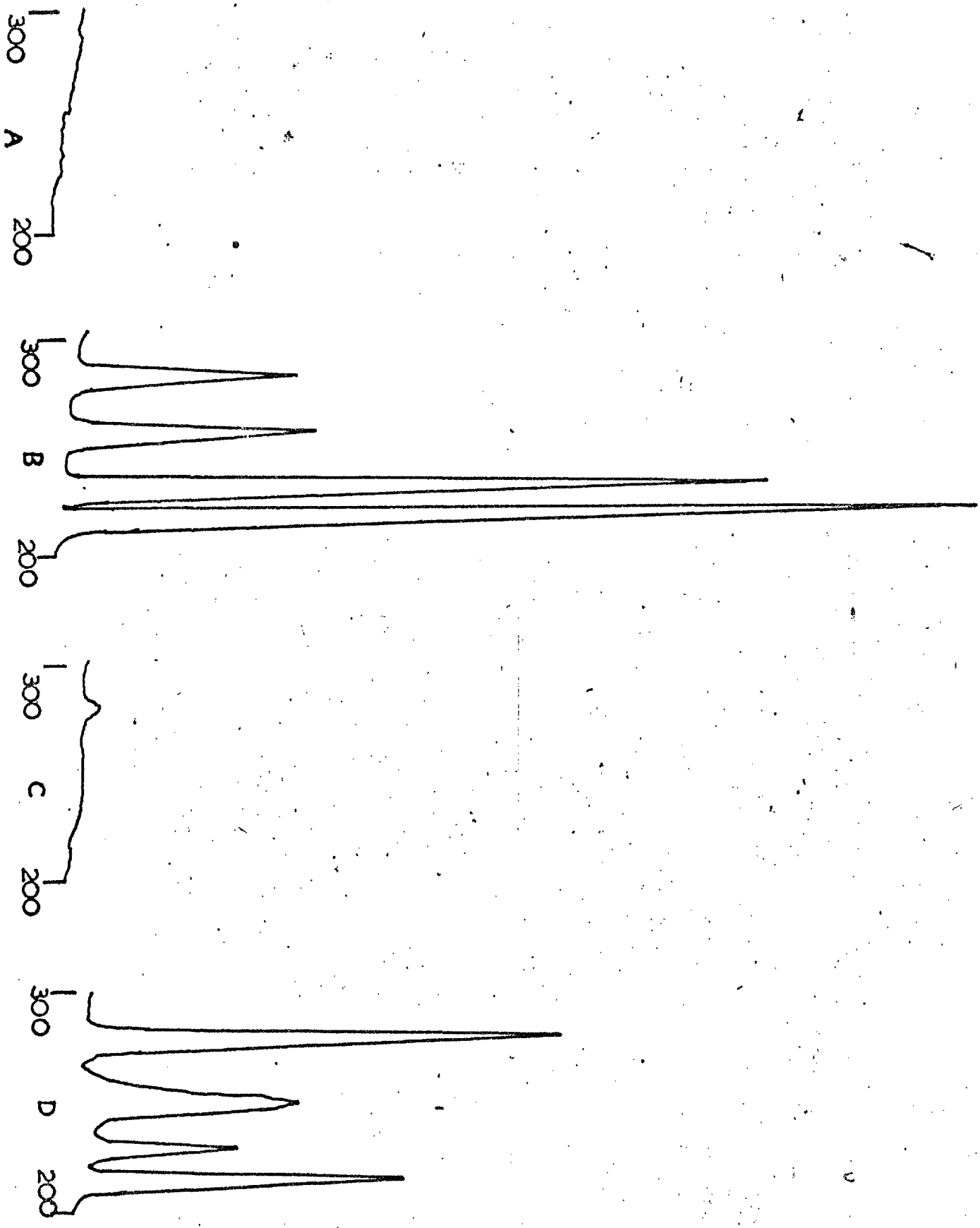
8.3.1 Initial experiments with Southern A1740

Two scans obtained for zinc-cadmium-iron-manganese atomic fluorescence between 205 and 285 nm in an air-hydrogen flame at different monochromator slit-widths, are shown in Figure 8.3. The wide slit-widths which were necessary, meant that only elements with fairly widely separated atomic fluorescence wavelengths could be used. Flame emissions cause a slope in the base-line at higher wavelengths, which also restricts the choice of elements which can be used with a scanning technique employing this instrument.

The effects of flame emission and scatter for the zinc 213.8 nm and cadmium 228.8 nm atomic fluorescence are illustrated in Figure 8.4. This shows that at these wavelengths scatter and flame emission are negligible.

FIGURE 8.3

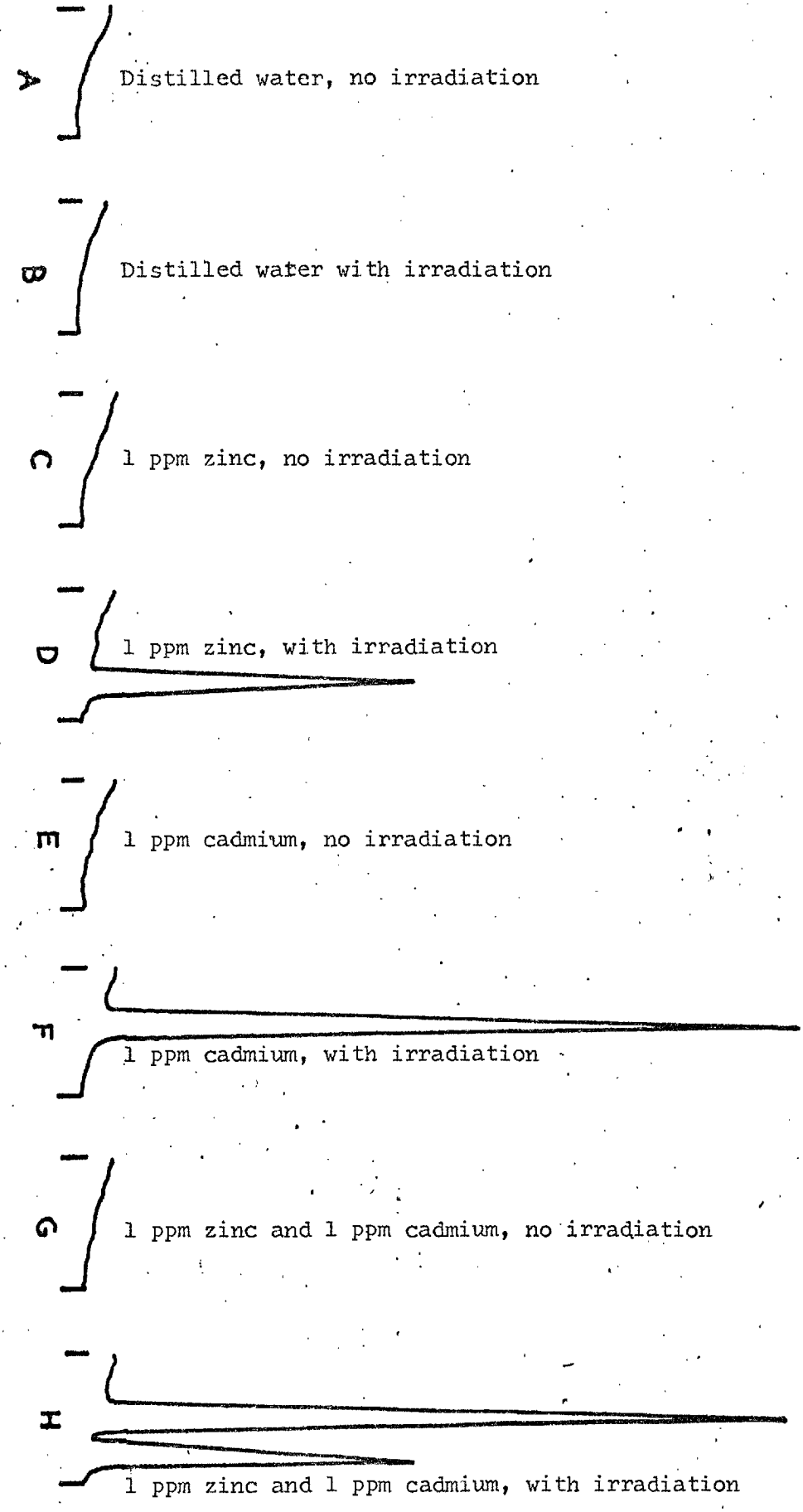
ATOMIC FLUORESCENCE SCANS BETWEEN 200 AND 300 NM FOR ZINC, CADMIUM, IRON AND MANGANESE



A. Distilled water, slit-width 3 nm, gain 10.
B. 0.1 ppm zinc, 0.1 ppm cadmium, 2 ppm iron and 0.5 ppm manganese, slit-width 3 nm, gain 10
C. Distilled water, slit-width 6 nm, gain 8.
D. 0.2 ppm zinc, 0.1 ppm cadmium, 5 ppm iron and 2 ppm manganese, slit-width 6 nm, gain 8.

FIGURE 8.4

ATOMIC FLUORESCENCE SCANS BETWEEN 200 AND 250 NM FOR ZINC AND CADMIUM



With the scanning speed of 75 nm min^{-1} available with this spectrometer, the peak heights were ca. 80% of the steady state signals, and standard deviations in peak height of ca. 6% were obtained.

8.3.2 Selection of operating parameters

The elements to be determined must be analysed in the same flame and under the same instrumental operating parameters. Since it is unlikely that the operating conditions will be optimal for all of the elements to be determined at one time, a compromise must be made, and either the optimal operating parameters for the least sensitively determined element, or the most favourable conditions for the majority of the elements will have to be selected.

The operating parameters used in this work were those which were found to be optimal for the majority of the elements to be determined. The optimal operating conditions for the multi-element determination of zinc, cadmium, nickel and cobalt are discussed below.

Flame conditions. In order to reduce both the flame background emission and the flame noise, and so to obtain a flat base-line for the wavelength scan, a low-background flame, such as argon-separated air-acetylene, is desirable. The flame was slightly fuel lean and flow rates of 0.6 dm^3 min^{-1} acetylene and 8 $dm^3 min^{-1}$ were used. A flow rate of 20 $dm^3 min^{-1}$ argon was necessary to separate this flame with the commercial separator, and 10 $dm^3 min^{-1}$ with the home-made separator. The part of the flame viewed by the monochromator was between 5 and 15 mm above the burner-head.

Monochromator slit-width. The monochromator slit-width must be selected so that the fluorescence lines of the elements whose atomic fluorescence is stimulated by the light source, do not overlap within the spectral band-pass. Preferably this should be arranged so that the peaks produced on the wavelength scan are completely separate, thus enabling more accurate measurements of the peak heights to be made. Since wide spectral band-passes are advantageous in atomic fluorescence, this places a restriction on the

elements which may be determined together in a scanning technique. The maximum monochromator slit-width of 0.3 mm, corresponding to a spectral band-pass of 1 nm, was used throughout this work.

Scanning speed. The speed used for wavelength scanning must be compatible with the response times of the amplification system and the chart recorder. Under certain circumstances it is possible that the scanning speed could also be dependant upon the monochromator slit-width. The response time of the Servoscribe chart recorder, which was slower than that of the amplifier, was ca. 1 second. In order to obtain a faithful response (i.e. peak height = steady state signal), a scanning speed of 25 nm min^{-1} was required. However, the initial experiments with the Southern A1740 spectrometer showed that considerably faster scanning speeds can be used without too greater loss in sensitivity or reproducibility. The chart recorder was operated on the 10 millivolt range at a speed of 30 mm min^{-1} (i.e. 1 nm on the chart paper represented a wavelength scan of 0.83 nm).

8.3.3 Wavelength scans for zinc-cadmium-nickel-cobalt

A typical atomic fluorescence wavelength scan, between 210 and 245 nm, obtained while nebulising a solution containing 0.1 ppm zinc, 0.1 ppm cadmium, 1 ppm nickel and 1 ppm cobalt, is shown in Figure 8.5. The wavelength range scanned includes the major resonance line of each of these elements. The actual scanning time for this wavelength scan was ca. 85 seconds, and the total time for such a determination for the four elements was ca. 100 seconds.

8.3.4 Detection limits

The detection limits obtained for the determination of zinc, cadmium, nickel and cobalt by scanning atomic fluorescence are given in Table 8.1. Due to the use of peak height measurement, the detection limits were defined as the concentration of the element in aqueous solution which produced a peak height equivalent to twice the standard deviation in peak height near the lower limit of the working range. These detection limits are of the same

FIGURE 8.5

ATOMIC FLUORESCENCE SCAN FOR ZINC, CADMIUM, NICKEL AND COBALT

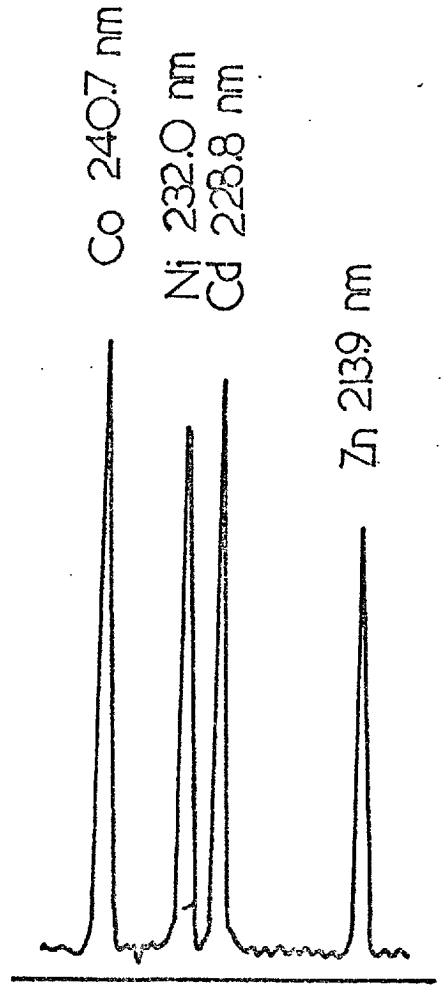


TABLE 8.1

ATOMIC FLUORESCENCE DETECTION LIMITS AND WORKING RANGES FOR ZINC, CADMIUM, NICKEL AND COBALT USING THE SCANNING TECHNIQUE.

Element	Wavelength nm	Working range ppm	Detection limit ppm
Zinc	213.8	0.02-1.5	0.003
Cadmium	228.8	0.02-1.0	0.002
Nickel	232.0	0.2-10	0.02
Cobalt	240.7	0.2-10	0.02

order as those previously obtained for these elements by conventional atomic fluorescence, using dual-element electrodeless discharge lamps and an argon-separated air-acetylene flame (see Table 6.1). Obviously, a direct comparison, even using identical instrumentation, is of little value, due to differences in the definitions of detection limits for scanning and conventional atomic fluorescence. However, it would appear that there is no significant reduction in sensitivity in the scanning technique.

8.3.5 Operating range

The operating range for an element in atomic fluorescence is normally taken as the range of concentrations over which the atomic fluorescence signal is linearly related to the concentration of that element which is nebulised into the flame (i.e. from the detection limit to the upper concentration limit). Atomic fluorescence operating ranges frequently cover several orders of magnitude, and to obtain a reasonable sensitivity over the whole of this concentration range, adjustments of the instrumental gain or of the power supply, and hence the intensity, of the spectral source must be made. Obviously, it is impractical to alter the instrumental operating parameters during a wavelength scan. This places a restriction on the composition of solutions which can be determined by the scanning technique, if a reasonably sensitive determination of each element is to be obtained. Thus more than one dilution of a sample may be necessary to obtain a complete analysis. This is the main outstanding problem with any multi-element technique involving atomic spectroscopy, and was referred to by Dagnall, Kirkbright, West and Wood (62,63) in relation to determinations with their multi-channel atomic fluorescence spectrometer.

For the purposes of this investigation, operating ranges with their lowest point ca. 10 times greater than the detection limits were selected, and calibration curves for each element obtained within these ranges, using one set of operating parameters. These calibration curves were linear, and the operating ranges used for zinc, cadmium, nickel and

cobalt are given in Table 8.1. These operating ranges are merely an example of those which are compatible for use together to enable a sensitive determination of each element to be made with one scan.

8.3.6 Interferences

The effects of 500 ppm concentrations of thirty-seven elements (Viz. Ag, Al, As, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Hg, In, K, Li, Mg, Mn, Na, Nb, Ni, Pb, Se, Si, Sm, Sn, Sr, Ta, Te, Th, Ti, V, W, Zn and Zr) on the atomic fluorescence wavelength scan produced by a solution containing 0.5 ppm zinc, 0.5 ppm cadmium, 5 ppm nickel and 5 ppm cobalt were investigated. These concentrations represented 1000 fold (weight) excesses on zinc and cadmium and 100 fold (weight) excesses on nickel and cobalt. No interference (i.e. less than $\pm$5% deviation in signal) was observed with any of these elements. These observations are in agreement with the results of previous atomic fluorescence interference studies for zinc (91), cadmium (36), nickel (111) and cobalt (64,111).

8.3.7 Scatter

Normally in atomic fluorescence it is possible to back off any signal produced by the reflection or scatter of the incident radiation. This is not possible in a scanning technique. However, with the optical arrangement used, no reflection or scatter was observed, except near the detection limit, when high gains were used or at extremely high concentration levels and even this was negligible.

8.3.8 Reproducibility

The percentage standard deviation in peak height for ten atomic fluorescence wavelength scans obtained while nebulising a solution containing 0.5 ppm zinc, 0.5 ppm cadmium, 5 ppm nickel and 5 ppm cobalt, over a period of one hour, with other solutions nebulised in between, was less than 3% for each of the four elements.

8.3.9 Wavelength scans for other combinations of elements

1. Selenium-nickel-tellurium-cobalt. A typical atomic fluorescence wavelength scan obtained while nebulising a solution containing 1000 ppm selenium, 1 ppm nickel, 10 ppm tellurium and 1 ppm cobalt, is shown in Figure 8.6. This scan was taken between 200 and 245 nm, and thus incorporates the major resonance lines of each of these elements.

2. Nickel-cobalt-iron-manganese. A typical atomic fluorescence wavelength scan obtained while nebulising a solution containing 1 ppm nickel, 1 ppm cobalt, 1 ppm iron and 0.5 ppm manganese, is shown in Figure 8.7. This scan was taken between 227 and 285 nm, and thus incorporates the major resonance line of each of these elements.

8.3.10 Scanning technique with a continuum source

An attempt was made to use a 500 watt xenon arc lamp as the spectral source for the scanning technique. This source had previously been used for the atomic fluorescence determination of several elements (137). The incident radiation from the xenon arc lamp was focussed on to the flame through a Techtron mechanical chopper. With this source, atomic fluorescence signals below 300 nm were particularly weak, as observed previously (137). Therefore, the elements used in this study of the scanning technique were copper (324.7 and 327.4 nm), chromium (357.9, 359.3 and 360.5 nm) and silver (328.0 and 338.0 nm). Even at these higher wavelengths the atomic fluorescence signals produced for these elements were comparatively small, and therefore, reasonably high concentrations had to be used. This enhanced the flame background and flame noise, which in any case are greater at these wavelengths than below 300 nm, and so made it impossible to obtain satisfactory atomic fluorescence scans.

8.4 CONCLUSION

A scanning technique for multi-element determinations by atomic fluorescence spectroscopy in conjunction with dual-element electrodeless discharge lamps appears to be a feasible method of analysis for a number of

FIGURE 8.6

ATOMIC FLUORESCENCE SCAN FOR SELENIUM, TELLURIUM, NICKEL AND COBALT

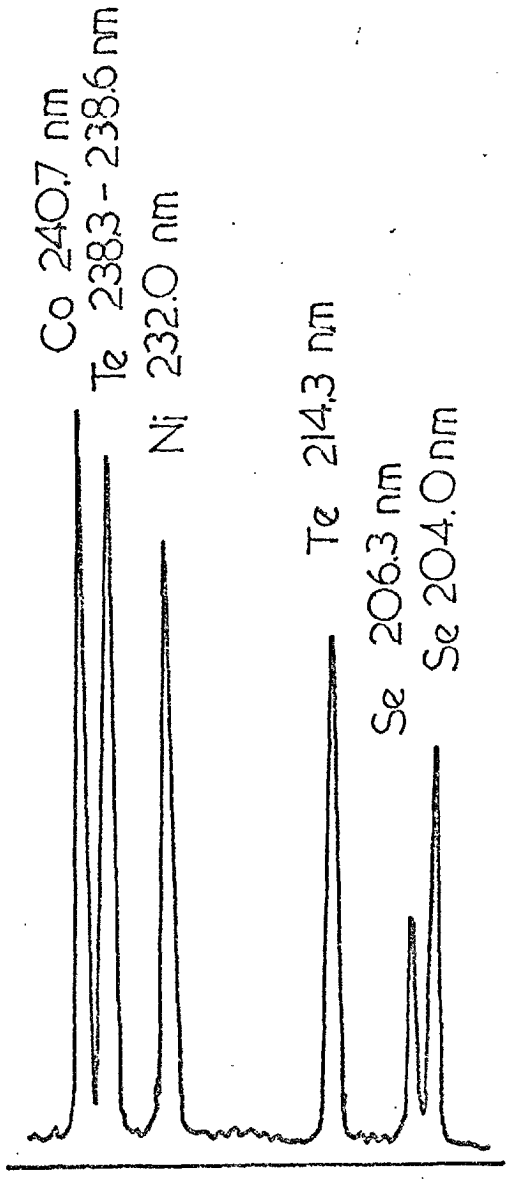
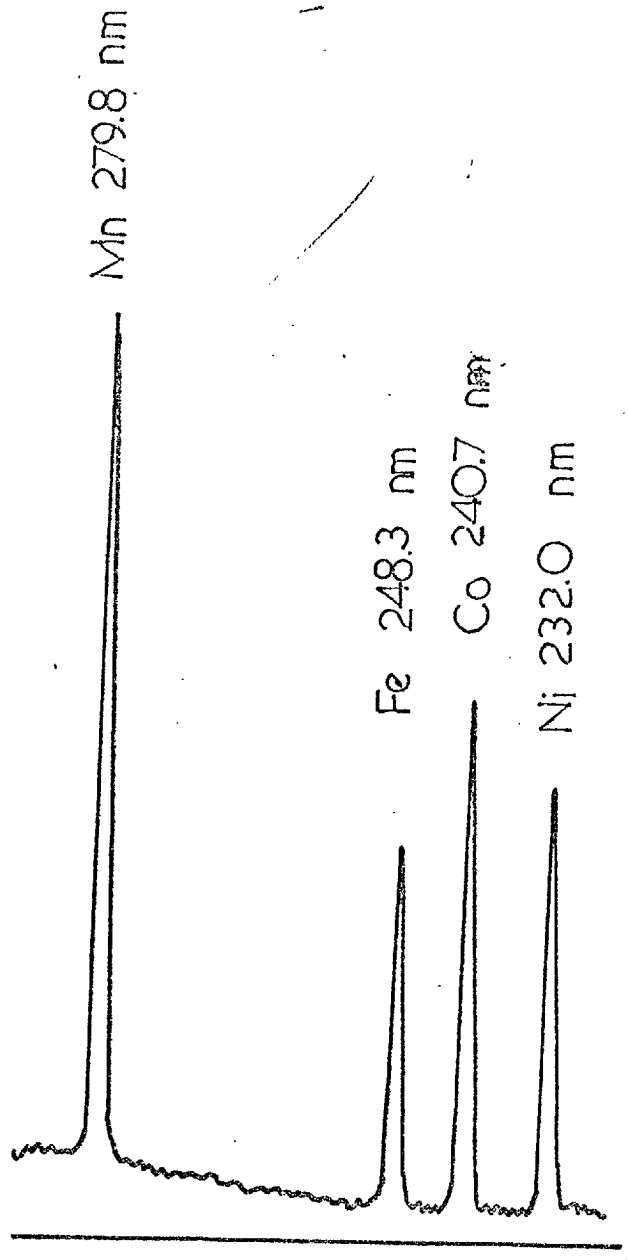


FIGURE 8.7

ATOMIC FLUORESCENCE SCAN FOR NICKEL, COBALT, IRON AND MANGANESE



combinations of elements. The procedure is simple and all of the instrumentation is commercially-available. The sensitivity and selectivity of the technique appear to be as good as for conventional atomic fluorescence with the same type of source and flame.

The time taken for a multi-element determination of zinc, cadmium, nickel and cobalt by the scanning technique is ca. 100 seconds, while that for selenium, tellurium, nickel and cobalt is ca. 140 seconds, and that for nickel, cobalt, iron and manganese is ca. 150 seconds. These times may be improved upon by using a faster scanning speed without too great a loss in sensitivity or reproducibility.

The main disadvantage of the technique, as with any multi-element atomic spectrometric method, is that the solutions used must be of a limited concentration with respect to each element, to avoid more than one dilution, and hence more than one determination of each sample.

The two-port power divider is used in this investigation of the scanning technique for two dual-element electrodeless discharge lamps with two different elements in each. An alternative is to use two lamps with one common element (e.g. lead-cadmium and lead-zinc). This would effectively double the intensity of lead radiation directed on to the flame; lead being the least sensitively determined of these three elements.

The sensitivity of the scanning technique could be improved by placing a curved mirror on the opposite side of the flame to the electrodeless discharge lamps.

The number of elements which can be determined by the scanning technique could be increased by the use of a continuum source. The main difficulty which was found with this was the low intensity of continuum sources. It is probable that an aluminium ellipse (114) would give a ten-fold increase in sensitivity with a continuum source. If the scanning atomic fluorescence technique could be made viable with a continuum source, it is

possible that combined atomic fluorescence/atomic emission scanning could be undertaken. Combined atomic fluorescence/atomic emission determinations have already been carried out, using a continuum source with conventional instrumentation (132).

CHAPTER 9

THE DETERMINATION OF MERCURY BY NON-DISPERSIVE ATOMIC FLUORESCENCE SPECTROSCOPY USING THE CARBON FILAMENT ATOM RESERVOIR

9.1 INTRODUCTION

The advantages to be found in the use of non-flame atom reservoirs for analytical atomic fluorescence spectroscopy, and the various non-flame devices which have been employed, have recently been reviewed (162). The first carbon filament atom reservoir was developed by West and Williams (79). A number of modifications of this atom reservoir, including a commercially-available version (Varian Techtron Pty. Ltd., Carbon Rod Atomiser, Model 61), have been extensively used for both atomic absorption and atomic fluorescence analysis (57-61,83,238-254). Although almost forty elements have been determined by atomic absorption with the carbon filament atom reservoir, only about a dozen have so far been determined by atomic fluorescence (57-61, 79,83,242,244). The absolute detection limits obtained by atomic fluorescence were generally of the order of 10^{-12} grams for 1 μl of solution (i.e. 0.001 ppm in the solution). The atomic absorption analyses of several trace elements in oils (240,243,253), clinical and biological materials (60,249-252), soils (245) and pigments (246) have been reported, whilst the only atomic fluorescence application of the carbon filament atom reservoir is the determination of lead in blood (60).

Optical filters in conjunction with a solar-blind photomultiplier have been employed in place of a monochromator in several atomic fluorescence investigations, using flame cells (44,45,62,63,66,70,71,103). The most important advantage in the use of optical filters is that the atomic fluorescence from a large solid angle may be directed on to the photomultiplier. This chapter describes the atomic fluorescence determination of mercury with the carbon filament atom reservoir, together with an optical filter and a solar-blind photomultiplier in place of the monochromator. An absolute detection limit of 5×10^{-11} grams (i.e. 0.05 ppm in the solution) has been previously reported for the determination of mercury at 253.7 nm with the carbon filament atom reservoir, and using a spectrometer fitted with a monochromator (59).

9.2 EXPERIMENTAL

9.2.1 Apparatus

9.2.1.1 General arrangement

The general arrangement of the instrumentation used for the atomic fluorescence determination of mercury is illustrated in Figure 9.2.

9.2.1.2 Source and incident optics

A 240 mm long by 5 mm internal diameter electrodeless discharge lamp, containing ca. 100 mg of mercury and 3 torr of argon (198), was operated at ca. 25 watts incident power in a three-quarter wave resonant cavity, powered from a Microtron 200 microwave generator. Two 35 mm diameter biconvex lenses of focal length 70 mm were used to focus the radiation from the electrodeless discharge lamp to a point just above the notch at the centre of the carbon rod. Initially the resonant cavity and the two lenses were supported on a metal framework directly above the carbon filament. However, this led to the reflection of the incident radiation from the carbon rod onto the photomultiplier. When the carbon rod was heated this reflection decreased and produced an apparent absorption signal, which masked the atomic fluorescence signal. This optical arrangement has been used previously for resonance fluorescence (242,244) when this effect was not observed. The resonant cavity and lenses were finally mounted on a metal framework horizontally and at right angles to the optical bar. This optical arrangement has the disadvantage that the end-caps of the electrodes prevent some of the incident radiation from being directed onto the atomic population. A modification of the carbon filament atom reservoir, involving the use of split end-caps to overcome this disadvantage, is described in Chapter 10. The radiation from the ends of the electrodeless discharge lamp, which protruded from the resonant cavity, was shielded from the photomultiplier by a screen.

FIGURE 9.1

CARBON FILAMENT ATOM RESERVOIR

A. Base

B. Water-cooled electrodes

C. Laminar flow box

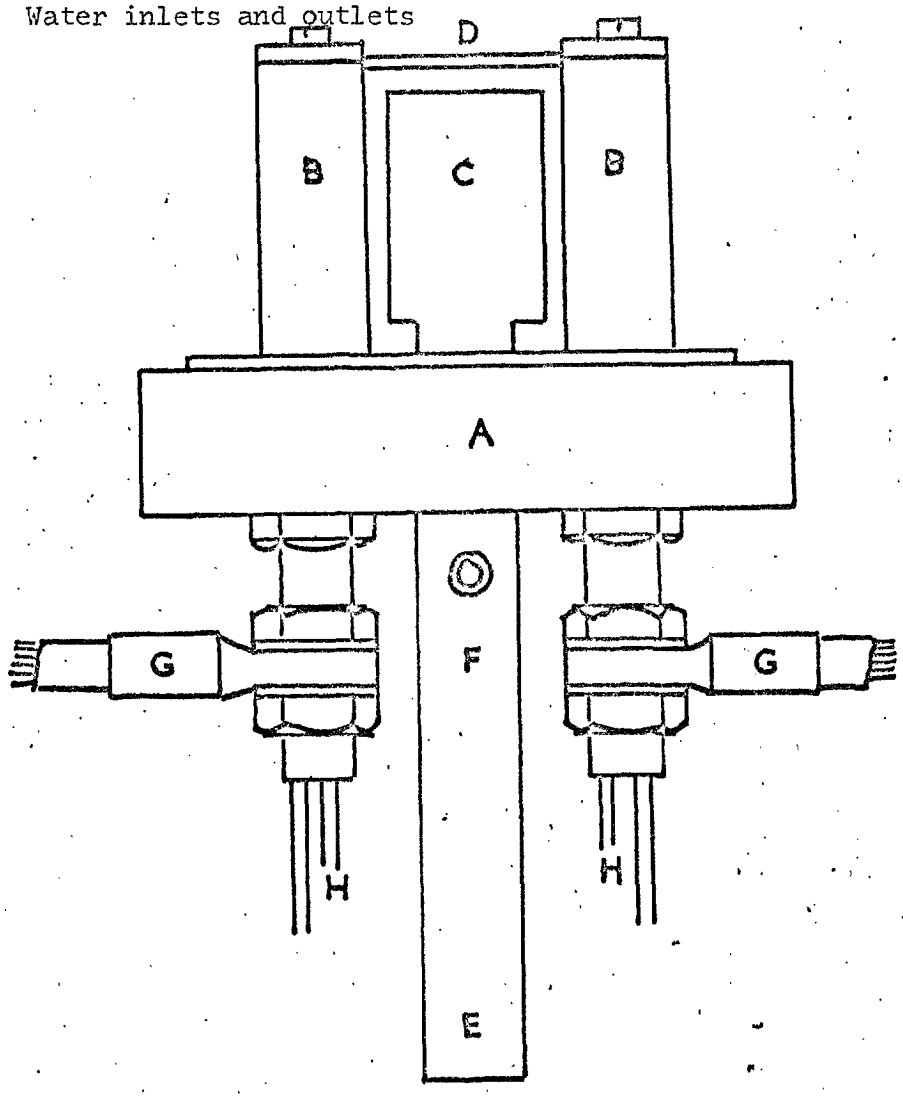
D. Carbon filament

E. Support stem

F. Inlet for shielding gas

G. Transformer terminals

H. Water inlets and outlets



9.2.1.3 Carbon filament atom reservoir

A diagram of a carbon filament atom reservoir of the type used in this investigation is shown in Figure 9.2. This was as described previously by Alder and West (83), except that the water cooling system for the electrodes had been modified so that both electrodes were cooled separately and the link between the electrodes was eliminated. The power supply to the carbon filament was from the mains via a Variac transformer to a Keston transformer, capable of delivering up to 100 amps at 5-8 volts. The carbon filament atom reservoir was mounted on a saddle on the optical bar so that the carbon rod was at right angles to the direction of the measured fluorescent radiation.

9.2.1.4 Optics and photomultiplier

A third biconvex lens of the same dimensions as those described above, was mounted in a lens holder on a saddle on the optical bar 14 mm from the carbon filament, to focus the atomic fluorescence onto the photomultiplier. A 25 mm diameter optical filter (Baird Atomic Ltd., Type 14-08-7) was held in a cardboard mount on the front of the photomultiplier. This filter peaked at 250±3 nm and gave greater than 50% of its peak transparency for a band of 7-10 nm. The transparency of the filter was 10-15% at its peak wavelength. An EMI 9616B solar-blind photomultiplier was mounted on a saddle on the optical bar 14 mm behind the biconvex lens. The power supply was a Brandenburg Model 472R photomultiplier power supply.

9.2.1.5 Amplifier and recorder

The signal from the photomultiplier was fed to an operational amplifier circuit based on a Philbrick type PF85AU amplifier. The circuit of the amplification system is shown in Figure 9.3. This gave x10, x30 and x100 amplification, a variable gain and an input offset. The output from the amplifier was fed to a Servoscribe chart recorder.

9.2.2 Reagents

Mercury stock solution (1000 ppm). 0.1354 g of A.R. grade mercuric chloride were dissolved in deionised water. 5 cm^3 of A.R. grade hydrochloric

FIGURE 9.2

INSTRUMENTAL ARRANGEMENT FOR NON-DISPERSIVE ATOMIC FLUORESCENCE WITH THE CARBON FILAMENT ATOM RESERVOIR

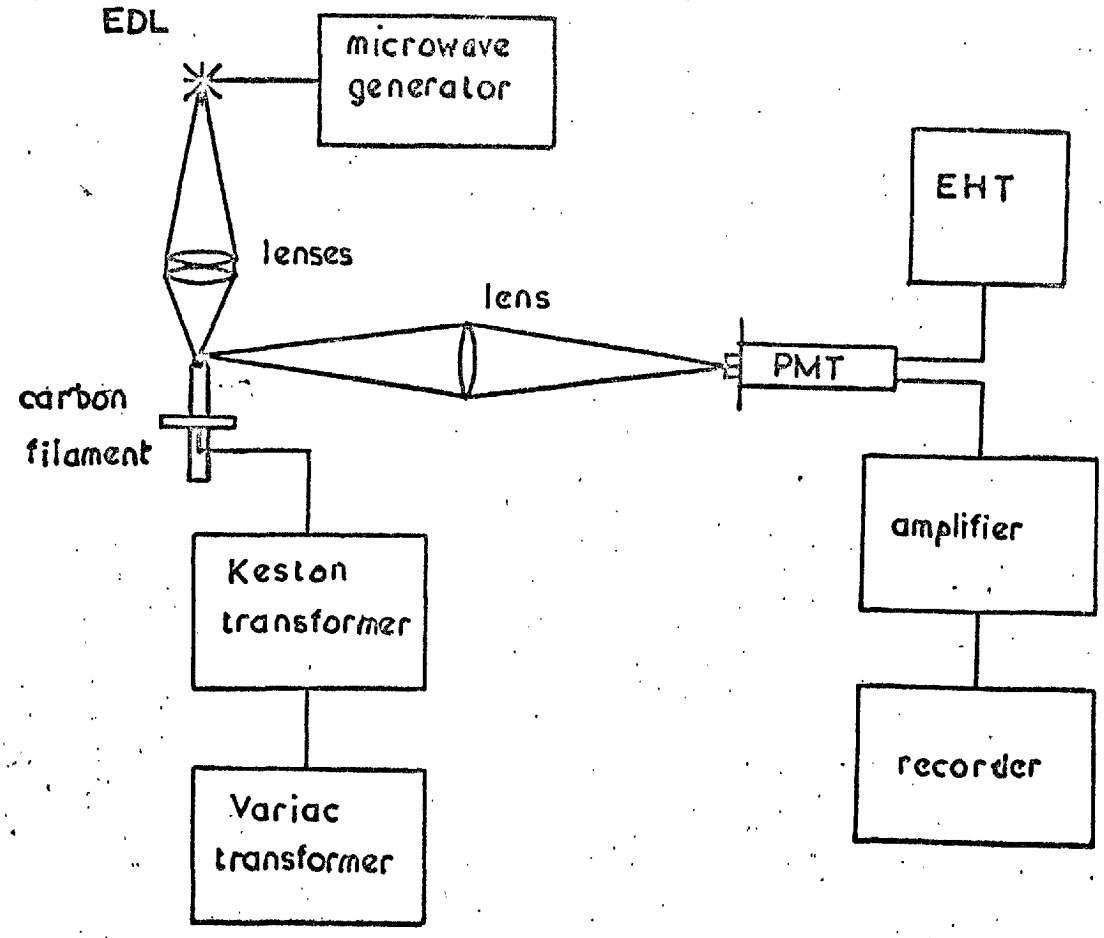
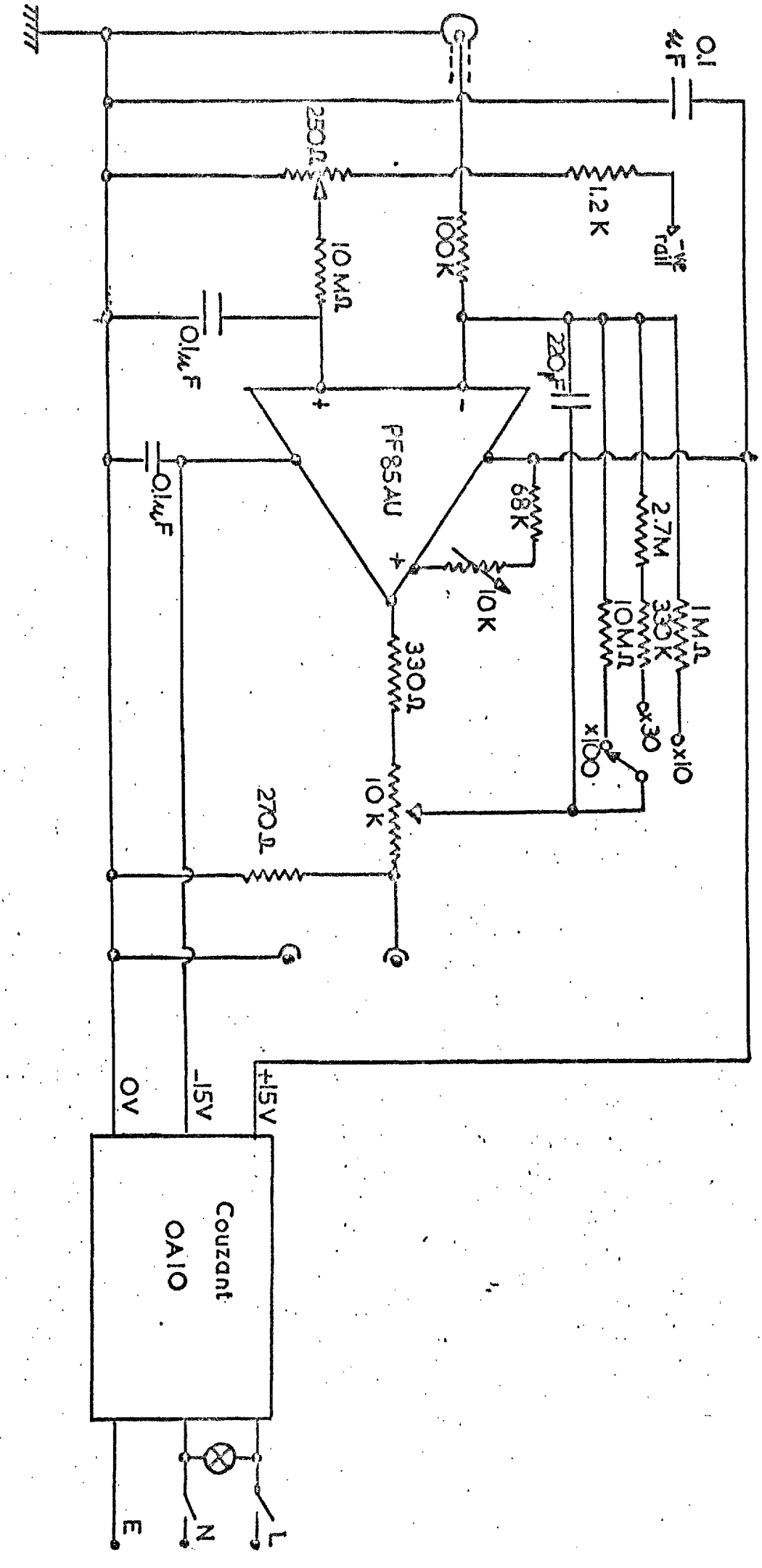


FIGURE 9.3 CIRCUIT DIAGRAM OF OPERATIONAL AMPLIFIER



acid were added and the solution diluted to 100 cm^3 with deionised water. This solution was diluted as required immediately before use.

9.2.3 Procedure

The general procedure for the operation of the carbon filament atom reservoir has been described several times (57-59,83), and will only be outlined here. The argon sheathing gas and the cooling water to the electrodes were turned on. A 1 µl aliquot of the sample solution was transferred to the notch at the centre of the carbon rod, using a 1 µl micro-pipette. The micro-pipette had previously been treated with 'Repelcote' water repellant. The filament current was switched on and off as quickly as possible, to heat the filament to 150-200 ^{o}C to evaporate the sample solution. After a few seconds the Servoscribe chart recorder was switched on at 600 mm min^{-1} and the filament current switched on for ca. 3 seconds to heat the filament to ca. 1400 ^{o}C to atomise the sample. The atomic fluorescence peak height on the recorder chart was measured.

9.3 RESULTS AND DISCUSSION

9.3.1 Performance of sheathing gas box

The performance of a new type of sheathing gas box for use with the carbon filament atom reservoir, which had been designed in the departmental workshop, was evaluated. This box had one ca. 2 mm wide slot immediately beneath the carbon rod. The carbon rod was weighed initially and after ten heatings. An argon flow rate of 4 dm^3 min^{-1} was used. The filament current was switched on ten times for ca. 5 seconds, with twenty seconds cooling time in between each heating. The loss in weight of the rod with the new type of sheathing box was between 16 and 20%. This compares with 2% with a conventional sheathing box and 20% without inert gas sheathing. The poor performance of this type of sheathing gas box was attributed to the entrainment of air with the inert gas.

9.3.2 Determination of mercury

The instrumental operating parameters employed for the determination of mercury were as given below: argon flow rate 3.5 dm^3 min^{-1}, power supply to photomultiplier 60% on scale, amplification x100 and chart recorder 2 millivolt range. Under these operating conditions the mercury atomic fluorescence peaks appeared ca. 1 second after the filament current had been switched on. A second peak, due to the glowing of the carbon rod, appeared after ca. 2 seconds. Therefore, the atomic fluorescence peak was completely separate. A detection limit of 0.25 ppm (2.5×10^{-10} g absolute detection limit) was obtained. The upper concentration limit was 10 ppm (10^{-8} g). This detection limit is five times worse than that previously reported for the atomic fluorescence determination of mercury with the carbon filament atom reservoir, using a spectrometer fitted with a monochromator (59). A ten-fold improvement in the detection limit would be expected, due to the removal of the monochromator, as was found with flame cells (65,66). However, the use of the filter would reduce the atomic fluorescence signal to 10-15% or less of its true value. Therefore, the detection limit of 0.25 ppm is of the order that would be expected with this instrumentation. It is possible that this could be improved upon by careful alignment of the optical components. The modification of the electrode end-caps described in Chapter 10 would also be an advantage.

9.4 CONCLUSION

The results obtained for the determination of mercury show that a monochromator is not necessary for atomic fluorescence analysis with the carbon filament atom reservoir, and a non-dispersive detection system, similar to those reported elsewhere for use with flame cells, may be employed. In the following discussion, which refers to some of the limitations of the instrumentation used, it should be noted that some of the components were selected primarily for use with the arrangement for the continuous operation of the carbon filament atom reservoir, which is described in Chapter 10, when

a continuous atomic fluorescence signal, rather than a transient signal, would be obtained.

The slow response time (ca. 1 second) of the Servoscribe chart recorder restricts the range of elements which may be determined with this instrumentation to the more volatile elements, which are easily atomised. The characteristics of the EMI 9616B solar-blind photomultiplier further limits the range of elements which may be determined to those with atomic fluorescence wavelengths below ca. 275 nm. In view of the above considerations, this instrumentation is only really suitable for the atomic fluorescence determination of a relatively small group of elements. However, this group includes zinc, cadmium, mercury, tellurium, selenium, arsenic and antimony, the trace determination of all of which is becoming increasingly important. The determination of these elements with non-dispersive instrumentation is advantageous since some of them have several atomic fluorescence wavelengths.

The range of elements which may be determined could be increased by the use of a fast response recorder, such as an oscillograph. The use of a different type of solar-blind photomultiplier, with more favourable characteristics, would also extend the range of elements which can be determined. However, the determination of elements with atomic fluorescence wavelengths above ca. 320 nm would require the use of a conventional photomultiplier in conjunction with the relevant filter.

A completely non-dispersive system, without optical filters, is also possible, although this would require some shielding of the photomultiplier and the possible use of slits to reduce the background observed by the photomultiplier. This was found necessary with the non-dispersive system used with a flame cell, described in Chapter 11, when lower instrumental gains were used than those necessary with the carbon filament atom reservoir. The use of slits would reduce the field of view, and therefore, some of the advantage in the use of a non-dispersive system would be lost.

The emission from the hot carbon rod is also likely to be of more significance when no filter is used.

The use of objective mirrors in place of lenses for focussing the incident and fluorescenct radiation from a reasonably large solid angle, would overcome these difficulties, and should provide good results for completely non-dispersive atomic fluorescence determinations with the carbon filament atom reservoir.

CHAPTER 10

THE CONTINUOUS OPERATION OF THE CARBON FILAMENT ATOM RESERVOIR

10.1 INTRODUCTION

10.1.1 Advantages of continuous operation of the carbon filament atom reservoir

One of the major advantages to be found in the use of the carbon filament atom reservoir as a means of producing populations of atoms for atomic absorption and atomic fluorescence spectroscopy is that extremely small volumes may be used. This has been reflected in some of the applications of the carbon filament (e.g. clinical analysis (60,247,249-252)). Since discrete samples are used, producing transient absorption or fluorescence signals, fast-response amplifiers and recorders must be employed for the determination of all except the most volatile elements. Therefore, in certain applications, where large sample volumes are readily available, a continuous technique may be advantageous when compared with the discrete sampling method. This would certainly increase the versatility of the carbon filament atom reservoir.

A continuous sampling technique would mean that any analyses which may be carried out with a flame could also be carried out with the carbon filament atom reservoir. The carbon filament could be installed in many locations where a flame would be unacceptable, and so would make automatic on-line atomic spectrometric analysis a real possibility.

10.1.2 Sampling technique

Although a pneumatic nebuliser is normally used with flames to introduce the sample solution, a number of other methods have been suggested. These have been reviewed previously (255-257).

The use of platinum wire for the introduction of the sample solution into a flame was first reported by Mitscherlich in 1862 (258). The sample solution was drawn up a bunch of small platinum wires by capillary action. Various other applications of platinum wires and gauzes as means of sample introduction have been described (259-262). A length of stainless

steel wire is used as the sample transport system in a number of Pye-Unicam liquid chromatographs (263). The application of this sample transport system to the continuous operation of the carbon filament atom reservoir is described in this chapter.

10.2 APPARATUS

10.2.1 General instrumentation

The general arrangement of the instrumentation required for the continuous operation of the carbon filament atom reservoir is illustrated in Figure 10.1. The electrodeless discharge lamp and power supply, optical filter, focussing lenses, optical bar, power supply to the carbon filament, solar-blind photomultiplier and power supply, operational amplifier and chart recorder were as described in Chapter 9, when used with the conventionally operated carbon filament atom reservoir. The additional equipment and the modifications necessary for the continuous system are discussed below.

10.2.2 Carbon filament

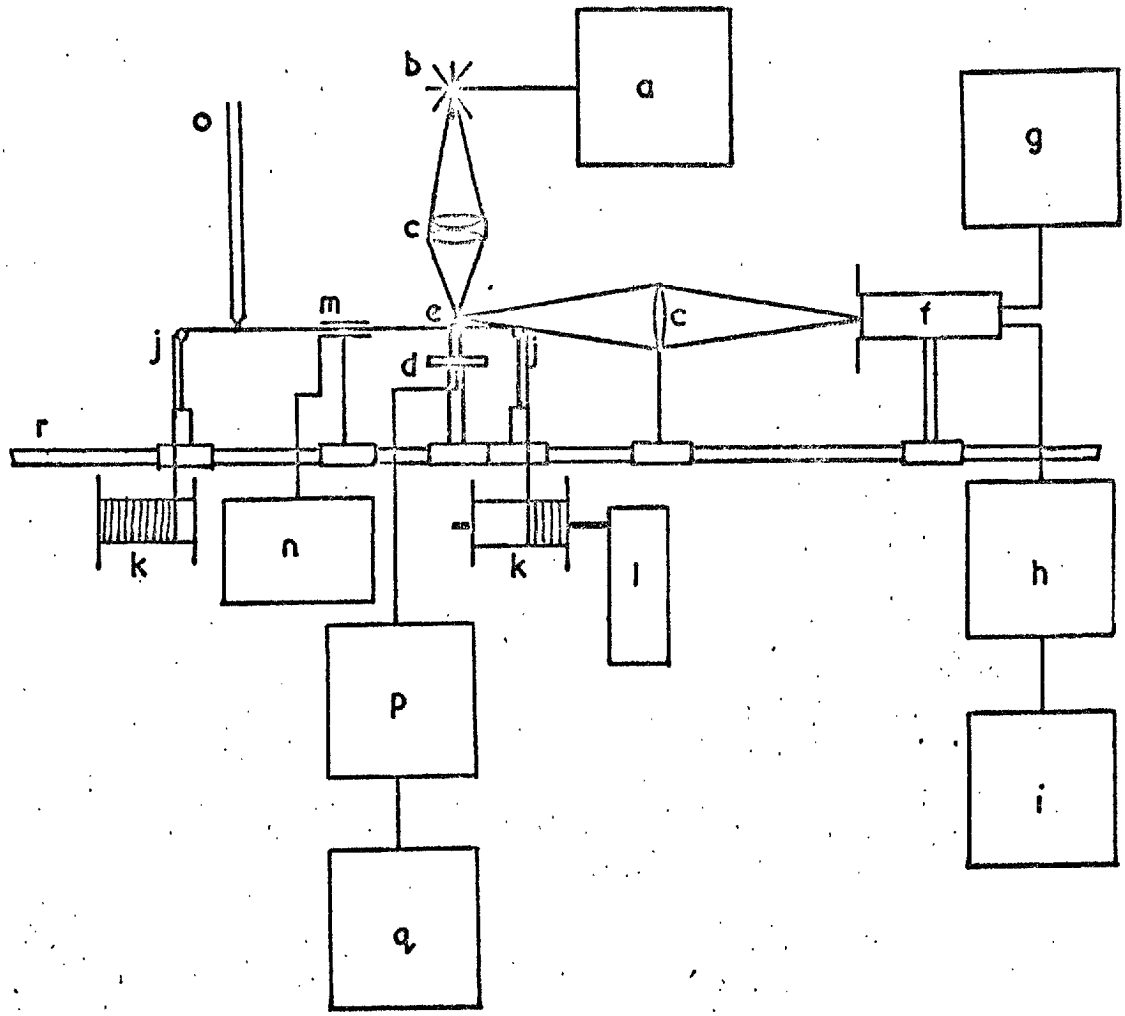
Since the carbon filament will be operated continuously at high temperatures for comparatively long periods, the 2 mm diameter carbon rod normally used was considered to be inadequate, due to the relatively short life-time of this size of rod. Therefore, 4 mm diameter carbon rod was employed, with a groove filed in the top, large enough for the transport wire to pass through without touching the rod. This arrangement is shown in Figure 10.2. The possibility of drilling a hole through the centre of the carbon rod for the transport wire to pass through (i.e. a mini-Massmann type rod (60,249-254)) was also considered. However, this design of rod is not really practical for atomic fluorescence determinations, and each time the replacement of the carbon rod became necessary the transport wire would have to be threaded through the hole in the rod.

10.2.3 Carbon filament holder

The only alteration necessary to the standard type of carbon filament holder was the enlargement of the electrode end-caps to accommodate the 4 mm

FIGURE 10.1

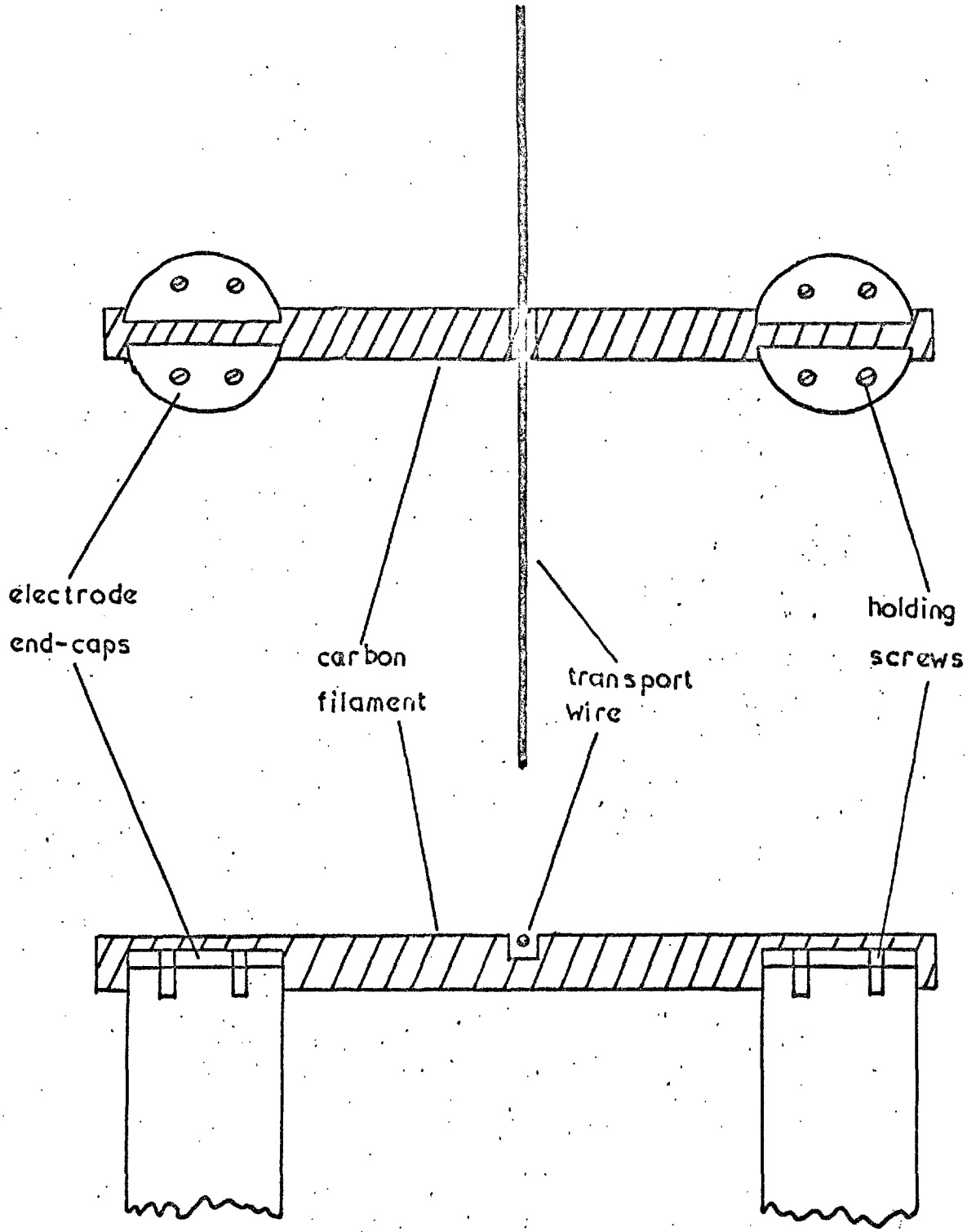
INSTRUMENTAL ARRANGEMENT FOR CONTINUOUS CARBON FILAMENT ATOM RESERVOIR



a. Microwave generator
b. Electrodeless discharge lamp
c. Lenses
d. Carbon filament atom reservoir
e. Wire
f. Solar-blind photomultiplier
g. E.H.T. supply
h. Operational amplifier
i. Servoscribe chart recorder
j. Pulley wheels
k. Winding spools
l. Drive motor
m. Heating coil
n. Simmerstat controller
o. Sample introduction
p. Keston transformer
q. Variac transformer

FIGURE 10.2

MODIFIED CARBON FILAMENT



diameter carbon rod. The opportunity was taken to design some split-end-caps, with counter-sunk holding screws, which enabled the carbon rod to be elevated above the level of the end-caps. This is illustrated in Figure 10.2. This modification allowed the instrumentation to be arranged so that the beam of incident radiation was in the same horizontal plane as the measured fluorescent radiation, instead of the normal practice of directing the incident radiation onto the carbon rod from above. (For clarity the normal arrangement is shown in Figure 10.1). The modified optical arrangement has the advantages of preventing the periodic sooting of the focussing lenses by small particles of carbon, and reducing the reflection of the incident radiation from the carbon rod onto the photomultiplier.

10.2.4 Transport wire

A ca. 9 mile length of ca. 0.12 mm diameter stainless steel wire and winding spools (Pye Unicam Ltd., Cambridge, U.K. Part 792269), which are normally employed as the sample transport system in a number of Pye liquid chromatograph arrangements (263), were used for an initial investigation of the continuous operation of the carbon filament atom reservoir. Stainless steel is not the ideal material for the transport wire, since the range of elements which may be determined is restricted to the more volatile elements which are not contained in the stainless steel. Higher melting point wire, manufactured from elements such as hafnium, tantalum or tungsten would be preferable, but the cost of such wire is prohibitive. A long length of wire was chosen in preference to a shorter continuous loop, since the drive mechanism is considerably simplified, and there would be no unevenness in the wire where the join in the loop was fabricated. If in a later arrangement the more expensive high melting point wire was used, a continuous loop would probably be preferable in reducing the length of wire required, and hence the costs, in spite of the above disadvantages.

10.2.5 Drive mechanism

The optimal speed for driving the transport wire for the Pye liquid chromatograph arrangements is between 3 and 30 cm sec^{-1} (263). It is probable

that a range of speeds of this order will also be suitable for use with the continuous carbon filament atom reservoir, although the main factor determining the drive speed may well be the rate at which the sample can be atomised off the wire, rather than the rate at which the sample can be introduced onto the wire. The speed at which the sample is atomised off the wire will depend upon the volatility of the element which is being determined, and so if the system is to be used for a number of elements, a range of speeds will be required. Therefore, a variable speed motor would be preferable to a single constant speed motor, although the former may be subject to slight fluctuations due to variations in the mains electricity supply. A Citenco variable speed stirrer motor (Model KQPS 24) was employed to drive one of the winding spools. This provided a choice of speeds between 10 and 50 r.p.m., which in conjunction with the transport wire winding spools gave most of the desired range of speeds. Two pulley wheels were necessary to support the transport wire, one before the sample introduction point and one after the carbon filament. The latter of these pulleys was spring loaded to maintain a constant tension in the transport wire, where it passes over the carbon rod.

10.2.6 Sample introduction

In the Pye liquid chromatograph arrangements the sample solution is introduced onto the transport wire via a narrow vertical stainless steel tube. The end of the tube is split, and the transport wire passes through the split and becomes coated with the sample solution, which runs down the tube at a fixed rate. An alternative system is to pass the transport wire through a trough containing the sample solution, in which the wire would become wetted. A further possibility is to use capilliary action to coat the transport wire. The sample solution would pass up a capilliary and coat the wire which touches the top of the capilliary.

10.2.7 Sample evaporation

Normally with the carbon filament atom reservoir the sample is evaporated on the carbon rod in an initial heating stage before atomisation.

This is not possible with a continuous system. Therefore, a heating coil, controlled by a Simmerstat heater control, was placed immediately in front of the carbon rod, to evaporate the sample solution.

10.3 CONCLUSION

Due to prolonged delays in the departmental workshops, the necessary drive mechanism has not yet been constructed, and so the proposed system for the continuous operation of the carbon filament atom reservoir has not yet been tested.

CHAPTER 11

THE USE OF A NON-DISPERSIVE ATOMIC FLUORESCENCE SPECTROMETER FOR THE DETERMINATION OF ZINC IN SOIL EXTRACTS AND NON-FERROUS METAL ALLOYS

11.1 INTRODUCTION

The advantages to be found in the use of non-dispersive detection systems in atomic fluorescence spectroscopy were discussed in Chapter 2. After some preliminary investigations of non-dispersive atomic fluorescence spectroscopy (43,171), Larkins and Willis (65,66) have described the construction and operation of a simple non-dispersive atomic fluorescence spectrometer. These workers have used this spectrometer for the determination of approximately thirty elements, in each case attaining better detection limits than those obtained with similar instrumentation incorporating a monochromator. The respective detection limits for zinc were 0.0003 ppm and 0.003 ppm (65), in an air-acetylene flame with a high-intensity hollow cathode lamp. Vickers et al (172) have also made an extensive study of non-dispersive atomic fluorescence.

This chapter describes the use of the instrumentation which was described in Chapter 9, in conjunction with an argon-separated air-acetylene flame, for the determination of zinc in soil extracts and non-ferrous metal alloys by non-dispersive atomic fluorescence spectroscopy.

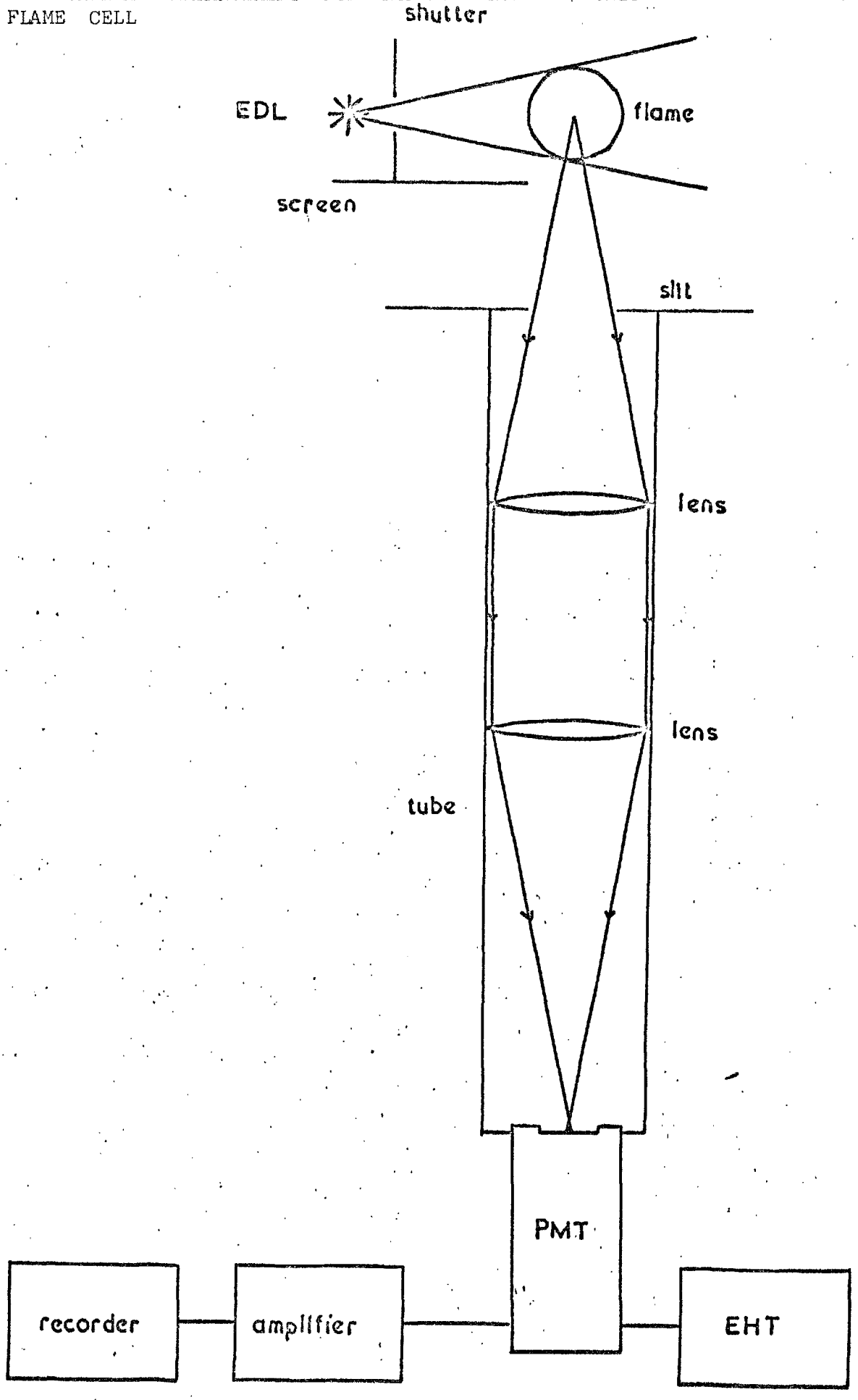
11.2 EXPERIMENTAL

11.2.1 Apparatus

The general arrangement of the instrumentation for non-dispersive atomic fluorescence spectroscopy is shown in Figure 11.1.

The spectral source was a zinc electrodeless discharge lamp, operated at 60 watts incident power in a three-quarter wave resonant cavity which was powered from a Microtron 200 microwave generator. A slightly fuel-lean argon-separated air-acetylene flame was supported on the modified Unicam SP900 air-acetylene burner and nebuliser unit, described in Chapter 3. The EMI 9616B solar-blind photomultiplier was used without an optical filter. The photomultiplier power supply, operational amplifier and chart recorder were as described in Chapter 9. The burner, lenses and photomultiplier were arranged on the optical bar. A slit of 12 mm diameter was positioned 35 mm

FIGURE 11.1
INSTRUMENTAL ARRANGEMENT FOR NON-DISPERSIVE ATOMIC FLUORESCENCE WITH A FLAME CELL



from the centre of the flame. The light path from this slit to the photomultiplier was enclosed in a metal tube to reduce the background radiation and the area of the flame observed. The shutter arrangement, described in Chapter 3, was used in conjunction with the electrodeless discharge lamp.

The atomic absorption measurements were made with a Techtron AA4 atomic absorption spectrometer, using an air-acetylene flame burning on a 100 mm long path burner. The spectral source was a zinc hollow cathode lamp operated at the manufacturers recommended power. A monochromator slit-width of 0.1 mm was used.

11.2.2 Reagents

Zinc stock solution (1000 ppm). 1.0000 g of A.R. grade zinc metal was dissolved in the minimum volume of A.R. grade hydrochloric acid and diluted to 1 dm^3 with distilled water. This solution was diluted as required immediately before use.

2.5% (v/v) acetic acid solution. 25 cm^3 of A.R. grade glacial acetic acid were dissolved and diluted to 1 dm^3 with distilled water.

Strontium chloride solution. 30.43 g of A.R. grade strontium chloride were dissolved and diluted to 100 cm^3 with distilled water.

Hydrochloric acid, nitric acid and sulphuric acid. A.R. grade.

11.2.3 Procedure for the analysis of soils

The extraction technique previously employed by Dagnall, Kirkbright, West and Wood (63) was employed. 2 g of the air-dried soil were weighed into a 250 cm^3 stoppered conical flask. 80 cm^3 of the 2.5% (v/v) acetic acid solution were added. The flask was shaken overnight (ca. 16 hours) with a mechanical agitator. The solution was filtered and washed into a 100 cm^3 volumetric flask. 1.5 cm^3 of the strontium chloride solution were added and the solution diluted to volume with distilled water. This procedure was carried out in duplicate for each soil sample.

A 10 ppm zinc solution was prepared from the 1000 ppm zinc stock solution. A series of standard solutions between 0.1 and 1.0 ppm were prepared

by transferring 10, 5, 2 and 1 cm^3 aliquots of this solution into a series of 100 cm^3 volumetric flasks. 80 cm^3 of the 2.5% (v/v) acetic acid solution and 1.5 cm^3 of the strontium chloride solution were added and the solutions diluted to volume. A blank solution was prepared containing 80 cm^3 of 2.5% (v/v) acetic acid solution and 1.5 cm^3 strontium chloride solution for every 100 cm^3 of the solution.

The blank solution was nebulised into the argon-separated air-acetylene flame. With the radiation from the electrodeless discharge lamp blocked off, the thermal emission signal was backed off, using the input offset on the operational amplifier. The flame was illuminated with the radiation from the source, and no increase in signal was observed. The highest concentration standard solution was nebulised, and with the radiation from the source blocked off, there was no significant increase in the thermal emission signal. The flame was illuminated and the atomic fluorescence signal measured. This procedure was repeated with the other standard and sample solutions. As usual in atomic fluorescence determinations a standard solution was measured in between each unknown solution.

11.2.4 Procedure for the analysis of non-ferrous metal alloys

For alloys containing 0.03 to 0.5% zinc 0.1-0.2 g of the metal alloy was weighed into a 100 cm^3 beaker. 5 cm^3 of A.R. grade hydrochloric acid and 2.5 cm^3 of A.R. grade nitric acid were added. The beaker was covered with a watch glass and heated to dissolve the alloy in the usual manner. (For sample B.C.S. 300 2.5 cm^3 of A.R. grade hydrochloric acid, 2.5 cm^3 of A.R. grade nitric acid and 2.5 cm^3 of A.R. grade sulphuric acid were necessary to dissolve the alloy). When all of the alloy had dissolved, the solution was diluted to ca. 50 cm^3 with distilled water and filtered through a filter paper, collecting the filtrate and washings in a 100 cm^3 volumetric flask. The solution was diluted to volume with distilled water. 10 cm^3 of this solution was pipetted into a 100 cm^3 volumetric flask and diluted to volume with distilled water. For alloys of different zinc

concentrations, proportionate weights of sample were taken or dilutions carried out so that the final solution contained 0.1-1.0 ppm of zinc.

A series of zinc standard solutions between 0.1 and 1.0 ppm were prepared by diluting the zinc stock solution with distilled water.

The standard and sample solutions were nebulised into the flame as for the soil analysis. The atomic fluorescence signals of the sample solutions were compared with those of the standard solutions.

11.3 RESULTS AND DISCUSSION

11.3.1 Analysis of soil extracts

The calibration curve for the range used was linear and passed through the origin. The results for the determination of zinc by non-dispersive atomic fluorescence spectroscopy in eight soils are compared with results obtained by the standard atomic absorption procedure in Table 11.1.

11.3.2 Analysis of non-ferrous metal alloys

The results for the determination of zinc in a number of different non-ferrous metal alloys, mainly from the B.C.S. range, are given in Table 11.2, together with the certificate values.

11.4 CONCLUSION

The above results illustrate the application of non-dispersive atomic fluorescence spectroscopy to the analysis of technical materials. The results obtained for the determination of zinc in soils and a variety of non-ferrous metal alloys compare favourably with those by standard analysis.

The working range used for the calibration curve (0.1-1.0) is about one thousand times greater than the detection limit which should be obtainable in an argon-separated air-acetylene flame (e.g. In Table 6.1, a detection limit of 0.001 ppm with a zinc-cadmium dual-element electrodeless discharge lamp). This high working range was necessary since the instrumentation employed was not particularly suitable for use with a non-dispersive flame technique. The d.c. amplification system was designed for measuring the less noisy signal produced with the carbon filament atom reservoir, with very

TABLE 11.1

ATOMIC FLUORESCENCE DETERMINATION OF ZINC IN SOILS.

SOIL SAMPLE	ATOMIC ABSORPTION (ppm)	NON-DISPERSIVE ATOMIC FLUORESCENCE (ppm)
1	0.7	0.5
2	1.5	1.4
3	19.0	19.3
4	2.6	2.5
5	1.5	1.4
6	4.2	4.2
7	4.8	4.9
8	13.2	13.5

TABLE 11.2

ATOMIC FLUORESCENCE DETERMINATION OF ZINC IN NON-FERROUS METAL ALLOYS

SAMPLE	STANDARD ANALYSIS[a] %	NON-DISPERSIVE ATOMIC FLUORESCENCE %
B.C.S. 179/1 High tensile brass	35.5	36.0
B.C.S. 180/1 Cupro-nickel	0.05	0.049
----- Copper alloy	0.049	0.047
Nimonic 90 Nickel-base alloy	0.002	0.003
B.C.S. 307 Ce-Zn-Zr-Mg alloy	2.08	2.02
B.C.S. 304 Aluminium bronze	0.60	0.59
B.C.S. 207/1 Bronze	1.81	1.75
B.C.S. 183/3 Leaded gun-metal	3.25	3.22
B.C.S. 364 Leaded bronze	0.13	0.14
B.C.S. 300 Aluminium alloy	5.98	6.05

[a] Certificate values for B.C.S. samples. Nimonic 90 standard analysis by Firth Brown Research Laboratories and Copper alloy standard analysis by Imperial Metal Industries Ltd.

little background emission. The results would obviously be greatly improved by the use of an a.c. amplification system, which would allow for smaller amounts of zinc to be sensitively determined.

The use of this far from ideal instrumentation and the attainment of the results reported in Tables 11.1 and 11.2 probably help to show the value of non-dispersive atomic fluorescence more than if instrumentation similar to that reported previously (65,172) had been used. There are obviously a number of atomic spectrometers in use, which are no more suitable for non-dispersive atomic fluorescence than the instrumentation used in the above study, and this work shows that reasonable results could be obtained even with these instruments.

The excellent results which may be obtained by non-dispersive atomic fluorescence would suggest that in the future this technique will be widely used for determinations in technical materials.

REFERENCES

1. A.C.G. MITCHELL and M.W. ZEMANSKY, 'Resonance, Radiation and Excited Atoms', Cambridge Univ. Press (1934)

2. P. PRINGSHEIM, 'Fluorescence and Phosphorescence', Interscience (1949).

3. R.W. WOOD, Proc. Am. Acad. 9(1904) 396.

4. A. TERENIN, Z. f. Phys. 31 (1925) 26.

5. C. BOECKNER, Bureau of Stand. Journ. Res. 5 (1930) 13.

6. A. BOGROS, Compt. Rend. 183 (1926) 124.

7. J. FRIDRICHSON, Z. f. Phys. 64 (1930) 43.

8. R.W. WOOD, 'Researches in Physical Optics I and II', Columbia Univ. Press (1913 and 1919)

9. N. PONOMAREV and A. TERENIN, Z. f. Phys. 37 (1926) 95.

10. E.L. NICHOLS and H.L. HOWES, Phys. Rev. 22 (1923) 425.

11. E.L. NICHOLS and H.L. HOWES, Phys. Rev. 23 (1924) 472.

12. R.M. BADGER, Z. f. Phys. 55 (1929) 56.

13. R. MANKOPFF, Verhandl. Deutsch. Phys. Ges. 14 (1933) 16.

14. A.L. BOERS, C.T.J. ALKEMADE and J.A. SMIT, Physica 22 (1956) 358.

15. C.T.J. ALKEMADE, in E.R. LIPPINATT and M. MARGOSHES (editors) 'Proc. Xth. Colloquium Spectroscopium Internationale', Spartan (1963) 143.

16. H.P. HOOYMAYERS and C.T.J. ALKEMADE, J. Quant. Spectry. Rad. Transfer 6 (1966) 501.

17. H.P. HOOYMAYERS and C.T.J. ALKEMADE, J. Quant. Spectry. Rad. Transfer 6 (1966) 847.

18. D.R. JENKINS, Proc. Roy. Soc. A293 (1966) 493.

19. D.R. JENKINS, Proc. Roy. Soc. A303 (1968) 453.

20. D.R. JENKINS, Proc. Roy. Soc. A303 (1968) 467.

21. D.R. JENKINS, Proc. Roy. Soc. A306 (1968) 413.

22. D.R. JENKINS, Proc. Roy. Soc. A313 (1969) 551.

23. J.W. ROBINSON, Anal. Chim. Acta 24 (1961) 254

24. J.D. WINEFORDNER and T.J. VICKERS, Anal. Chem. 36 (1964) 161.

25. J.D. WINEFORDNER and R.A. STAAB, Anal. Chem. 36 (1964) 165.

26. R.M. DAGNALL, K.C. THOMPSON and T.S. WEST, Anal. Chim. Acta 36 (1966) 269.

27. R.F. BROWNER, R.M. DAGNALL and T.S. WEST, Talanta 16 (1969) 75.

28. J.D. WINEFORDNER and J.M. MANSFIELD, in G.G. GUILBAULT (editor) 'Fluorescence - Theory, Instrumentation and Practice', Arnold (1967).

29. N. OMNETTO and G. ROSSI, Spectrochim. Acta 24B (1969) 95.

30. R.M. DAGNALL, K.C. THOMPSON and T.S. WEST, Talanta 14 (1967) 1151.

31. C.T.J. ALKEMADE, J. Pure Appl. Chem. 23 (1970) 73.

32. J.D. WINEFORDNER, M.L. PARSONS, J.M. MANSFIELD and W.J. McCARTHY, Spectrochim. Acta 23B (1967) 37.

33. P.J.T. ZEEGERS, R. SMITH and J.D. WINEFORDNER, Anal. Chem. 40 (1968) 26A(13).

34. H.P. HOOYMAYERS, Spectrochim. Acta 23B (1968) 567.

35. P.J.T. ZEEGERS and J.D. WINEFORDNER, Spectrochim. Acta 26B (1971) 161.

36. R.M. DAGNALL, T.S. WEST and P. YOUNG, Talanta 13 (1966) 803.

37. G.I. GOODFELLOW, Rep. U.K. At. Energ. Auth. A.W.R.E. O-87/66 (1967).

38. G.I. GOODFELLOW, Anal. Chim. Acta 36 (1966) 132.

39. J.M. MANSFIELD, J.D. WINEFORDNER and C. VEILLON, Anal. Chem. 37 (1965) 1049.

40. T.L. MARTIN, F.M. HAMM and P.B. ZEEMAN, Anal. Chim. Acta 53 (1971) 437

41. N. OMNETTO and G. ROSSI, Anal. Chim. Acta 40 (1968) 195.

42. K.C. THOMPSON and G.D. REYNOLDS, Analyst 96 (1971) 771.

43. T.J. VICKERS and R.M. VAUGHT, Anal. Chem. 41 (1969) 1476.

44. P.D. WARR, Talanta 17 (1970) 543.

45. P.D. WARR, Talanta 18 (1971) 234.

46. J.D. WINEFORDNER and R.A. STAAB, Anal. Chem. 36 (1964) 1367.

47. R. KLAUS, Z. Klin. Chem. 4 (1966) 299

48. D.N. ARMENTROUT, Anal. Chem. 38 (1966) 1235.

49. D.C. MANNING and P. HENEAGE, At. Absorpt. Newsl. 7 (1968) 80.

50. U.I. BELYAEV, A.V. KARYAKIN and A.M. PCHELINTSEV, Zh. Anal. Khim. 25 (1970) 852, via J. Anal. Chem. USSR 25 (1970) 735.

51. U.I. BELYAEV and A.M. PCHELINTSEV, Zh. Anal. Khim. 25 (1970) 2094, via J. Anal. Chem. USSR 25 (1970) 1799.

52. U.I. BELYAEV and A.M. PCHELINTSEV, Zh. Anal. Khim. 25 (1970) 2238, via J. Anal. Chem. USSR 25 (1970) 1922.

53. A.M. PCHELINTSEV, U.I. BELYAEV, A.V. KARYAKIN and T.A. KOVESHNICKOVA, Zh. Anal. Khim. 26 (1971) 1355, via J. Anal. Chem. USSR 26 (1971) 1209

54. J.I. DINNIN and A.W. HELZ, Anal. Chem. 39 (1967) 1489

55. J.I. DINNIN, Anal. Chem. 39 (1967) 1491.

56. N. OMNETTO and G. ROSSI, Talanta 16 (1969) 263.

57. J. AGGETT and T.S. WEST, Anal. Chim. Acta 55 (1971) 349.

58. J. AGGETT and T.S. WEST, Anal. Chim. Acta 57 (1971) 15.

59. D. ALGER, R.G. ANDERSON, I.S. MAINES and T.S. WEST, Anal. Chim. Acta 57 (1971) 271.

60. M.D. AMOS, P.A. BENNETT, K.G. BRODIE, P.W. LUNG and J.P. MATOUSEK, Anal. Chem. 43 (1971) 211.

61. R.G. ANDERSON, I.S. MAINES and T.S. WEST, Anal. Chim. Acta 51 (1970) 355.

62. R.M. DAGNALL, G.F. KIRKBRIGHT, T.S. WEST and R. WOOD, Analyst 97 (1972) 245.

63. R.M. DAGNALL, G.F. KIRKBRIGHT, T.S. WEST and R. WOOD, Anal. Chem. 43 (1971) 1765.

64. B.FLEET, K.V. LIBERTY and T.S. WEST, Anal. Chim. Acta 45 (1969) 205.

65. P.L. LARKINS, Spectrochim. Acta 26B (1971) 477.

66. P.L. LARKINS and J.B. WILLIS, Spectrochim. Acta 26B (1971) 491.

67. D.C. MANNING and P. HENEAGE, At. Absorpt. Newsl. 6 (1967) 124.

68. J.MATOUSEK and V. SYCHRA, Anal. Chim. Acta 49 (1970) 175.

69. J. MATOUSEK and V. SYCHRA, Anal. Chem. 41 (1969) 518.

70. D.G. MITCHELL and A. JOHANSSON, Spectrochim. Acta 25B (1970) 175.

71. D.G. MITCHELL and A. JOHANSSON, Spectrochim. Acta 26B (1971) 677.

72. J.W. ROBINSON and C.J. HSU, Anal. Chim. Acta 43 (1968) 109.

73. R. SMITH, R.C. ELSER and J.D. WINEFORDNER, Anal. Chim. Acta 48 (1969) 35.

74. V. SYCHRA and J. MATOUSEK, Anal. Chim. Acta 52 (1970) 376.

75. V. SYCHRA and J. MATOUSEK, Talanta 17 (1970) 363.

76. V. SYCHRA, P.J. SLEVIN, J. MATOUSEK and F. BEK, Anal. Chim. Acta 52 (1970) 259.

77. T.S. WEST and X.K. WILLIAMS, Anal. Chem. 40 (1968) 335.

78. T.S. WEST and X.K. WILLIAMS, Anal. Chim. Acta 42 (1968) 29.

79. T.S. WEST and X.K. WILLIAMS, Anal. Chim. Acta 45 (1969) 27.

80. H. MASSMANN, Spectrochim. Acta 23B (1968) 215.

81. J.V. SULLIVAN and A. WALSH, Spectrochim. Acta 21 (1965) 721.

82. R.M. LOWE, Spectrochim. Acta 26B (1971) 201.

83. J.F. ALDER and T.S. WEST, Anal. Chim. Acta 51 (1970) 365.

84. M.P. BRATZEL, R.M. DAGNALL and J.D. WINEFORDNER, Appl. Spectrosc. 24 (1970) 517.

85. M.P. BRATZEL, R.M. DAGNALL and J.D. WINEFORDNER, Anal. Chim. Acta 48 (1969) 197.

86. L. BREWER and J.B. TELLINGHUISEN, J. Chem. Phys. 54 (1971) 5133.

87. R.F. BROWNER, R.M. DAGNALL and T.S. WEST, Anal. Chim. Acta 46 (1969) 207.

88. R.F. BROWNER, R.M. DAGNALL and T.S. WEST, Anal. Chim. Acta 50 (1970) 375.

89. M.S. CRESSER and T.S. WEST, Anal. Chim. Acta 51 (1970) 530

90. M.S. CRESSER and T.S. WEST, Spectrosc. Lett. 2 (1969) 9.

91. M.S. CRESSER and T.S. WEST, Anal. Chim. Acta 50 (1970) 517.

92. R.M. DAGNALL, G.F. KIRKBRIGHT, T.S. WEST and R. WOOD, Anal. Chim. Acta 47 (1969) 407.

93. R.M. DAGNALL, G.F. KIRKBRIGHT, T.S. WEST and R. WOOD, Anal. Chem. 42 (1970) 1029.

94. R.M. DAGNALL, G.F. KIRKBRIGHT, T.S. WEST and R. WOOD, Analyst 95 (1970) 425.

95. R.M. DAGNALL, M.R.G. TAYLOR and T.S. WEST, Lab. Pract. 20 (1971) 209.

96. R.M. DAGNALL, M.R.G. TAYLOR and T.S. WEST, Spectrosc. Lett.1 (1968) 397.

97. R.M. DAGNALL, K.C. THOMPSON and T.S. WEST, Talanta 15 (1968) 677.

98. R.M. DAGNALL, K.C. THOMPSON and T.S. WEST, Talanta 14 (1967) 557.

99. R.M. DAGNALL, K.C. THOMPSON and T.S. WEST, Talanta 14 (1967) 551.

100. R.M. DAGNALL, K.C. THOMPSON and T.S. WEST, Talanta 14 (1967) 1467.

101. L. EBDON, G.F. KIRKBRIGHT and T.S. WEST, Anal. Chim. Acta 47 (1969) 563.

102. L. EBDON, G.F. KIRKBRIGHT and T.S. WEST, Talanta 17 (1970) 965.

103. R.C. ELSER and J.D. WINEFORDNER, Appl. Spectrosc. 25 (1971) 345.

104. H.A. FULTON, K.C. THOMPSON and T.S. WEST, Anal. Chim. Acta 51 (1970) 373.

105. T.H. GLENN, M.P. BRATZEL and J.D. WINEFORDNER, Anal. Chem. 43 (1971) 1769.

106. D.N. HINGLE, G.F. KIRKBRIGHT and T.S. WEST, Analyst 93 (1968) 522.

107. R.S. HOBBS, G.F. KIRKBRIGHT and T.S. WEST, Talanta 18 (1971) 859.

108. G.F. KIRKBRIGHT, P. RAO and T.S. WEST, Anal. Lett.2 (1969) 465.

109. J.M. MANSFIELD, M.P. BRATZEL, H.O. NORGORDON, D.O. KNAPP, K.E. ZACHA and J.D. WINEFORDNER, Spectrochim. Acta 23B (1968) 389.

110. G.B. MARSHALL and T.S. WEST, Anal. Chim. Acta 51 (1970) 179.

111. J.D. NORRIS and T.S. WEST, Anal. Chim. Acta 55 (1971) 359.

112. J.D. NORRIS and T.S. WEST, Anal. Chim. Acta 59 (1972) 355.

113. J.D. NORRIS and T.S. WEST, Anal. Chim. Acta 59 (1972) 474.

114. M. SHULL and J.D. WINEFORDNER, Anal. Chem. 43 (1971) 799.

115. M.D. SILVESTER and W.J. McCARTHY, Anal. Lett.2 (1969) 305.

116. M.D. SILVESTER and W.J. McCARTHY, Spectrochim. Acta 25B (1970) 229.

117. R. SMITH, C.M. STAFFORD and J.D. WINEFORDNER, Canadian Spectrosc. 14 (1969) 38.

118. K.E. ZACHA, M.P. BRATZEL, J.D. WINEFORDNER and J.M. MANSFIELD, Anal. Chem. 40 (1968) 1733.

119. K.E. ZACHA, M.P. BRATZEL, J.D. WINEFORDNER and J.M. MANSFIELD, Anal. Chem. 41 (1969) 1315.

120. T.S. WEST, Min. Sci. and Engng. (1970) 31.

121. D.O. COOKE, R.M. DAGNALL and T.S. WEST, Anal. Chim. Acta 56 (1971) 17.

122. D.O. COOKE, R.M. DAGNALL and T.S. WEST, Anal. Chim. Acta 54 (1971) 381

123. D.O. COOKE, Ph.D. Thesis, Univ. of London (1971)

124. R.F. BROWNER, R.M. DAGNALL and T.S. WEST, Anal. Chim. Acta 45 (1969) 163.

125. R.M. DAGNALL and M.D. SILVESTER, Anal. Chem. 44 (1972) 204.

126. R.M. DAGNALL, M.D. SILVESTER and T.S. WEST, Talanta 18 (1971) 1103.

127. R.M. DAGNALL and T.S. WEST, Appl. Optics 7 (1968) 1287.

128. W.C. SCHRENK, S.E. VALENTE and K.E. SMITH, Appl. Spectrosc. 26 (1972) 108.

129. K.C. THOMPSON and P.C. WILDY, Analyst 95 (1970) 772.

130. P.C. WILDY and K.C. THOMPSON, Analyst 95 (1970) 562.

131. M.P. BRATZEL, R.M. DAGNALL and J.D. WINEFORDNER, Anal. Chim. Acta 52 (1970) 157.

132. R.L. MILLER, L.M. FRASER and J.D. WINEFORDNER, Appl. Spectrosc. 25 (1971) 477.

133. C. VEILLON, J.M. MANSFIELD, M.L. PARSONS and J.D. WINEFORDNER, Anal. Chem. 38 (1966) 204.

134. D.H. COTTON and D.R. JENKINS, Spectrochim. Acta 25B (1970) 283.

135. D.W. ELLIS and D.R. DEMERS, A.C.S. Advan. in Chem. 73 (1968) 326.

136. D.W. ELLIS and D.R. DEMERS, Anal. Chem. 38 (1966) 1943.

137. M.S. CRESSER and T.S. WEST, Spectrochim. Acta 25B (1970) 61.

138. S.J. PEARCE, L.de GALAN and J.D. WINEFORDNER, Spectrochim. Acta 23B (1968) 793.

139. T.J. VICKERS and S.P. MERRICK, Talanta 15 (1968) 873.

140. V.I. MUSCAT and T.J. VICKERS, Anal. Chim. Acta 57 (1971) 23.

141. V.I. MUSCAT, T.J. VICKERS and A. ANDREN, Anal. Chem. 44 (1972) 218.

142. A.M.C. HUSSEIN and G. NICKLESS, Talk at I.A.A.S.C. Sheffield (1969).

143. L.M. FRASER and J.D. WINEFORDNER, Anal. Chem. 43 (1971) 1693.

144. D.R. JENKINS, Spectrochim. Acta 23B (1967) 167.

145. T.J. VICKERS and R.M. VAUGHT, Anal. Chem. 41 (1969) 1476.

146. G.F. KIRKBRIGHT, A. SEMB and T.S. WEST, Talanta 14 (1967) 1011.

147. G.F. KIRKBRIGHT, A. SEMB and T.S. WEST, Talanta 15 (1968) 441.

148. D.N. HINGLE, G.F. KIRKBRIGHT and T.S. WEST, Analyst 94 (1969) 864.

149. D.N. HINGLE, G.F. KIRKBRIGHT and T.S. WEST, Talanta 15 (1968) 199.

150. R.S. HOBBS, G.F. KIRKBRIGHT, M. SARGENT and T.S. WEST, Talanta 15 (1968) 997.

151. R.S. HOBBS, G.F. KIRKBRIGHT and T.S. WEST, Analyst 94 (1969) 554.

152. G.F. KIRKBRIGHT, M. SARGENT and T.S. WEST, Talanta 16 (1969) 1467.

153. G.F. KIRKBRIGHT, M. SARGENT and T.S. WEST, At. Absorpt. Newsl. 8 (1969) 34.

154. G.F. KIRKBRIGHT, M. SARGENT and T.S. WEST, Talanta 16 (1969) 245.

155. K.M. ALDOUS, R.F. BROWNER, R.M. DAGNALL and T.S. WEST, Anal. Chem. 42 (1970) 939.

156. D.N. HINGLE, G.F. KIRKBRIGHT, M. SARGENT and T.S. WEST, Lab. Pract. 18 (1969) 1069.

157. G.F. KIRKBRIGHT and T.S. WEST, Appl. Optics 7 (1968) 1305.

158. M.S. CRESSER and P.N. KELIHER, Intern. Lab. (1971) 17.

159. M.D. AMOS, P.A. BENNETT and K.G. BRODIE, Resonance Lines 2 (1970) 3

160. R.F. BROWNER and D.C. MANNING, Anal. Chem. 44 (1972) 843.

161. C. VEILLON and M. MARGOSHES, 'Proc. XIIIth Colloquium Spectroscopium Internationale' Hilger (1968) 284.

162. G.F. KIRKBRIGHT, Analyst 96 (1971) 609.

163. R.F. BROWNER, Ph. D. thesis, Univ. of London (1970).

164. P. BENNETTI, N. OMNETTO and G. ROSSI, Appl. Spectrosc. 25 (1971) 57

165. M. SHULL and J.D. WINEFORDNER, Appl. Spectrosc. 25 (1971) 97.

166. P.L. BOAR and J.V. SULLIVAN, Fuel 46 (1967) 47.

167. P.L. BOAR and J.V. SULLIVAN, Fuel 46 (1967) 230.

168. B.S. RAWLING and J.V. SULLIVAN, Trans. Instn. Min. Metall. 76 (1967) 238.

169. J.V. SULLIVAN, A.B. TIMMS and P.A. YOUNG, Proc. Austral. Instn. Min. Metall. 226 (1968) 31.

170. A. WALSH, J. PURE Appl. Chem. 23 (1970) 1.

171. P.L. LARKINS, R.M. LOWE, J.V. SULLIVAN and A. WALSH, Spectrochim. Acta 24B (1969) 187.

172. T.J. VICKERS, P.J. SLEVIN, V.I. MUSCAT and L.T. FARIAS, Anal. Chem. 44 (1972) 930.

173. D.O. COOKE R.M. DAGNALL, B.L. SHARP and T.S. WEST, Spectrosc. Lett. 5 (1971) 91.

174. R.M. DAGNALL, B.L. SHARP and T.S. WEST, Nature (Phys. Sci.) 234 (1971) 69.

175. D. ALGER, R.M. DAGNALL, B.L. SHARP and T.S. WEST, Anal. Chim. Acta 57 (1971) 1.

176. J.D. WINEFORDNER, V. SVOBODA and L. CLINE, C.R.C. Crit. Rev. Anal. Chem. 1 (1970) 233.

177. G.F. KIRKBRIGHT and T.S. WEST, Chem. Brit. 8 (1972) in press.

178. E.E. PICKETT and S.R. KOIRTYOHANN, Spectrochim. Acta 23B (1967) 235

179. E.E. PICKETT and S.R. KOIRTYOHANN, Spectrochim. Acta 23B (1968) 673

180. S.R. KOIRTYOHANN and E.E. PICKETT, Spectrochim. Acta 24B (1969) 325

181. V.A. FASSEL and D.W. GOLIGHTLY, Anal. Chem. 39 (1967) 466.

182. M.S. CRESSER, P.B. JOSHIPURA and P.N. KELIHER, Spectrosc. Lett. 3 (1970) 267.

183. R.N. KNISELEY, C.C. BUTLER and V.A. FASSEL, Anal. Chem. 41 (1969) 1494.

184. H.L. KAHN, A.C.S. Advan. in Chem. 73 (1968) 183.

185. H.L. KAHN, At. Absorpt. Newsl. 7 (1968) 5.

186. 'Technique and applications of atomic absorption', PERKIN-ELMER, Norwalk (1971).

187. G.F. KIRKBRIGHT, T.S. WEST and P.J. WILSON, At. Absorpt. Newsl. 11 (1972) 53.

188. Literature on AA4 and AA5 spectrometers, VARIAN TECHTRON, Melbourne.

189. K. KINSON, R.J. HODGES and C.B. BELCHER, Anal. Chim. Acta 29 (1963) 134.

190. M. YANAGISAWA, M. SUZUKI and T. TAKEUCHI, Anal. Chim. Acta 52 (1970) 386.

191. J.T.H. ROOS and W.J. PRICE, Spectrochim. Acta 26B (1971) 441.

192. J.E. ALLAN, Spectrochim. Acta 18 (1962) 259.

193. L. BARNES, Anal. Chem. 38 (1966) 1083.

194. R. DYCK, At. Absorpt. Newsl. 4 (1965) 170.

195. V.A. FASSEL, R.W. SLACK and R.N. KNISELEY, Anal. Chem. 43 (1971) 186.

196. H.A. BRYAN and J.A. DEAN, Anal. Chem. 29 (1957) 1289.

197. N. OMNETTO and G. ROSSI, Spectrochim. Acta 25B (1970) 297.

198. M.S. CRESSER, Ph. D. thesis Univ. of London (1970)

199. W.F. MEGGERS, C.H. CORLISS and B.F. SCRIBNER, 'Tables of Spectral Line Intensities', N.B.S. MONOGRAPH 32 Part I, Washington (1961).

200. C.E. MOORE, 'Atomic Energy Levels, derived from the Analyses of Optical Spectra', N.B.S. Circular 467 Vol. 2, Washington (1952).

201. M. JONES, G.F. KIRKBRIGHT, L. RANSON and T.S. WEST, Anal. Chim. Acta in press.

202. V.A. FASSEL, J.A. RASMUSAN and T.G. COWLEY, Spectrochim. Acta 23B (1968) 579.

203. J.E. ALLAN, Spectrochim. Acta 24B (1969) 13.

204. D.C. MANNING and F. FERNANDEZ, At. Absorpt. Newsl. 7 (1968) 24.

205. S. SLAVIN and T.W. SATTUR, At. Absorpt. Newsl. 7 (1968) 99.

206. D.C. MANNING, At. Absorpt. Newsl. 10 (1971) 97.

207. M.L. PARSONS, W.J. McCARTHY and J.D. WINEFORDNER, Appl. Spectrosc. 20 (1966) 223.

208. M.I.T. Wavelength Tables (1969 edition), Mass. Inst. of Tech. (1969).

209. D. KOLIHOVA and V. SYCHRA, Anal. Chim. Acta 59 (1972) 477.

210. I. RUBESKA and M. MIKSOVSKY, At. Absorpt. Newsl. 11 (1972) 57.

211. M. YANAGISAWA, M. SUZUKI and T. TAKEUCHI, Anal. Chim. Acta 47 (1969) 121.

212. C.R. WALKER, O.A. VITA and R.W. SPARKS, Anal. Chim. Acta 47 (1969) 1.

213. W.G. JONES and A. WALSH, Spectrochim. Acta 16 (1960) 249.

214. H. MASSMANN, Z. Instr. 71 (1963) 225.

215. L.R.P. BUTLER and A. STRASHEIM, Spectrochim. Acta 21 (1965) 1207.

216. C. SEBENS, W. SLAVIN and J. VOLLMER, At. Absorpt. Newsl. 3 (1964) 165.

217. D.C. MANNING, D. TRENT and J. VOLLMER, At. Absorpt. Newsl. 4 (1965) 234.

218. C. SEBENS, W. SLAVIN and J. VOLLMER, At. Absorpt. Newsl. 4 (1965) 306.

219. F.J. FERNANDEZ, D.C. MANNING and J. VOLLMER, At. Absorpt. Newsl. 8 (1969) 117.

220. K.C. THOMPSON, Spectrosc. Lett. 3 (1970) 59.

221. T.S. WEST, J. Pure Appl. Chem. 23 (1970) 99.

222. K.M. ALDOUS, Ph. D. thesis, Univ. of London (1970).

223. M.S. CRESSER, H.J. MATTHEWS and T.S. WEST, unpublished results.

224. M.S. CRESSER, J.D. NORRIS and T.S. WEST, unpublished results.

225. A.T. GRZESIAK, J.D. NORRIS and T.S. WEST, unpublished results.

226. G.B. MARSHALL and A.C. SMITH, Analyst 97 (1972) 447.

227. A. WALSH, 'Proc. XIIIth Colloquium Spectroscopium Internationale' Hilger (1968) 257.

228. J.B. DAWSON, D.J. ELLIS and R. MILNER, Spectrochim. Acta 23B. (1968) 695.

229. D.O. COOKE, R.M. DAGNALL, H.N. JOHNSON, G.F. KIRKBRIGHT and T.S. WEST, Lab. Pract. 21 (1972) 171.

230. R. MAVRODINEAU and R.C. HUGHES, Appl. Optics 7 (1968) 1281.

231. A. STRASHEIM and H.G.C. HUMAN, Spectrochim. Acta 23B (1967) 265.

232. F. BRECH, 'Proc XIIIth Colloquium Spectroscopium Internationale' Hilger (1968) 294.

233. F. BRECH, 'Proc. XIVth Colloquium Spectroscopium Internationale' Hilger (1969) 1191.

234. C.T.J. ALKEMADE and J.M.W. MILATZ, Appl. Sci. Res. B4 (1955) 289.

235. J.A. BOWMAN, J.V. SULLIVAN and A. WALSH, Spectrochim. Acta 22 (1966) 205.

236. R.M. LOWE, Spectrochim. Acta 24B (1969) 191.

237. H.V. MALMSTADT and E. CODOS, Paper 132 Pittsburgh Conf. on Anal. Chem. and Appl. Spectrosc. (1972)

238. R.G. ANDERSON, H.N. JOHNSON and T.S. WEST, Anal. Chim. Acta 57 (1971) 281.

239. L. EBDON, G.F. KIRKBRIGHT and T.S. WEST, Anal. Chim. Acta 58 (1972) 39.

240. J.F. ALDER and T.S. WEST, Anal. Chim. Acta 58 (1972) 331.

241. K.W. JACKSON and T.S. WEST, Anal. Chim. Acta 59 (1972) 187.

242. L. EBDON, G.F. KIRKBRIGHT and T.S. WEST, Anal. Chim. Acta, in press.

243. J.F. ALDER and T.S. WEST, Anal. Chim. Acta, in press.

244. L. EBDON, G.F. KIRKBRIGHT and T.S. WEST, Talanta, in press.

245. A.C. OBORNE and T.S. WEST, Proc. Soc. for Anal. Chem., in press.

246. K.W. JACKSON and T.S. WEST, Anal. Chem., in press.

247. M. GLENN, J. SAVORY, L. HART, T.H. GLENN and J.D. WINEFORDNER, Anal. Chim. Acta 57 (1971) 263.

248. T.W. STEELE and B.D. GUERIN, Analyst 97 (1972) 77.

249. J.P. MATOUSEK and B.J. STEVENS, Clin. Chem. 17 (1971) 363.

250. J.P. MATOUSEK and B.J. STEVENS, Clin. Chem. 17 (1971) 1210.

251. H.L. KAHN, Clin. Chem. 17 (1971) 1209.

252. N.B. KUBASICK, M.T. VOLOSIN and M.H. MURRAY, Clin. Chem. 18 (1972) 410.

253. K.G. BRODIE and J.P. MATOUSEK, Anal. Chem. 43 (1971) 1557.

254. M.P. BRATZEL, C.L. CHAKRABARTI and R.E. STURGEON, Anal. Chem.44 (1972) 372.

255. R. MAVRODINEAU and H. BOITEUX, 'Flame Spectroscopy', Wiley (1965).

256. R.L. MITCHELL, Comm. Bur. Soil Sci. Tech. Comm. 44 (1948).

257. A. WALSH, in F. Twyman 'Metal Spectroscopy', Griffen (1951).

258. A. MITSCHERLICH, Ann. Physik u Chem. 116 (1862) 499.

259. J.M. EDER and E. VALENTA, Klasse Kais Akad. Wiss Wien. (1863) 467.

260. F.H. GOOCH and T.S. HART, Am. J. Sci. 42 (1891) 448.

261. F.H. GOOCH and J.I. PHINNEY, Am. J. Sci. 44 (1892) 392.

262. K. HELLER, K. PEH and F. GURTLER, Z. Pflanzenernahr. Dung. u Bodenk A, 35 (1934) 215.

263. Pye Liquid Chromatograph Sales Literature, Pye Unicam Ltd., Cambridge.