

SOME ANALYTICAL ASPECTS OF ATOMIC FLUORESCENCE
SPECTROSCOPY

by

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ABSTRACT

The flame atomic fluorescence and flame atomic emission spectroscopy of aluminium, germanium, molybdenum, silicon, titanium, vanadium and zirconium in a nitrogen or argon separated nitrous oxide-acetylene flame have been investigated. Microwave-excited electrodeless discharge tubes were prepared and used for the excitation of the atomic fluorescence. Atomic fluorescence emission was not obtained for titanium or zirconium, but the sensitivities for aluminium, germanium, silicon and vanadium were an order of magnitude better than for the corresponding atomic absorption sensitivities.

Optimum conditions for the determination of each element by either emission technique, where applicable, have been obtained, and the effects of 100-fold excesses of diverse ions were studied for interference. The flame atomic emission determinations for each element suffered from severe interferences, but the atomic fluorescence determination of aluminium, germanium, silicon and vanadium was virtually interference free. The molybdenum fluorescence signal was considerably more prone to interference but was much less seriously affected than atomic emission.

A method for the determination of ionisation contours of an element within a flame has been investigated. The percentage ionisation of an element has been related to the temperature of the element's atomic population and to the flame by the Saha Ionisation Equilibrium Equation. Effective ionisation temperature profiles were obtained for the air-acetylene and for the unseparated and the argon and nitrogen separated nitrous oxide-acetylene flames at different fuel:support gas stoichiometries.

Some recommendations for extending the scope and accuracy of flame temperature measurements have been made in the final chapter, as well as suggestions for increasing the selectivity of atomic fluorescence spectroscopy.

ACKNOWLEDGEMENTS

The work presented in this thesis is entirely original except where due reference is made. No part of the work has been submitted previously for any other degree. The work was carried out in the Chemistry Department of the Imperial College of Science and Technology, between September 1968 and August 1970.

I should like to thank my supervisors, Drs G. F. Kirkbright and R. M. Dagnall and Professor T. S. West for their invaluable help and encouragement throughout this project, and to members of the analytical spectroscopy research group for helpful discussions.

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A handwritten signature in cursive script, reading "Roger Wood", with a horizontal line drawn underneath the name.

Roger Wood

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CHAPTER 1. INTRODUCTION TO FLAME ATOMIC SPECTROSCOPY

The use of flame spectroscopy as a routine instrumental technique for trace element analysis has recently become widespread. For the purposes of this thesis the term analytical flame spectroscopy encompasses three techniques; atomic absorption (A.A.S.), atomic fluorescence (A.F.S.) and flame atomic emission spectroscopy (F.E.S.). With the development of increasingly more sophisticated equipment the range of elements which may be quantitatively determined by flame spectroscopy has also increased; to date about 68 elements may be determined by at least one of the flame spectroscopic techniques. Although each technique may possess its own advantages for a particular analysis, there has been very little practical comparison of the advantages and disadvantages of each technique for the determination of a given element.

1.1: Scope of Work to be Investigated

The work which is presented in this thesis forms two separate and distinct parts (a) the investigation of the analytical flame spectroscopic properties of several refractory elements and (b) the determination of some flame temperature profiles.

The determination of refractory elements is of great importance in the practical analysis of many samples, e.g. the analysis of trace elements in steels. Such analyses have generally employed atomic emission or atomic absorption spectroscopy to determine the trace element present. However, these two techniques often suffer from either matrix element interferences or lack of sensitivity or both.

The sensitivity of determinations by atomic fluorescence spectroscopy has been predicted (1, 2) to be greater than that of flame atomic emission spectroscopy in the same flame for those elements whose principal resonance lines are at wavelengths less than 300 nanometers (nm). Similarly it is expected that A.F.S. and F.E.S. sensitivities will be comparable for those elements with principal resonance lines in the region 300 to 350 nm. Many of the refractory elements have resonance lines which lie in this latter region and so the possibility of determining these elements by atomic fluorescence spectroscopy was investigated. Their determination was compared in terms of sensitivity and selectivity with the corresponding determinations by F.E.S. and A.A.S., and a practical correlation has been observed for the theoretical prediction of sensitivity dependence upon wavelength reported above. The use of

both hollow cathode lamps (H.C.L.) and microwave-excited electrodeless discharge tubes (E.D.T.) to stimulate fluorescence radiation was studied for each refractory element. Throughout the studies the high-temperature nitrous oxide-acetylene flame was employed as the atom reservoir. This flame has been reported to possess a sufficiently high temperature and reducing atmosphere to produce good atomisation of the refractory elements (3-6).

The second part of the work reported here concerns the study of the percentage ionisation contours of the atoms of an element within different flames, and describes an attempt to relate the percentage ionisation found to the effective ionisation temperature for that part of the flame. The ionisation temperature can be predicted accurately from the percentage ionisation of the atoms of an element if the total electron concentration and the partial pressure of the atoms of the element employed is known. The validity of the calculation also depends upon thermal equilibrium conditions being established within the flame, the ideal gas law and the Saha equation for the ionisation of an element.

The variations in the degree of ionisation of the atoms of an element within air-acetylene and gas shielded and conventional premixed nitrous oxide-acetylene flames

of different stoichiometries were observed both with respect to height and width, and these values were then related to the flame temperature profiles.

1.II: Theory

A brief résumé of the theory of atomic emission and atomic absorption and a more comprehensive survey of the theory of atomic fluorescence spectroscopy is presented in this thesis. These sections have not been presented in detail because, with the exception of atomic fluorescence, the theoretical and historical aspects of each technique have been extensively documented in the literature (7-19). The theoretical considerations for the principal atom reservoirs used (separated and unseparated nitrous oxide-acetylene flames) and the sources employed for the stimulation of fluorescence radiation (electrodeless discharge tubes) is also presented.

1.II.1: Flame Atomic Emission Spectroscopy

Flame atomic emission spectroscopy is the oldest of the three flame spectroscopic techniques; the technique developed from early eighteenth century observations of the colour imparted to flames by the addition of metallic

salts. Atomic emission spectroscopy usually refers to the measurement of the radiation emitted from thermally excited atoms. The theory of atomic spectroscopy was developed in the early part of this century concurrent with the development of the modern atomic theory.

The integrated emission intensity of a line, if self-absorption and induced emission are neglected, is given by,

$$\int I_{\lambda} d\lambda = C N_j f$$

where

N_j is the number of atoms in the excited state involved in the transition responsible for the line.

f is the oscillator strength - a measure of the average number of electrons/atoms capable of transition.

C is a constant dependent on the dispersing and detecting systems.

Assuming that the atomic vapour is in thermal equilibrium at temperature T , the number of atoms N_j in the excited state j of excitation energy E_j is given by,

$$N_j = N_0 \frac{P_j}{P_0} \exp (-E_j/KT)$$

where

N_0 is the number of atoms in the ground state.

K is the Boltzmann constant.

P_j and P_o are the statistical weights for the excited and ground states respectively (for the atom $P = 2J + 1$, where J is the quantum number for total angular momentum of the electron for the ground state).

There have been many definitive texts on flame atomic emission spectroscopy, principally those of Herrmann and Alkemade (7), Alkemade (8), Mavrodineanu and Boiteux (9) and Dean and Rains (10).

1.II.2: Atomic Absorption Spectroscopy

Atomic absorption phenomena were first observed in the nineteenth century by Fraunhofer in the spectrum of the sun. It was not until the work of Walsh (11) in 1953 and Alkemade and Milatz (12, 13) in 1955, however, that atomic absorption spectroscopy was proposed as a generally applicable analytical method, although Woodson (14) in 1939 had described an atomic absorption instrument for the determination of mercury in air.

Atomic absorption spectroscopy is based on the measurement of the absorption of resonance radiation by free atoms in the gaseous state, i.e. of spectral lines corresponding to the transition of atoms between the ground and excited states. These transitions have been treated quantitatively, and from them a relationship

between absorbance and atomic concentration has been developed. The relationship between the integrated absorption and concentration in the general case where N_ν (the number of atoms cm^{-3} capable of absorption in the range $\nu + d\nu$ to ν) is much greater than N_j is given by,

$$\int K d\nu = \frac{\lambda^2 P_i}{8\pi P_1} \cdot N_\nu A_{ji}$$

where

$\int K d\nu$ is the integrated absorption, K being the absorption coefficient of the atomic vapour at frequency ' ν '.

λ is the wavelength at the centre of the absorption line. P_i and P_j are the statistical weights, where 'i' denotes the initial state involved in the transition and 'j' the excited state.

A_{ji} is the Einstein coefficient of spontaneous emission for the $j \longrightarrow i$ transition.

If absorption by resonance lines only is considered (this is generally the case) N_ν is equal to N , the total number of atoms cm^{-3} . Similarly A_{ji} becomes equal to $1/\tau$, where ' τ ' is the average lifetime of an atom in the excited state 'j'.

The theory of atomic absorption spectroscopy using continuum and sharp-line sources has been well documented

(11, 15). There have been many definitive texts on atomic absorption spectroscopy, principally those by Mavrodineanu and Boiteux (9), Dean and Rains (10), Elwell and Gidley (16), Ramirez-Munoz (17), Slavin (18) and Rubeska and Moldan (19).

1.II.3: Atomic Fluorescence Spectroscopy

a. Introduction

Atomic fluorescence spectroscopy, the most recently proposed of the three flame atomic spectroscopic techniques, is based upon the absorption of radiation by an atomic vapour to produce excited atoms in that vapour, and the measurement of the radiation emitted when a fraction of the atoms lose their energy by a radiational process. The process was first observed in 1905 by Wood (20) who succeeded in exciting the fluorescence of the D-lines of sodium vapour. Wood called this phenomenon 'fluorescence resonance radiation' because it was predicted from the classical theory of a light wave vibrating with the same frequency as the dipole oscillations of the medium. Fluorescence resonance radiation was observed for mercury, lithium, cadmium, zinc and many other elements very soon after the initial discovery. This early work has been summarized by Mitchell and Zemansky (21). The early studies employed quartz cells to contain the atomic

vapour under low pressure. Atomic fluorescence flame spectroscopy, in which the atomic vapour is contained in a flame reservoir, has developed more recently. The atomic fluorescence of metal atoms in flames was first observed in 1924 by Nichols and Howes (22). They detected atomic fluorescence from calcium, strontium, barium, lithium and sodium in a Bunsen flame; later Badger (23) in 1927 detected the fluorescence of thallium, mercury, magnesium, copper, silver, cadmium and sodium in the same flame.

In 1962 Alkemade (24) outlined the possible mechanisms of excitation and deactivation of atoms in flames and determined the quantum efficiency of the sodium 589.0 nm line by measurement of the atomic fluorescence of sodium. He also suggested that there were possible analytical applications of the technique. Winefordner and co-workers (25-28) developed and published in 1964/65 the first analytical method which employed atomic fluorescence spectroscopy. Over the past five years interest in the technique has expanded greatly and a substantial number of papers have been published about the theory and applications of atomic fluorescence.

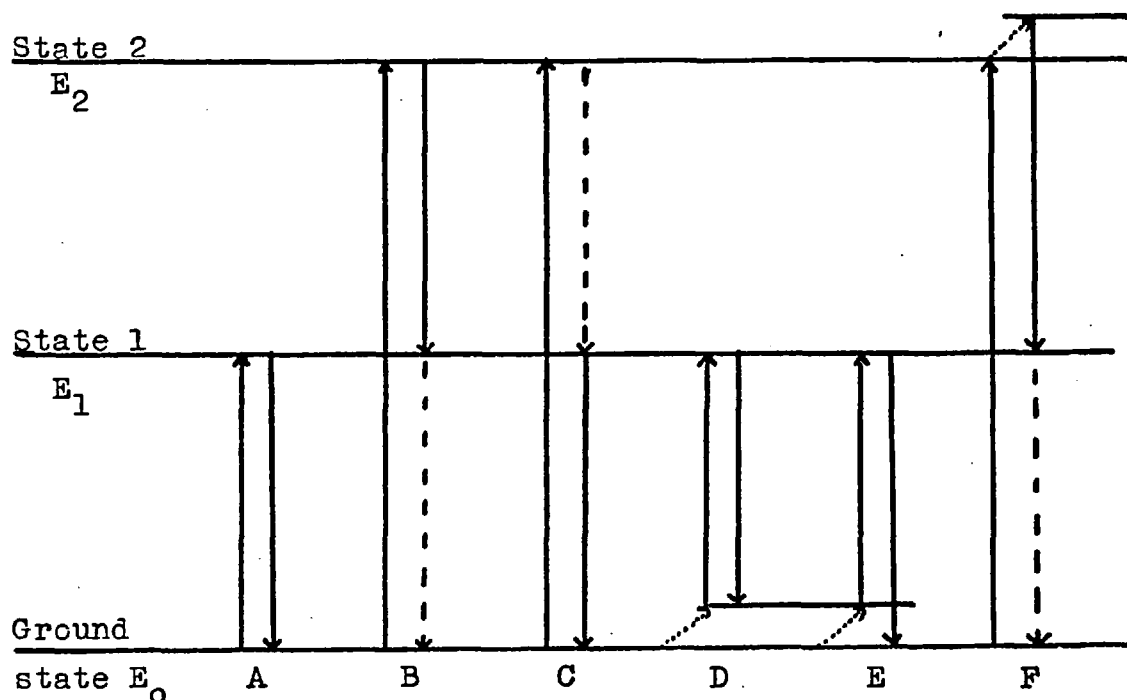
b. Types of Atomic Fluorescence Radiation

There are seven types of atomic fluorescence (21, 25,

29, 30) which have been observed, and these are illustrated in Figure 1.

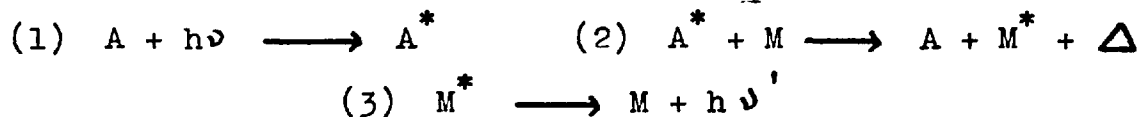
1. Resonance fluorescence results when atoms are excited from the ground electronic state to an excited electronic state and then undergo radiational deactivation to the ground state re-emitting radiation of the same energy which was absorbed. The most intense resonance fluorescence generally occurs from the first excited state of an atom. The transition probabilities for resonance lines are usually much greater than for other transitions; resonance fluorescence intensities are generally significantly greater than the intensities observed with other types of atomic fluorescence; it has thus been, and will probably continue to be, the most interesting type of atomic fluorescence to the analytical chemist. All the atomic fluorescence work presented in this thesis has utilized atomic resonance fluorescence.

2. Direct line fluorescence results when an atom is raised to an excited state considerably above the ground electronic state and then undergoes a radiational transition to a lower excited state (not the ground state), e.g. direct line fluorescence occurs in the emission of the Tl 535.0 nm line after excitation of thallium atoms by the Tl 377.6 nm line.



$\updownarrow$ radiational deactivation or activation processes
 $\downarrow$ (dashed) non-radiational deactivation processes
 $\rightarrow$ (dotted) thermal activation processes

Sensitized fluorescence:



(A: atom or molecule in high concentration; donor)

(M: atom in low concentration; acceptor)

Figure 1: Types of atomic fluorescence. A: resonance. B: direct line. C: stepwise. D: thermally assisted resonance. E: thermally assisted anti-Stokes. F: thermally assisted direct line.

3. Thermally assisted direct line fluorescence occurs when an atom is raised to an upper excited state by the acquisition of both radiational and thermal energy, and becomes deactivated in the usual direct line fluorescence manner. An example of thermally assisted direct line fluorescence is the excitation of bismuth atoms by the 206.2 nm line and the subsequent re-emission at the 293.8 nm line.

4. Stepwise line fluorescence results when an atom is excited to an electronic state above the first excited electronic state, then undergoes deactivation (usually radiationless) to a lower excited state, and finally undergoes the fluorescence transition to a lower state (often the ground state). An example of stepwise fluorescence occurs in the emission of the sodium 589.0 nm line after excitation of sodium atoms by the sodium 330.3 nm doublet.

5. Thermally assisted resonance fluorescence and 6. thermally assisted anti-Stokes fluorescence. In both processes atoms in the ground electronic state are thermally excited to a metastable level just above the ground state level, and are then excited to an upper electronic level by the absorption of radiation. In the case of the resonance fluorescence the atom re-emits to

the metastable state, and for the anti-Stokes fluorescence, re-emits to the ground state (anti-Stokes because the radiation emitted is of shorter wavelength (or greater energy) than that absorbed). These phenomena have been demonstrated for indium and gallium.

7. Sensitized fluorescence occurs when donor atoms (or molecules) are excited by means of an external light source and the excited donor species collide with the sample atom (acceptor) transferring energy and exciting the sample atom which then undergoes radiational deactivation to exhibit atomic fluorescence. This type of fluorescence has never been of analytical use with flame atom reservoirs because the concentration of donor atoms necessary for energy transfer can never be made sufficiently large for efficient transfer of energy. An example of sensitized fluorescence is the excitation of mercury vapour at the 253.7 nm line, transference of energy to thallium atoms which re-emit at their 377.6 and 535.0 nm lines.

c. Theory

There have been extensive reviews of the theory of atomic fluorescence published (21, 24, 31, 32); a résumé only has been presented in this thesis.

i. The Profile of Atomic Absorption Lines

The absorption of radiation by atoms occurs over a very narrow frequency interval called an atomic absorption line; the line profile and half-width are determined by broadening parameters. The absorption of radiation results in the electronic activation of an atom from the ground electronic state (or occasionally from metastable states just above the ground state level) to an upper electronic state. The excited atom has a life-time of about 10^{-8} seconds and then undergoes a non-radiational deactivation via collisions with flame gas molecules, or via a radiational deactivation, which is emitted isotropically, and called atomic fluorescence.

The intensity of radiation which is transmitted through an absorbing atomic vapour (diagrammatically represented in Figure 2) is given by,

$$I_{\nu} = I_{\nu}^0 \exp(-k_{\nu} L) = I_{\nu}^0 10^{-0.43 k_{\nu} L}$$

where

I_{ν} is the intensity of the transmitted radiation.

I_{ν}^0 is the intensity of the incident radiation.

' ν ' is the frequency of the incident and transmitted radiation.

L is the atomic absorption path length, in cms.

k_{ν} is the atomic absorption coefficient.

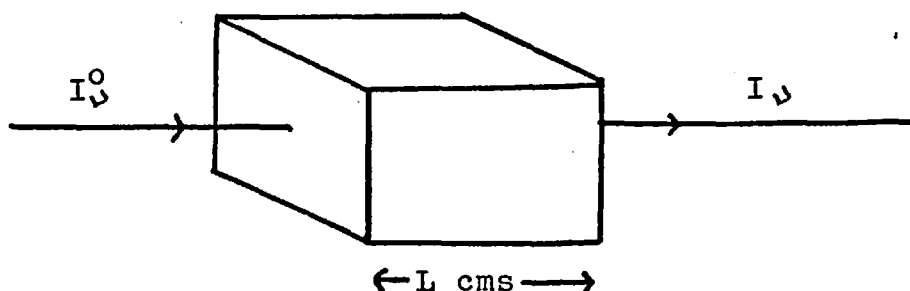


Figure 2: Diagrammatic representation of incident and transmitted radiation through an atomic vapour.

The exponent in the right-hand expression is more commonly called the absorbance, extinction or the optical density.

The broadening of a spectral line results in the absorption of radiation by atoms over a finite frequency rather than an infinitely narrow frequency interval. The half-width, Δ_ν , of an atomic absorption line is defined as the half-width of the plot of k_ν vs. ν ; it is the width of the absorption line profile at $k_{\max}/2$, where $k_{\max}$ is the maximum (or peak) atomic absorption coefficient.

The major causes of spectral line broadening of atoms in flames are Doppler broadening (thermal agitation of the absorbing or emitting atoms), collisional broadening (perturbation of the absorbing or emitting species by foreign gas atoms or molecules), resonance broadening (similar to collisional broadening but from collisions

between the absorbing or emitting atoms), natural broadening (from the finite life-time of an atom in its excited state) and Stark broadening (splitting of the atomic line on application of an electric field --- not significant for flames, hollow cathode lamps or electrodeless discharge tubes). The natural half-width of resonance lines ~~is~~ ^{is} about 10^{-5} nm (33) and the Doppler (about 0.008 nm half-width) and collisional half-widths (between 0.001 and 0.01 nm) are added quadratically to give the total half-width of the line.

ii. The Atomic Absorption Coefficient

The atomic absorption coefficient k_ν in cm^{-1} can be expressed by the Voigt profile expression which accounts for line broadening due to a Gaussian effect (Doppler broadening) and a Lorentzian effect (collisional and natural broadening). A simplified Voigt profile expression is given as,

$$k_\nu = \frac{k^0_{ap}}{\pi}$$

where

'a' is the damping constant defined by $(\ln 2)^{\frac{1}{2}}$ times the ratio of collisional half-width to Doppler half-width. p is a complex function of the types of broadening (values are available in tables (34)).

k^0 is the atomic absorption coefficient at frequency ν_0 .

for the pure Doppler broadening case; k^0 is given by,

$$k^0 = \frac{2 (\ln 2)^{\frac{1}{2}} \lambda_0^2 g_u N_1 A_t}{(8\pi)^{1.5} \Delta \nu_D g_l}$$

where

λ_0 is the wavelength in cm at the line centre.

'g''s are the statistical weights of the upper (u) and lower (l) energy levels involved in the transition.

N_1 is the concentration of atoms in the lower energy level (ground state) in atoms cm^{-3} in the flame.

$\Delta \nu_D$ is the Doppler half-width in seconds $^{-1}$.

A_t is the probability of the transition $u \rightarrow l$ in seconds $^{-1}$.

iii. The Total Absorption Factor A_T for Radiation Absorbed from a Line Source

The total absorption factor A_T represents the half-width of radiation absorbed by an isolated spectral line from a narrow line source and is given by (35),

$$A_T = \int_0^{\Delta \nu_s (\pi)^{\frac{1}{2}} 2 (\ln 2)^{\frac{1}{2}}} [1 - \exp(-k \nu L)] d\nu$$

where the limits are over the half-width of the source line $\Delta \nu_s$ in seconds $^{-1}$. The total absorption can be pictorially represented by the area under any of the curves

shown in Figure 3, as is the variation of A_T with atomic concentration.

The total absorption factor for radiation absorbed from a continuous source may also be derived to give a similar expression (21) but this has not been presented in this thesis as only line sources have been employed here as radiation sources for atomic fluorescence.

The above expression for A_T may be evaluated for small optical densities (small values of $k_\nu L$ at all frequencies) and for large optical densities near the line centre. At small optical densities,

$$A_T = \int_0^{\Delta\nu_S(\pi)^{\frac{1}{2}}2(\ln 2)^{\frac{1}{2}}} [1 - \exp(-k_\nu L)] d\nu$$

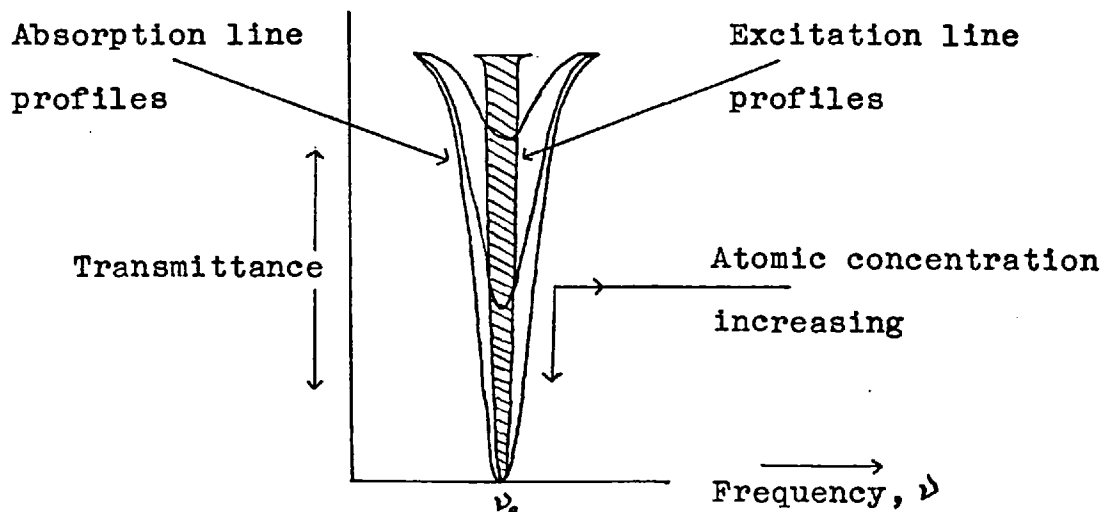
$$= L \int_0^{\Delta\nu_S(\pi)^{\frac{1}{2}}/2 (\ln 2)^{\frac{1}{2}}} k_\nu d\nu$$

and as k_ν is approximately constant over the narrow interval $\Delta\nu_S$,

$$A_T = \frac{(\pi)^{\frac{1}{2}} k^0 L \delta \Delta\nu_S}{2 (\ln 2)^{\frac{1}{2}}}$$

where δ is the factor to correct broadening of the absorption line by factors other than Doppler broadening.

Low Atomic Concentration



High Atomic Concentration

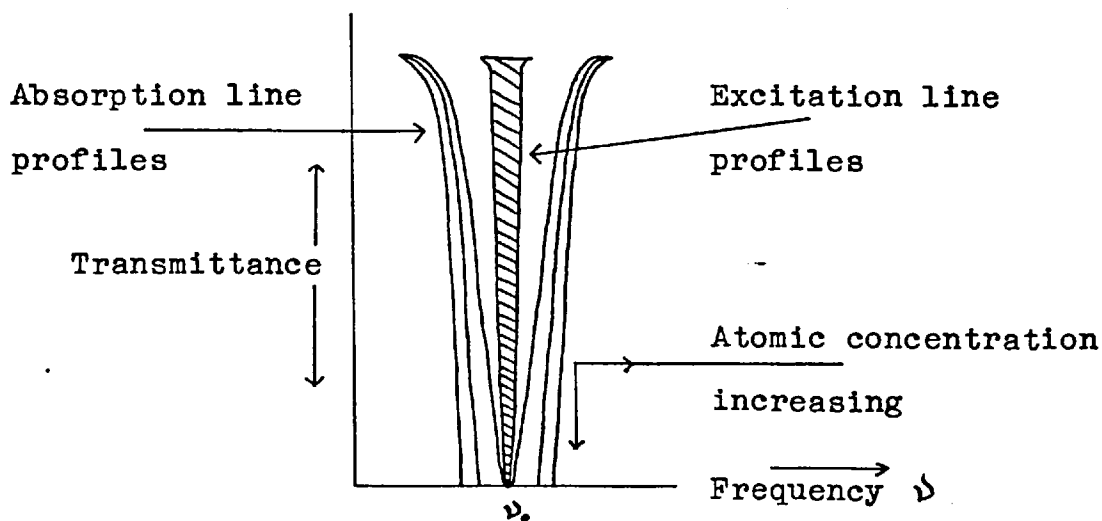


Figure 3: Pictorial representation of total absorption with a narrow line source.

At large optical densities A_T is given by

$$A_T = \int_0^{\Delta\nu_S(\pi)^{1/2}/2 (\ln 2)^{1/2}} d\nu$$

$$= \frac{\Delta\nu_S(\pi)^{1/2}}{2(\ln 2)^{1/2}}$$

The factor $(\pi)^{1/2}/2 (\ln 2)^{1/2}$ is needed to convert from a Gaussian to a triangular half-width to use in the calculation of A_T , i.e. the area shown in Figure 3.

iv. Intensity of Atomic Fluorescence

The intensity of atomic fluorescence radiation (36) is dependent upon the intensity of the exciting radiation, the ratio of the excitation source line or band half-width ($\Delta\nu_S$, in seconds⁻¹) to the absorption line half-width ($\Delta\nu_A$, in seconds⁻¹), the diameter of the absorption cell and the solid angle over which excitation occurs, the atomic concentration of the absorbing atoms, the efficiency of converting the absorbed energy to fluorescence radiation and the spectral parameters such as frequency of the absorption line, the transition probability and the extent of line broadening. A schematic diagram of an atomic fluorescence spectrophotometer is shown in Figure 4 which indicates the absorption cell (flame) diameter and solid angles. It will be assumed

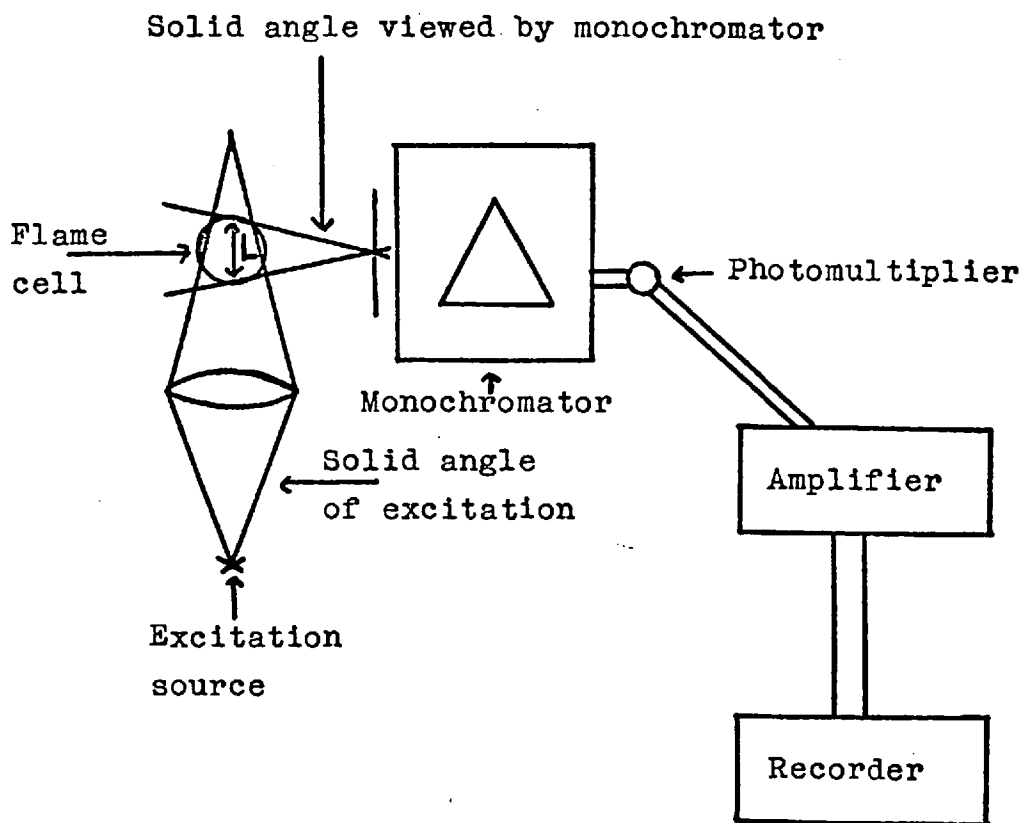


Figure 4: Schematic representation of atomic fluorescence spectrophotometer.

that the source of excitation has a greater area than the flame cell, which is within the solid angle over which excitation occurs, and that the flame cell is within the solid angle of radiation Ω_f subtended by the monochromator entrance slit.

Assuming the above conditions the integrated atomic fluorescence expression for a spectral line is given by,

$$I_F = \frac{I_A \phi}{4\pi}$$

where

I_F is the fluorescence intensity (watts cm^{-2} ster $^{-1}$).

I_A is the total intensity absorbed by the spectral line which results in activation of the fluorescence state (the upper level involved in the fluorescence process).

ϕ is the total power of the fluorescence transition, i.e. watts emitted by the fluorescence process to watts absorbed causing the fluorescence process.

The intensity absorbed I_A is given by,

$$I_A = \Omega_A \sum I_i^0 A_{T_i}$$

where

Ω_A is the solid angle over which excitation occurs, and is dependent upon the monochromator entrance slit parameters.

I_i^0 and A_{T_i} are the incident intensity of the exciting

radiation (watts cm^{-2} ster $^{-1}$ second) and the total absorption factor in seconds $^{-1}$ for the absorption line causing fluorescence stimulation. If, as is the case in all the fluorescence determinations presented in this thesis, resonance absorption-resonance fluorescence is considered, then,

$$I_A = \Omega_A I^0 A_T$$

where

I^0 and A_T are for the resonance absorption process.

The intensities of line sources are generally listed as integrated intensities (in watts cm^{-2} ster $^{-1}$); to obtain I^0 for a line source the integrated intensity is divided by the line half-width. The expressions for I_F for small and large optical densities when $\Delta\nu_S < \Delta\nu_A$ using a line source are derived by substitution of A_T in the above equation. These are given below,

Small optical density,

$$I_F = \frac{2(\ln 2)^{\frac{1}{2}} I_L^0 \Omega_A \lambda_0^2 g_u A_t N_L}{32 \pi^{2.5} g_l \Delta\nu_D} \quad [1.1]$$

Large optical density,

$$I_F = \frac{I_L^0 \Omega_A}{4} \quad [1.2]$$

where

I_L^0 is the integrated intensity of a line source (in watts cm^{-2} ster $^{-1}$).

v. Growth Curves

The growth curves of $\log I_F$ vs. $\log N_1$ for a given element using a sharp line source to stimulate fluorescence can be predicted from equations [1.1] and [1.2]. The curve would be expected to have a slope of 1.00 at low N_1 and 0.0 at high N_1 . It would be expected that as N_1 increases so ϕ will decrease because of quenching processes. A complete derivation of the theoretical atomic fluorescence growth curves and an explanation of some of the deviations which are observed practically have been published by Winefordner and co-authors (36, 37).

vi. General

An adequate review has been published by Winefordner and Mansfield (31) on the variations of atomic concentration with flame temperature and sample concentration introduced into the flame gases. They also describe the experimental system (see Figure 4), possible sources of excitation of fluorescence radiation, and experimental conditions including a review of detection limits and the selectivity of atomic fluorescence.

1.II.4: The Nitrous Oxide-Acetylene Flame

The separated and unseparated nitrous oxide-acetylene

flames have been the principal atom reservoirs employed throughout the work presented in this thesis. This flame is of particular use in the determination by flame atomic spectroscopy of elements which form refractory oxides because it attains a high temperature without an excessive burning velocity, and when fuel-rich, exhibits the strongly reducing properties necessary to support the existence of free atoms of many elements whose oxides are thermally stable.

The advantages of the nitrous oxide-acetylene flame for atomic spectroscopy were first demonstrated by Willis (38) in 1965. Since that time the use and characteristics of the flame have been extensively studied by many workers, principally by Kirkbright, West and co-workers (4-6, 39) and Koirttyohann and Pickett (3, 40, 41).

Because of its high temperature (ca 3,000°K) the flame shows intense background emission from the flame species and reactions in the outer zone (principally from the OH species and the reaction $\text{CO} + \text{O} = \text{CO}_2 + h\nu$ (4)). Separation of the slightly fuel-rich nitrous oxide-acetylene flame may be achieved; this removes the background emission due to the diffusion zone which surrounds the primary region. This separation may be achieved by use of a quartz tube placed over the burner

mounting (4) or by a stream of inert gas flowing parallel to the flame (5, 6). The use of separated flames has been reviewed by Kirkbright and West (42).

The slightly fuel-rich flame exhibits intense emission from the CN red and violet systems within the interconal zone of the flame. The CN radical has been, until the present time, accepted as the agent for the reduction of metal oxides to metallic atoms by the removal of atomic oxygen in the equilibrium,



In the unseparated flame the reducing zone is restricted by the entrainment of atmospheric air; however, upon either mechanical or inert-gas separation, the reducing zone is considerably extended and this is instrumental in the maintenance of a substantially greater population of ground state atoms of an aspirated element. This leads to substantially greater sensitivities being observed in the separated flame.

1.II.5: Electrodeless Discharge Tubes

Although the history of electrodeless discharge tubes is comparatively long (high frequency E.D.T.'s were first discovered by Hittorf in 1884 (43)), it is only in the 1950's and '60's that they have been employed as line

sources for the analytical atomic spectroscopy techniques. Prior to this their main use was as line sources for wavelength calibration and spectral investigations. The developement of electrodeless discharge tubes has been adequately described by Thompson (32), as has their preparation and basic principles.

CHAPTER 2. EXPERIMENTAL

Chapter 2 outlines the apparatus used throughout the work presented in this thesis. The experimental arrangement used for the determination of several refractory elements by atomic fluorescence, atomic absorption and flame atomic emission spectroscopy is described in detail. Where the apparatus has been modified from that commercially available the modification has been described, and justification for the alteration given.

2.1: Apparatus

The instrument used throughout these studies was a Techtron AA4 atomic absorption spectrophotometer fitted with a Servoscribe recorder, which was used on the 0-10 mV range. The use of this instrument for atomic fluorescence measurements has been described elsewhere (44, 45). A diagram of the apparatus as it was employed in the atomic fluorescence spectroscopy mode is shown in Figure 5. Spectra were scanned with a 6 r.p.m. synchronous motor geared to the diffraction grating drive-shaft to produce a scanning speed of $7.5 \text{ nm minute}^{-1}$. The discharge of the electrodeless discharge tubes employed for excitation of the atomic fluorescence was maintained using a

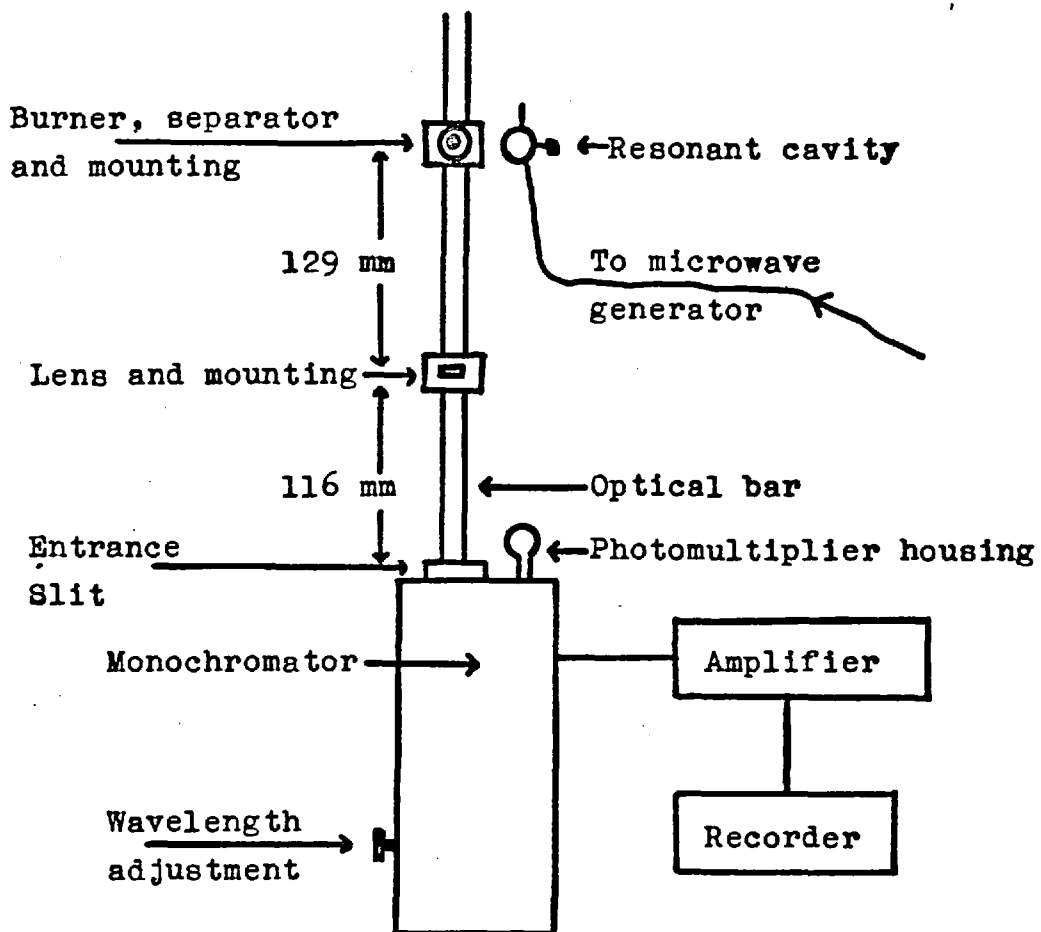


Figure 5: Diagrammatic representation of the Techtron AA4 flame spectrophotometer when used for atomic fluorescence measurements.

Microtron 200 microwave generator ($2,450 \pm 25$ MHz) (Electro-medical Supplies Ltd, Wantage) which was electronically modulated at 285 Hz in phase with the Techtron amplification. The synchronous modulator of the Techtron amplifier was phased to the modulated signal from the E.D.T. by means of the synchronisation pulse provided by the Microtron modulator unit (variable 0 to 5 volts peak to peak square wave). This signal was fed to the Techtron AA4 amplifier via the 5-pin DIN input socket provided to permit the use of a mechanical chopper. A quarter wave or a three-quarter wave Broida-type cavity (Electro-medical Supplies Ltd, Wantage) was employed, and the discharge was initiated with a high-frequency 'Tesla' vacuum-tester.

The advantages of electronically modulated electrodeless discharge tubes for atomic fluorescence and atomic absorption spectroscopy have been described in detail elsewhere (46, 47). The three different modulation systems for atomic fluorescence are:-

- i) electronic modulation of the source,
- ii) mechanical modulation of the source by placing a mechanical chopper between the flame and the source,
- iii) measurement of the fluorescence signal on top of the flame atomic emission from the flame by placing a

mechanical chopper between the flame and the monochromator.

Systems (ii) and (iii) have several disadvantages. In system (ii) the size of the mechanical chopper reduces the amount of energy reaching the flame from the discharge tube by the small physical size of the chopper orifice, and for the necessity for the source to be a considerable distance from the flame (inverse-square law effect, only partially compensated by focussing). When system (iii) is employed the fluorescence signal is obscured in many instances by the very intense background radiation emitted by the nitrous oxide-acetylene flame and the flame atomic emission from the species being investigated.

Electronic modulation of the source permitted the source to be placed up to the burner mounting and this precluded the detection of flame atomic emission with the a.c. amplification system employed.

2.II: Burners

A Techtron AA4 50 mm path-length, high-temperature burner (AB 40) was employed with the nitrous oxide-acetylene flame for the atomic absorption measurements. Flame atomic emission and fluorescence measurements were made using a circular burner designed for a nitrous oxide-acetylene flame, with facilities for flame separation by

nitrogen and argon by gas shielding. This burner is similar to that described in detail elsewhere (48) with the exception that for these studies the flame was supported at a circular slot of dimensions 11 mm internal diameter and 0.75 mm width. The acetylene and nitrous oxide supplies to either burner were regulated by the gas control unit on the AA4 flame spectrophotometer.

2.III: Nebulizer

The indirect nebulizer of the Techtron was modified by the insertion of a 500 mm length of 10 mm internal diameter plastic tubing between the nebulizing chamber and the burner mounting. This was found to give greater stability of signal because there was a complete pre-mixing of gases before combustion. Gaydon and Wolfhard (49) have suggested that the burner tube between the mixing point of the gases (nebulizer) and the burner head must be sufficiently long to enable good mixing and for steady flow conditions to be established. For air flames a tube at least 300 mm long, and for fast-burning mixtures lengths up to 900 mm have been recommended. A brief study for both the air-acetylene and nitrous oxide-acetylene flames was undertaken and the results of these are summarized below.

The flame atomic emission of a $10 \mu\text{g ml}^{-1}$ sodium solution at 589.0 nm in the air-acetylene flame was recorded, with the additional length of tube both inserted and removed. A similar experiment was repeated for the nitrous oxide-acetylene flame utilizing $100 \mu\text{g ml}^{-1}$ vanadium solution at 438.7 nm. The comparison of signal-to-noise was obtained in each case. The spectral band-pass used in each case was 0.33 nm, with the most appropriate amplifier E.H.T. gain for each solution.

The air-acetylene flame:	signal:noise ratio
with tube inserted	100:1
without tube inserted	88:1

The nitrous oxide-acetylene flame:	
with tube inserted	100:1
without tube inserted	64:1

As would be expected from theoretical considerations of burning velocities adequate mixing of the gases has occurred for the comparatively slow burning gases using the standard Techtron nebulization arrangement. However, a significant reduction in the signal-to-noise ratio would be expected using the nebulizer modification for gases with a higher burning velocity.

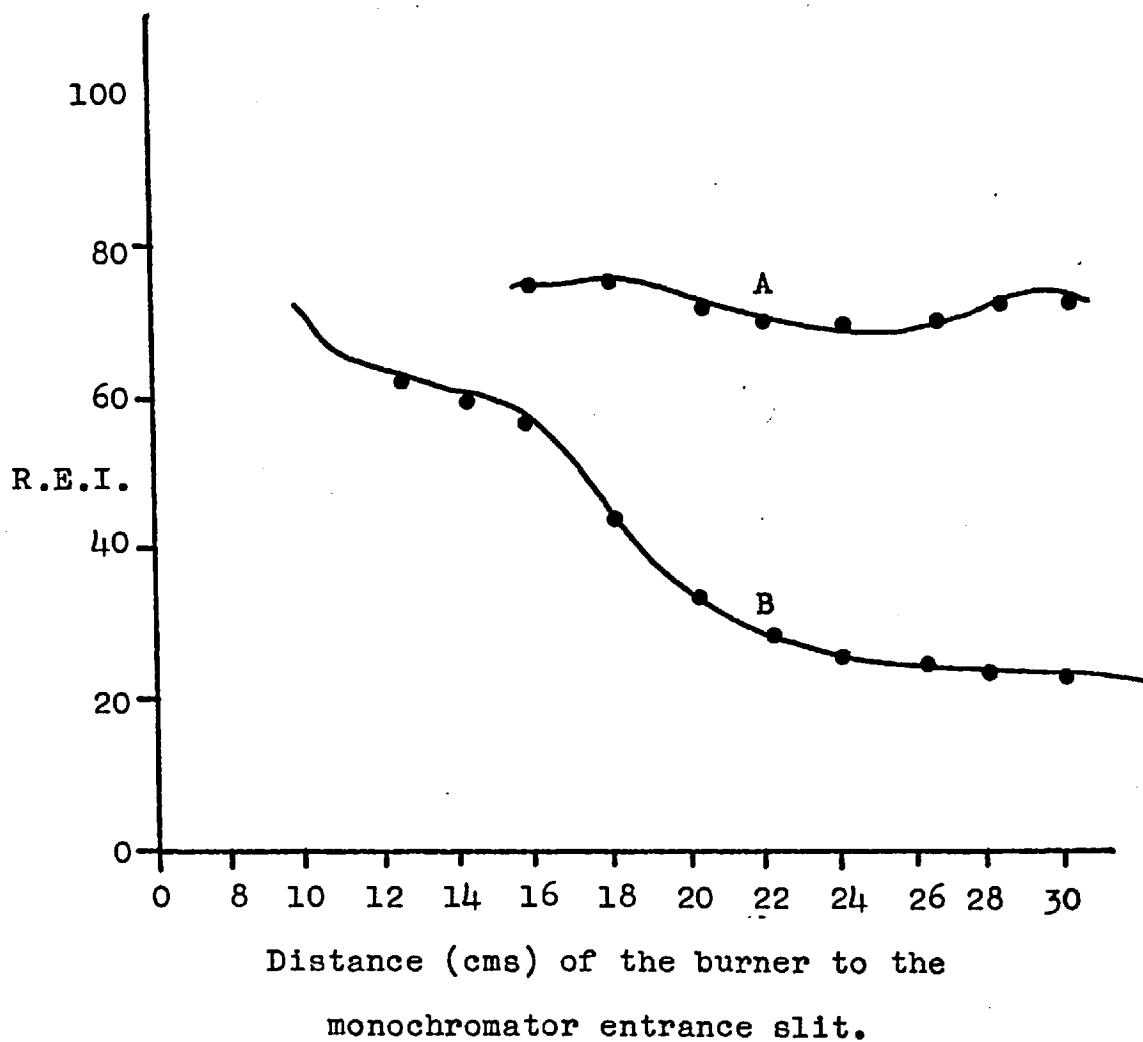
2.IV: Optical Arrangement

In the atomic fluorescence studies the flame was irradiated by an electrodeless discharge tube placed at right angles to the line from the flame to the monochromator entrance slit. The tube and cavity were shielded to prevent any radiation falling directly upon the entrance slit. The discharge tube was placed in the resonant cavity, which in turn was placed as close to the flame as possible. A 50 mm transparent silica disc was placed between the cavity and the flame to prevent disturbance of the flame by the draughts arising from the air cooling of the tube within the cavity. No focussing was used, the greatest fluorescence intensity being found with the simple arrangement described above. When a discharge tube that did not require air cooling for stable output was employed, the silica disc was removed because it was not 100 per cent transparent to ultra-violet radiation.

There were two possible alternative positions for the burner. One was to place the burner head as close to the monochromator entrance slit as possible. This proved to be ca 100 mm from the slit; placing the burner nearer prevented the use of the mechanical chopper and also caused a severe drift of signal as the flame was then situated too close to the photomultiplier housing.

In the second position the burner was placed 245 mm from the monochromator entrance slit and the radiation from the flame was focussed onto the slit using the convex lens (ca 63 mm focal length) supplied for use in atomic absorption with the spectrophotometer. The optimum distance of the burner from the monochromator entrance slit was determined in the following manner; a study of the different intensities from a standard solution of $10 \mu\text{g ml}^{-1}$ sodium was undertaken at 589.0 nm by flame atomic emission, using an air-acetylene flame supported at a conventional round emission burner. The amplifier E.H.T. gain and spectral band-width, 0.33 nm, were unchanged throughout the course of the determination. The results obtained are shown in Figure 6.

Curve A shows the emission intensities obtained when the burner was progressively moved away from the monochromator and the radiation from the flame was focussed onto the slit with the standard Techtron lens. The recommended distances (Techtron AA4 Instruction Manual), in which the centre of the burner head was set 245 mm from the monochromator entrance slit and the lens was placed in between the flame and the slit 116 mm from the slit, produced the greatest intensity. Curve B shows the decrease in emission intensity observed as the burner was



R.E.I. : Relative emission intensity.

Figure 6: The relative emission intensities of $10 \mu\text{g ml}^{-1}$ sodium at 589.0 nm obtained with different optical arrangements.

A: with focussing. B: without focussing.

moved away from the slit using no focussing. The emission intensities shown on Curve A are greater than those shown on Curve B, though with the burner head set at 100 mm from the flame the differences are minimal. In practice the radiation from the flame was focussed onto the monochromator entrance slit as this proved more convenient because there was less heating of the photomultiplier housing by the flame.

The effect of placing a small front-silvered concave mirror behind the flame opposite the source when obtaining fluorescence measurements was also investigated. It was found that in all cases the increase in fluorescence emission was accompanied by a corresponding increase in the background noise level. As only a small mirror was available the overall sensitivity gained was negligible, so its use was discontinued.

CHAPTER 3. THE DETERMINATION OF SOME REFRACTORY ELEMENTS BY FLAME ATOMIC SPECTROSCOPY

The characteristics of the determination of several refractory elements (aluminium, germanium, molybdenum, silicon, titanium, vanadium and zirconium) by atomic fluorescence spectroscopy utilizing an argon or nitrogen separated fuel-rich nitrous oxide-acetylene flame as atom reservoir and microwave-excited electrodeless discharge tubes as sources are presented in this chapter. An experimental comparison of the sensitivity and selectivity of the atomic fluorescence spectroscopic determination for each element has been made with those available by flame atomic emission and atomic absorption spectroscopy when the same instrumentation and flame were used. The characteristics which were observed for each element are described separately, but a general comparison of the spectroscopic techniques that were used and discussion of each element's determination are presented as a conclusion to the chapter.

Refractory elements may be defined, for the purposes of their determination by flame atomic spectroscopy, as those elements which form stable and long-lived oxide species within an analytically useful flame. Their atomic absorption and flame atomic emission characteristics

(which were obtained in a number of different flames) have been extensively studied and reported (3, 5, 6, 38, 41, 50-70). It has been found that the greatest sensitivity and selectivity was obtained for aqueous sample solutions when the nitrous oxide-acetylene flame is employed as the atom reservoir. The advantages which are obtained when this flame is used have been described previously in this thesis (pp 31). Similarly the detection limits for the determination of the refractory elements by atomic absorption and flame atomic emission may be improved by inert-gas separation of the nitrous oxide-acetylene flame (5, 6); the advantages which are gained upon separation have also been described previously (pp 32).

Standard equipment has been used whenever possible throughout the study, i.e. for the atomic absorption determinations standard Techtron hollow-cathode lamps were used in conjunction with a 50 mm slot burner. The respective high-intensity hollow-cathode lamps were available and employed in the silicon and aluminium determinations. The initial atomic fluorescence measurements were made with the respective hollow-cathode lamps, but in all cases negligible fluorescence intensity was observed. The procedure that was employed is

described in some detail in Section 3.1.1., and this was subsequently repeated for the other refractory elements.

3.1: THE DETERMINATION OF SILICON

The determination of silicon by atomic absorption spectroscopy in the conventional (38, 50-53) and the separated (5) nitrous oxide-acetylene flame, and by flame atomic emission in the separated nitrous oxide-acetylene flame (6) has been reported by a number of workers. In this Section the determination of silicon by atomic fluorescence is described, and this determination has been compared with that obtained by flame atomic emission and atomic absorption with the same equipment. The initial atomic fluorescence spectroscopy measurements were made with a high-intensity hollow-cathode lamp as source. The lamp intensity was found to be inadequate, and all subsequent determinations were obtained with an electrodeless discharge tube as the source. The experimental parameters for each technique were optimized, and the effect of diverse ions was studied.

3.I.1: The Atomic Fluorescence of Silicon using a High-Intensity Hollow-Cathode Lamp as Source

The use of a hollow-cathode lamp as source for atomic fluorescence has been previously reported, but only for silver (44), magnesium (71), and cobalt, iron and nickel (72), elements that are non-refractory in nature and that can be determined in relatively cool flames. The standard atomic fluorescence experimental arrangement previously described was employed with the burner ca 245 mm from the monochromator entrance slit. The hollow-cathode lamp was placed perpendicularly to the burner-slit axis, and mounted as close to the burner as was feasible.

It was found that a minimal signal was produced when a $1,000 \mu\text{g ml}^{-1}$ silicon solution was aspirated into the flame at 251.61 nm, with a spectral band-width of 0.99 nm. The overall detection limit, to be subsequently defined, was of the order of $200 \mu\text{g ml}^{-1}$ using the above arrangement. The use of a lens between the burner and lamp did not increase the signal intensity.

A far more intense source was therefore required for silicon atomic fluorescence emission excitation, and that source would have to be situated as close to the flame as possible; there was a distance of 80 mm between the cathode and quartz window of the hollow-cathode lamp. A

silicon electrodeless discharge tube would satisfy these requirements. At this stage it was impossible to determine if the signal obtained was fluorescence and not scatter from particulate matter in the flame.

3.I.2: The Preparation of Silicon Electrodeless Discharge Tubes

The silicon electrodeless discharge tubes used were prepared from elemental silicon and iodine by the same general procedure described for other elements (73). Some initial difficulty was experienced in the production of a silicon tube which would exhibit an intense stable discharge. A systematic study on the effect of varying the weight ratio of silicon to iodine on the intensity and stability of the emission at 251.6 nm was therefore undertaken. Silicon and iodine were taken in known weight ratios and ground to a fine powder with a pestle and mortar. Weighed amounts of the mixtures were placed in degassed silica tubing. The iodine was then degassed for a fixed length of time (2 minutes) and the tubing sealed in the usual manner with an argon filler-gas pressure of ca 1 torr. A comparison of the stability and intensity for each tube was obtained under identical conditions using the quarter wave cavity. The results are shown in Table I, and indicate that the most satisfactory

TABLE I

Characteristics of E.D.T.'s Prepared from Varying Weight

Ratios of Silicon:Iodine

Silicon:iodine weight ratio	Relative Intensity	Characteristics
50:1	1	Very stable
20:1	1	Very stable
10:1	20	Fairly stable
8.5:1	30	Stable with slight cooling
7:1	60	Stable with rapid cooling
1:1	10	Stable with rapid cooling

tubes were obtained with a silicon:iodine weight ratio of 7:1

The tubes used in the quarter wave cavity were ca 80 mm long and contained ca 5 mg of the 7:1 silicon:iodine mixture. These tubes produced the grèatest intensity and stability when operated at 100 Watts (5 W reflected power). Greater stability but less intensity was subsequently obtained at the same power input by use of the three-quarter wave cavity. It was always necessary to air-cool the tubes strongly to obtain stable silicon emission, which, under the above conditions, was bright blue.

3.I.3: Spectral Characteristics of Discharge Tube

The emission spectrum from a silicon discharge tube was obtained between 200 and 260 nm by placing the tube at that position employed for the hollow-cathode lamp when using the conventional experimental arrangement for atomic absorption and scanning the emission received by the monochromator. The only atomic silicon lines observed were those between 250 and 253 nm shown in Table II. The intensities obtained under the same instrumental conditions from a Techtron high-intensity hollow-cathode lamp are also shown; these were determined experimentally by replacing the tube and cavity in the above arrangement by the lamp. The line-to-background ratio for each source was obtained at the most intense line, i.e. 251.61 nm. The long period fluctuation and instantaneous noise were similar for both sources.

3.I.4: Reagents

a. Stock Silicon Solution, 1,000 $\mu\text{g ml}^{-1}$

1 g of pure silicon powder (Hopkin and Williams Ltd) was dissolved in sufficient cold concentrated hydrofluoric acid (25 mls AR grade, 40%) in a polythene bottle so that on dilution to 1 litre with distilled water the solution was 1 per cent with respect to hydrofluoric acid. Care

TABLE II

Principal Source Emission Characteristics

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
250.69	$^3P_1^o \longrightarrow ^3P_1$	2.1	89
251.43	$^3P_1^o \longrightarrow ^3P_0$	2.1	69
251.61 ^c	$^3P_1^o \longrightarrow ^3P_1$	6.4	100
251.92	$^3P_1^o \longrightarrow ^3P_1$	1.5	64
252.41	$^3P_0^o \longrightarrow ^3P_1$	2.0	70
252.85	$^3P_1^o \longrightarrow ^3P_1$	2.5	73
Line-to-background ratio at 251.61 nm		44:1	130:1
Long period fluctuation over 1 hour		$\pm 3\%$	$\pm 3\%$
Instantaneous noise over 1 minute		$\pm 1\%$	$\pm 1\%$
^a emission intensities expressed relative to intensity of 251.61 nm line from E.D.T.			
^b H.C.L. primary electrodes operated at 12 mA, secondary electrodes at 400 mA.			
^c most sensitive for atomic absorption			

was taken to ensure that no volatile silicon fluorides were allowed to escape throughout the dissolution process.

b. Diverse Ions

Stock 10 per cent solutions were prepared from analytical reagent grade salts of the elements. These stock solutions were subsequently used in all the interference studies reported in this thesis.

3.I.5: Spectral Characteristics

a. Flame Atomic Emission Measurements

The flame background and flame atomic emission spectra for silicon between 249 and 254 nm are shown in Figure 7 for the nitrogen separated nitrous oxide-acetylene flame. The flame background was not intense in this region, but on introduction of silicon into the flame significant atomic emission was observed. Flame atomic emission therefore provided good detection limits for silicon at 251.61 nm in the separated and unseparated flames. Lower detection limits were observed in the separated flame as a direct result of the lower background and noise levels in the interconal zone and because of the increased volume of the zone (6). It has also been shown that the atomic population of silicon increases on separation of a nitrous oxide-acetylene flame (5).

b. Atomic Fluorescence Measurements

The flame background and atomic emission from silicon

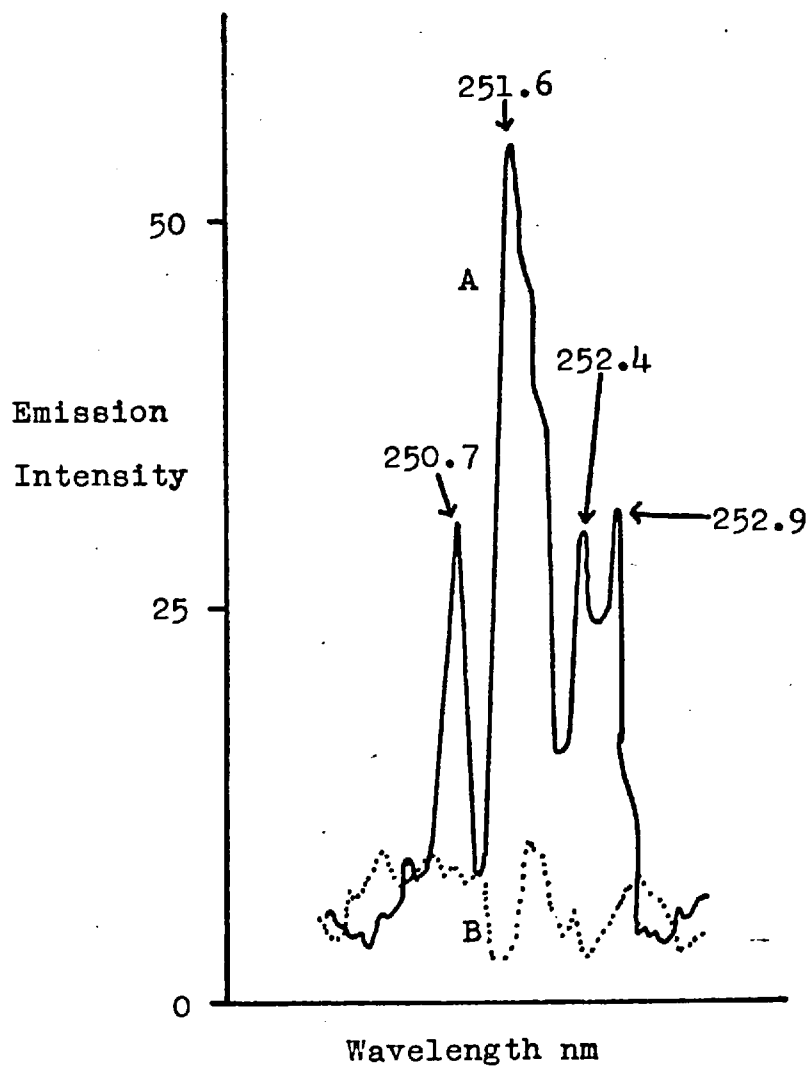


Figure 7: Flame atomic emission spectrum of A: $100 \mu\text{g ml}^{-1}$ silicon solution and B: water between 249 and 254 nm, 0.33 nm spectral band-width, scan speed $1.5 \text{ nm minute}^{-1}$.

constituted a d.c. signal at 251.61 nm received by the photomultiplier. In the prescence of this emission in the hot flame it was necessary to employ a modulated source and detector if appreciable sensitivity and good selectivity were to be obtained in the detection of silicon by atomic fluorescence spectroscopy. When atomic fluorescence measurements were made with the electronically modulated electrodeless discharge tube arrangement described previously, the relative fluorescence intensities at the various wavelengths shown in Figure 8 were obtained using the optimum acetylene flow-rate and height of observation in the flame. Negligible interference from the source was received at the monochromator slit by reflection from the burner assembly. The signals obtained at 251.61 nm when silicon solutions were introduced into the flame were assigned to silicon fluorescence rather than scatter from particulate material in the flame. The experimental evidence for this was,

- a) that appreciable absorption by silicon atoms was observed in atomic absorption spectroscopy with the same flame, source and samples,
- b) that the introduction of a $20,000 \mu\text{g ml}^{-1}$ solution of sodium tungstate into the flame caused no scatter of incident radiation from the silicon source and
- c) no scattered Hg 253.65 nm radiation was observed when

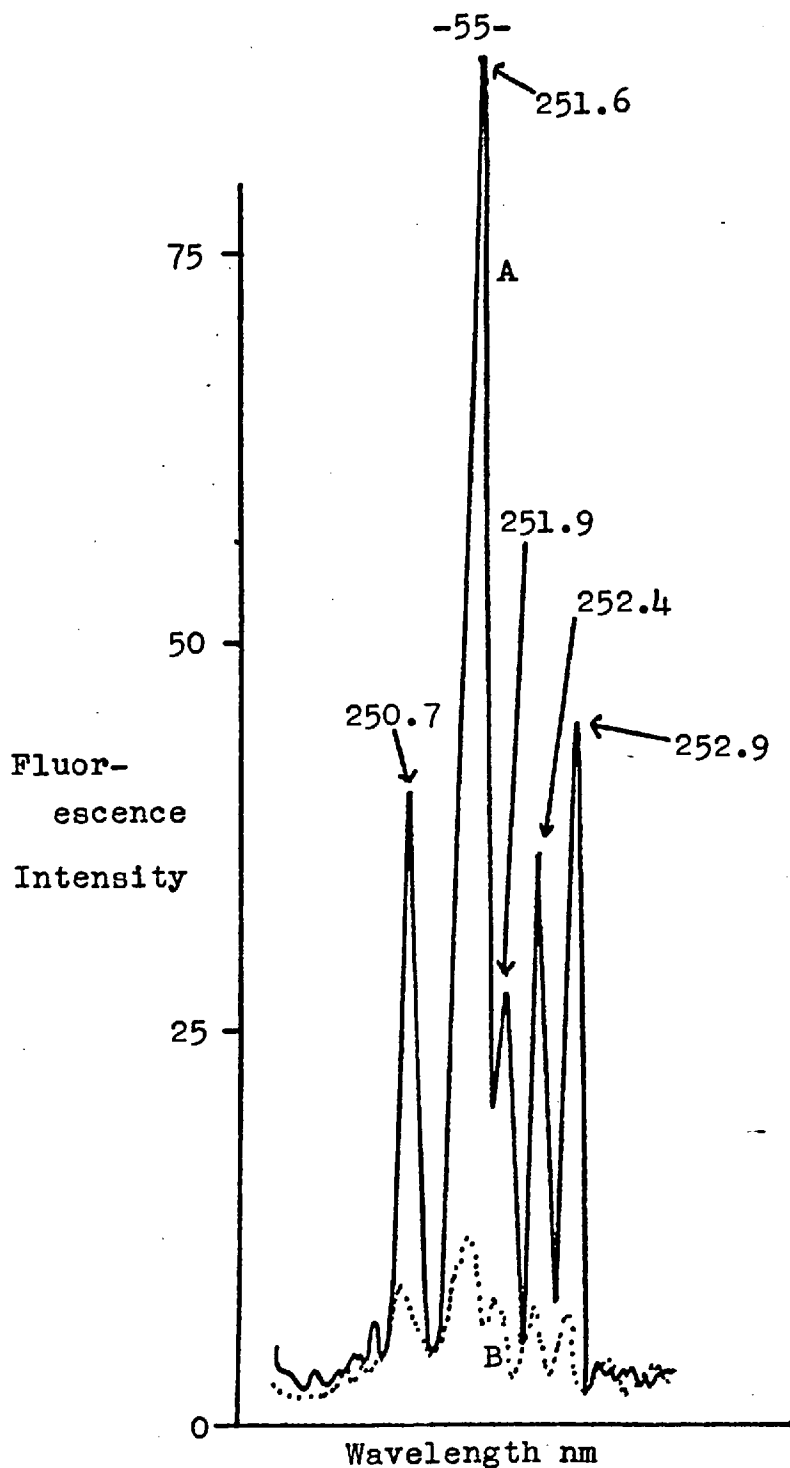


Figure 8: Atomic fluorescence emission spectrum of
A: $6,000 \mu\text{g ml}^{-1}$ silicon solution and B: water between
249 and 254 nm, 0.16 nm spectral band-width, scan
speed $1.5 \text{ nm minute}^{-1}$.

the silicon E.D.T. was replaced by an intense mercury E.D.T. and a $1,000 \mu\text{g ml}^{-1}$ silicon solution was aspirated into the flame.

The absence of interference from other elements in the determination of silicon under the conditions described also supported the assignment.

Figure 8 indicates that resonance fluorescence was observed at the principal silicon lines emitted from the source. The fluorescence at the 251.4 nm line ($^3\text{P}_0 \rightarrow ^3\text{P}_1$) was difficult to resolve from the more intense emission at 251.61 nm and so appeared as a small shoulder on the 251.61 nm emission. Figure 8 also shows that at the spectral band-width employed for greatest sensitivity, the monochromator transmitted the fluorescence radiation from all six lines, so that it was the integrated fluorescence intensity that was recorded as the analytical signal.

c. Atomic Absorption Measurements

The atomic absorption measurements were obtained with the Techtron recommended settings of band-width and lamp current (AA4 Instruction Manual). The spectral band-width employed was 0.16 nm (slit-width 50 μ). The primary electrodes were run at the recommended current of 12 mA, and the secondary electrodes at 400 mA.

3.I.6: Optimum Flame Operating Conditions

The flame operating conditions were chosen to produce the most intense fluorescence and flame atomic emission signals with the minimum background and noise; spectral band-widths of 0.99 nm (the maximum instrumental band-width) and 0.33 nm respectively were employed. The nitrous oxide flow-rate was maintained at a constant $5.8 \text{ l minute}^{-1}$ and the nitrogen or argon gas flow-rate was initially set at ca 10 l minute^{-1} , the minimum necessary to obtain effective separation of the flame. Under these conditions the effect of variation of the acetylene flow-rate on the atomic fluorescence and flame atomic emission from silicon was observed. Figure 9 shows that the maximum fluorescence and flame atomic emission intensities were observed when using ca $3.2 \text{ l minute}^{-1}$ and ca $3.0 \text{ l minute}^{-1}$ of acetylene respectively; these flow-rates were used for all further work.

With the optimum conditions described above the most intense fluorescence and flame atomic emission was observed in the red interconal zone immediately above the primary reaction zone. The burner height was adjusted so that the monochromator entrance slit viewed the interconal zone between 3-13 mm above the primary reaction zone.

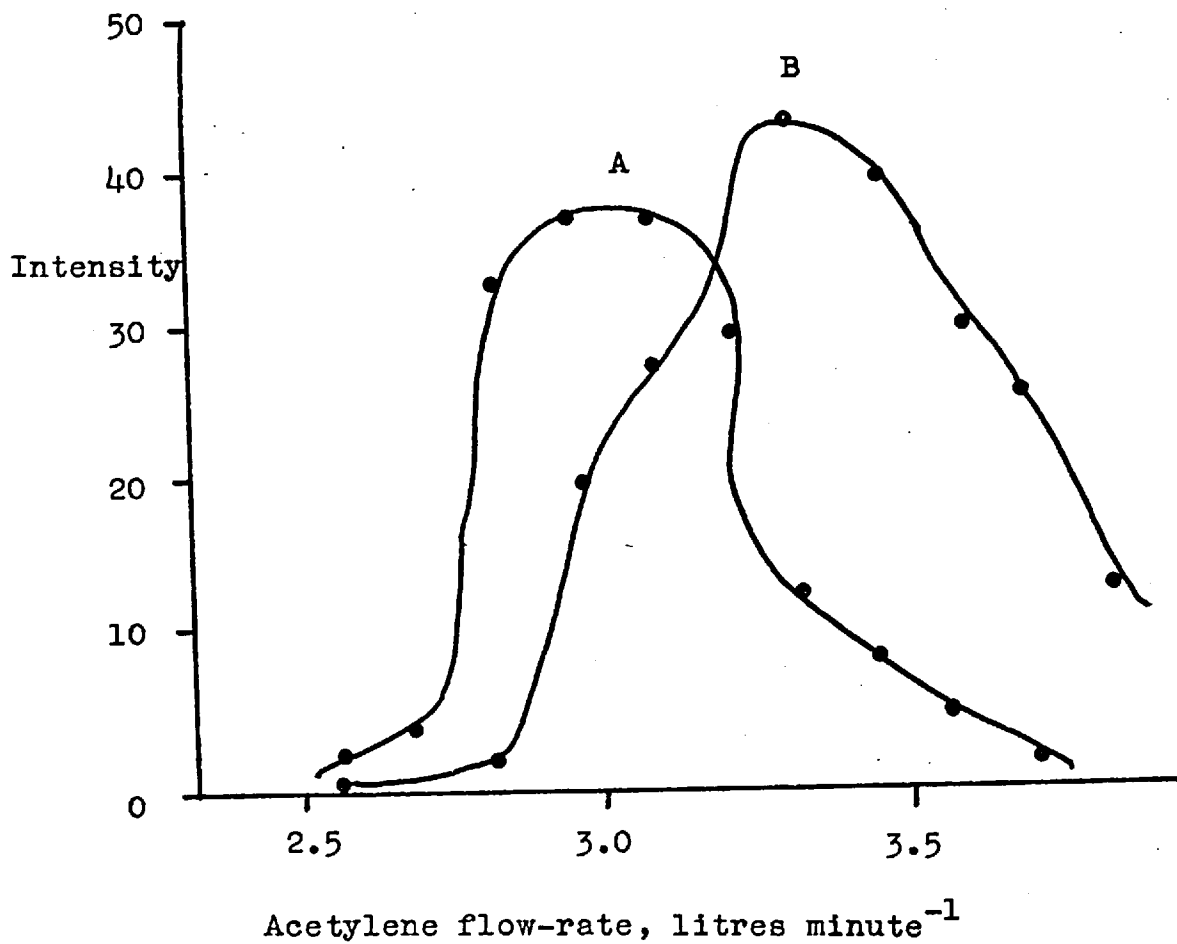


Figure 9: Effect of acetylene flow-rate of A: flame atomic emission intensity of $100 \mu\text{g ml}^{-1}$ silicon at 251.6 nm and B: fluorescence intensity of $50 \mu\text{g ml}^{-1}$ silicon at 251.6 nm. Nitrogen separated flames.

3.I.7: Detection Limits for Silicon by Flame Atomic Emission, Atomic Fluorescence and Atomic Absorption Spectroscopy

The limits of detection for silicon at 251.61 nm by atomic fluorescence and flame atomic emission were obtained for both the separated and unseparated flames. The detection limit for atomic absorption was determined at the standard Techtron 50 mm slot burner. The detection limit was defined as the concentration of silicon in aqueous solution required to produce a signal:noise ratio of unity. This definition has subsequently been employed throughout this thesis.

The detection limits that were observed are summarized in Table III, as well as the sensitivity of the atomic absorption determination (the sensitivity being conventionally defined as the concentration in aqueous solution in μg per ml necessary to produce an absorbance of 1 per cent). Similar sensitivities were obtained with either the hollow-cathode lamp or the electrodeless discharge tube as source.

3.I.8: Effect of Organic Solvent

A brief study of the effect of nebulizing silicon in an organic medium was undertaken. $100 \mu\text{g ml}^{-1}$ silicon

TABLE III

Detection Limits and Sensitivities for Silicon by Flame

Spectroscopy

Technique	<u>Detection Limit ($\mu\text{g ml}^{-1}$)</u>		
	Conventional	N ₂ sep.	Ar sep.
Flame atomic emission ^a	20	6	5
Atomic fluorescence ^a	2	0.7	0.55
Atomic absorption ^{ab}	4	-	-
Atomic absorption sensitivity ^{ab}	6 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron) ^{ab}	2.1 $\mu\text{g ml}^{-1}$		
^a wavelength 251.61 nm			
^b determined with conventional flame at commercial burner			

solutions were prepared with varying proportions of methanol-water as the solvent. The ratio methanol-water was varied between 0:100 and 99:1 , by volume.

The comparative atomic fluorescence signal was obtained at the same amplifier E.H.T. gain, and under the optimum conditions previously determined. The comparative signal intensities are shown in Table IV.

The increased signal intensity when the 99:1 methanol:water solvent was used resulted not only from the flame becoming more fuel rich, but also, probably, from an increased rate of nebulization caused by the surface

TABLE IV

Effect of Organic Solvent on Atomic Fluorescence Signal

Solution				Fluorescence Intensity
100 $\mu\text{g ml}^{-1}$	silicon, aqueous solution			34
"	"	50:50	MeOH:H ₂ O	35
"	"	75:25	MeOH:H ₂ O	34
"	"	99:1	MeOH:H ₂ O	77

Ratios by volume

tension effect. Although the fluorescence signal appeared to have doubled in almost 100 per cent organic solutions the background noise also increased by an equivalent amount which resulted in no increase in the detection limit. The use of organic solvents for atomic fluorescence was therefore not adopted.

3.1.9: Calibration Graphs and Precision

The calibration graphs obtained for the flame atomic emission and atomic fluorescence of silicon in the nitrogen separated flame under optimum conditions are shown in Figure 10. Linear calibration graphs were obtained for silicon flame atomic emission at 251.61 nm over the range 25 to 500 $\mu\text{g ml}^{-1}$. For atomic fluorescence linear calibration graphs were obtained over the range 2 to 100 $\mu\text{g ml}^{-1}$. Over the range 50 to 1,000 $\mu\text{g ml}^{-1}$ slight

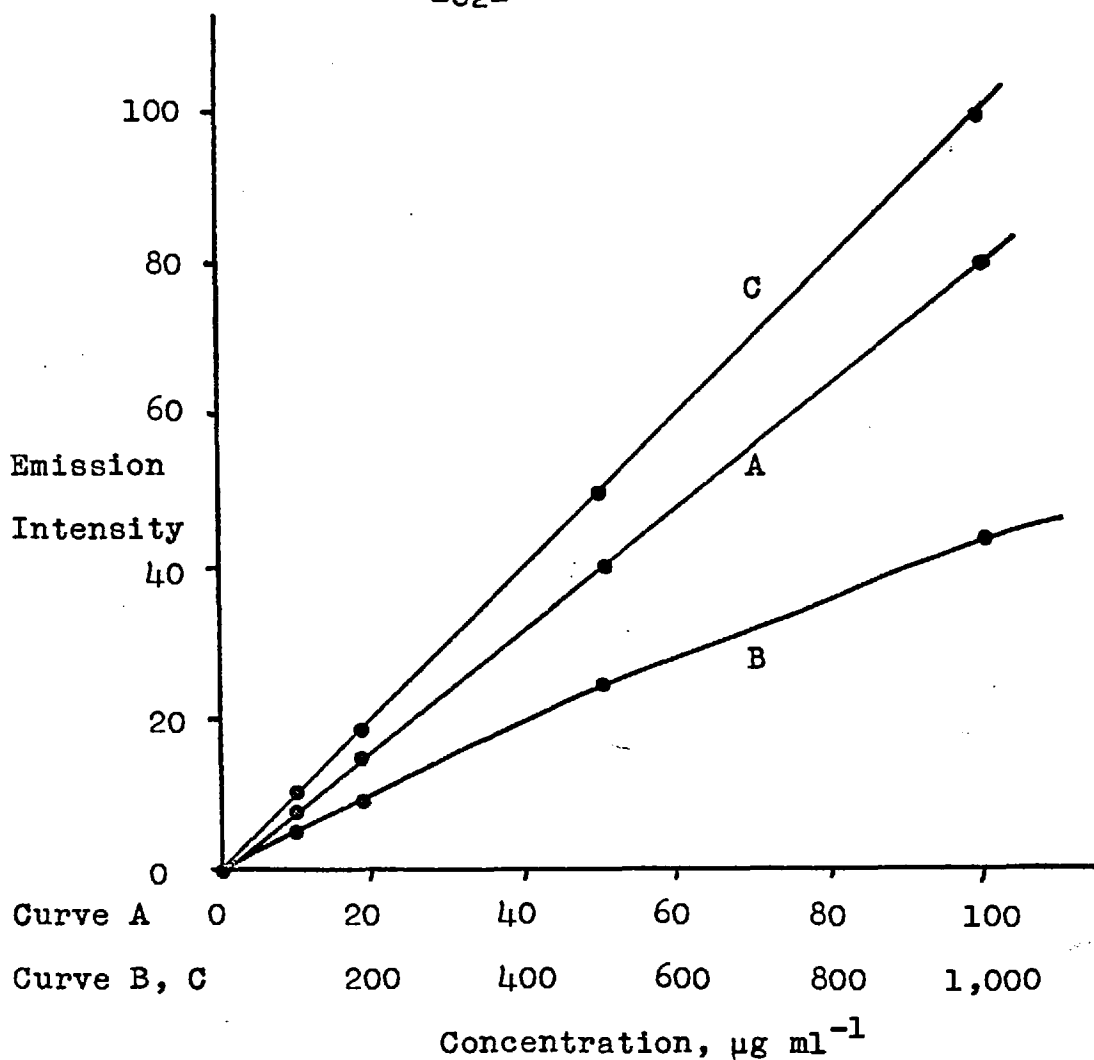


Figure 10: Calibration graphs for silicon atomic fluorescence, Curves A ($0-100 \mu\text{g ml}^{-1}$) and B ($0-1,000 \mu\text{g ml}^{-1}$) and silicon flame atomic emission, Curve C ($0-1,000 \mu\text{g ml}^{-1}$).

curvature towards the concentration axis was observed.

The repetitive introduction (10 times) of a 200 $\mu\text{g ml}^{-1}$ silicon solution into the separated flame under the optimal conditions indicated a standard deviation in the silicon flame atomic emission intensity at 251.61 nm of 2.02 per cent. Similar experiments with a 50 $\mu\text{g ml}^{-1}$ silicon solution resulted in a standard deviation of 1.8 per cent for the fluorescence measurements.

3.I.10: Interference Studies

The effect of 100-fold excesses by weight of a range of cations and anions on the intensity of the flame atomic emission and atomic fluorescence produced by 100 $\mu\text{g ml}^{-1}$ and 50 $\mu\text{g ml}^{-1}$ of silicon at 251.61 nm respectively was investigated; all readings were obtained with the optimal conditions for each technique. Diverse ions were considered not to interfere when they produced a variation in signal intensity of not greater than twice the standard deviation. The effect of each ion is summarized in Table V.

No interference was observed from any diverse ion on the atomic fluorescence intensity, but there were five instances of interference in flame atomic emission. It was assumed that these increases of signal were principally

TABLE V

Effect of Diverse Ions on Silicon Emission

Element	A.F.S. (50 $\mu\text{g ml}^{-1}$)	F.A.E. (100 $\mu\text{g ml}^{-1}$)
Al	No Interference	No Interference
Be	"	"
Cd	"	"
Co (II)	"	+ 700% ^a
Cr (III)	"	+ 550% ^a
Cu	"	No Interference
Fe (II)	"	+ 900% ^a
Hg (II)	"	No Interference
K	"	"
Mg	"	"
Mn (II)	"	"
Mo (VI)	"	"
Na	"	"
Ni	"	"
Pb	"	"
Te (IV)	"	"
V (V)	"	+ 1,000% ^a
W (VI)	"	+ 300% ^a
Zn	"	No Interference
Cl ⁻	"	"
NO ₃ ⁻	"	"
F ⁻	"	"
PO ₄ ³⁻	"	"

^aexistence of some spectral contribution to interference has been experimentally confirmed.

caused by spectral line interference from the diverse ion solution; a concentrated solution of the diverse ion without the presence of silicon produced a considerable atomic emission signal.

3.II: THE DETERMINATION OF GERMANIUM

Germanium has been determined by atomic absorption spectroscopy in the oxy-acetylene (54, 55) and nitrous oxide-acetylene flames (56, 57), by flame atomic emission in the nitrous oxide-acetylene flame (3, 41) and by atomic fluorescence spectroscopy in a nitrogen-oxygen-acetylene flame (74). An electrodeless discharge tube was used as the source in the latter determination; germanium fluorescence was observed, but no quantitative measurements were obtained.

In this study the initial atomic fluorescence determination of germanium was unsatisfactory because a hollow-cathode lamp was employed as the source for the excitation of the emission. More intense electrodeless discharge tube sources were prepared and employed in all subsequent determinations.

3.II.1: Preparation of Germanium Electrodeless Discharge Tubes

Germanium discharge tubes were produced from the

elemental metal and iodine by the same general procedure described for other elements (73). The most satisfactory tubes for use in the three-quarter wave cavity were found to be ca 40 mm long, and contained ca 2 mg of germanium and 2 mg of iodine; the optimum argon filler-gas pressure was found to be 4 torr. The tubes produced greatest intensity and stability when they were operated at 55 W (20 W reflected power). The tubes were slightly cooled by compressed air via the central slot of the cavity. When the tubes were operated under these conditions they exhibited a bright steel-blue emission.

3.II.2: Spectral Characteristics of the Discharge Tubes

The emission spectrum from a germanium discharge tube was obtained between 255 and 305 nm by the same general procedure as employed for silicon (Section 3.I.3.). The atomic germanium emission lines that were observed are shown in Table VI. The most intense line was found to be the 265.12-265.16 nm doublet, which could not be resolved with the instrumentation employed. The comparative intensities for a Techtron germanium hollow-cathode lamp, the line-to-background ratio at the most intense line and the noise characteristics for each source are also shown in Table VI.

TABLE VI

Principal Source Emission Characteristics

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
250.69	$^3P_1^o \longrightarrow ^3P_1$	0.3	23
265.12	$^3P_1^o \longrightarrow ^3P_2$ $^3P_1^o \longrightarrow ^3P_2$	0.8	100
265.16			
269.1	$^3P_1^o \longrightarrow ^3P_2$	0.2	16.7
270.9	$^3P_2^o \longrightarrow ^3P_1$	0.3	25.4
275.5	$^3P_1^o \longrightarrow ^3P_2$	0.4	32.8
303.9	$^1P_1^o \longrightarrow ^1D_2$	0.4	73.5
Line-to-background ratio at 265.1 nm		80:1	98:1
Long period fluctuation over 1 hour		$\pm 3\%$	$\pm 2\%$
Instantaneous noise over 1 minute		$\pm 1\%$	$\pm 1\%$
^a emission intensities expressed relative to intensity of 265.1 nm line from E.D.T.			
^b H.C.L. electrodes operated at 15 mA.			
^c most sensitive for atomic absorption			
^d doublet cannot be resolved with instrumentation employed			

3.II.3: Reagents, Stock Germanium Solution, 1,000 $\mu\text{g ml}^{-1}$

1.44 g of pure germanium dioxide (B.D.H. Ltd) was dissolved in 20 ml of 1 M potassium hydroxide solution, and diluted to 1 litre with distilled water and sufficient AnalaR hydrochloric acid to make the solution slightly acidic.

3.II.4: Flame Atomic Emission Measurements

The flame emission background and germanium flame emission spectra were obtained between 263 and 268 nm for the nitrogen separated nitrous oxide-acetylene flame; these spectra are shown in Figures 11 and 12. The flame emission background exhibits a broad peak (266.3 to 266.8 nm); this peak probably arises from either a weak OH band or from the band head of the fourth positive CO band system. Germanium flame atomic emission was readily observed when germanium was nebulized into the flame. The magnitude of the emission was considerably greater than the flame background emission at 265.1 nm, and its intensity was increased upon separation of the flame with argon.

3.II.5: Atomic Fluorescence Measurements

The germanium atomic fluorescence emission from the

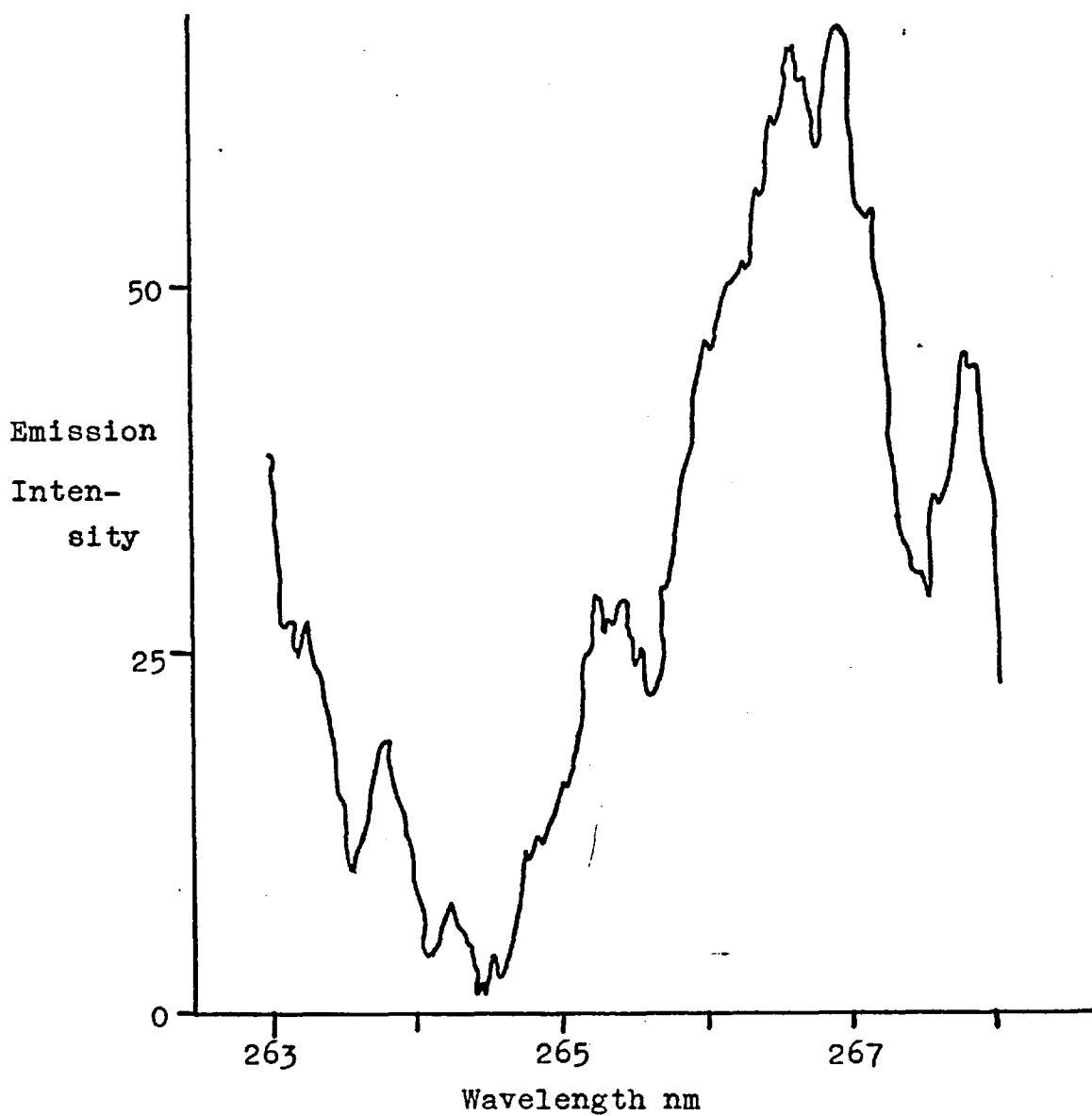


Figure 11: Emission spectrum of the flame background between 263 and 268 nm, 0.33 nm spectral band-width, scan speed 1.5 nm minute⁻¹.

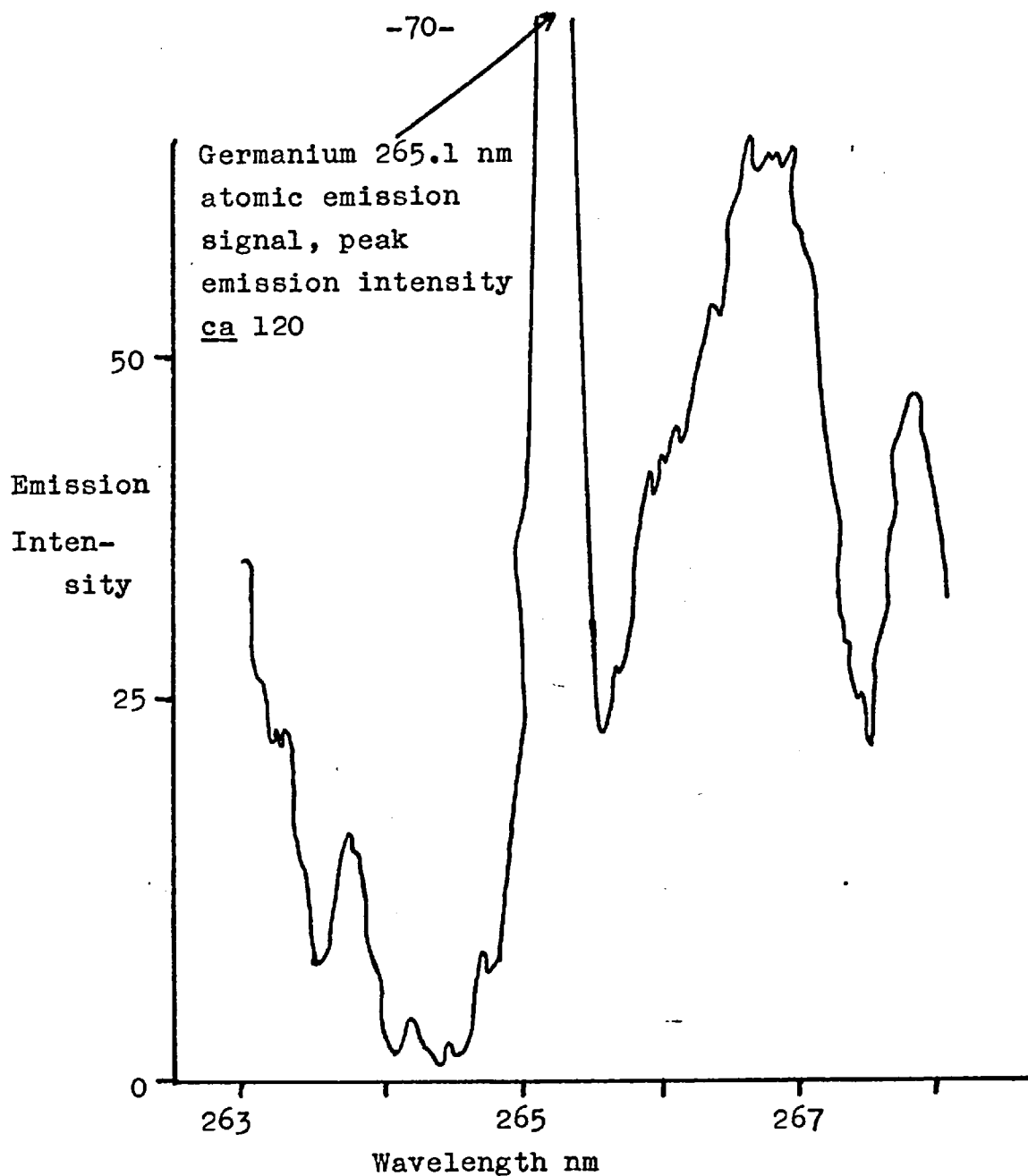


Figure 12: Flame atomic emission spectrum of $100 \mu\text{g ml}^{-1}$ germanium solution between 263 and 268 nm, spectral band-width 0.33 nm , scan speed $1.5 \text{ nm minute}^{-1}$.

nitrogen separated nitrous oxide-acetylene flame, when it had been optimized for acetylene flow-rate and height of observation in the flame, was scanned between 255 and 275 nm. The relative fluorescence intensities that were obtained are shown in Figure 13. The atomic emission obtained at 265.1 nm, when the germanium solutions were introduced into the flame and the discharge tube was in operation, was shown to be germanium fluorescence rather than scatter signals from the flame because (1) appreciable atomic absorption was observed in the atomic absorption spectroscopy of germanium with similar flame conditions, (2) the nebulization of a 20,000 $\mu\text{g ml}^{-1}$ sodium tungstate solution into the flame caused a negligible scatter of the incident radiation from the fluorescence source, (3) no scattered radiation from the mercury 253.6 nm line was observed when the germanium E.D.T. was replaced by an intense mercury E.D.T. and a 1,000 $\mu\text{g ml}^{-1}$ germanium solution was aspirated into the flame, and (4) the absence of interferences by diverse ions in the germanium atomic fluorescence interference study also indicated that scattered radiation was minimal.

Germanium atomic fluorescence arose from all the principal germanium lines that were scanned (Figure 13). The greatest emission occurred from the 265.12-265.16 nm doublet. The greatest fluorescence sensitivity was

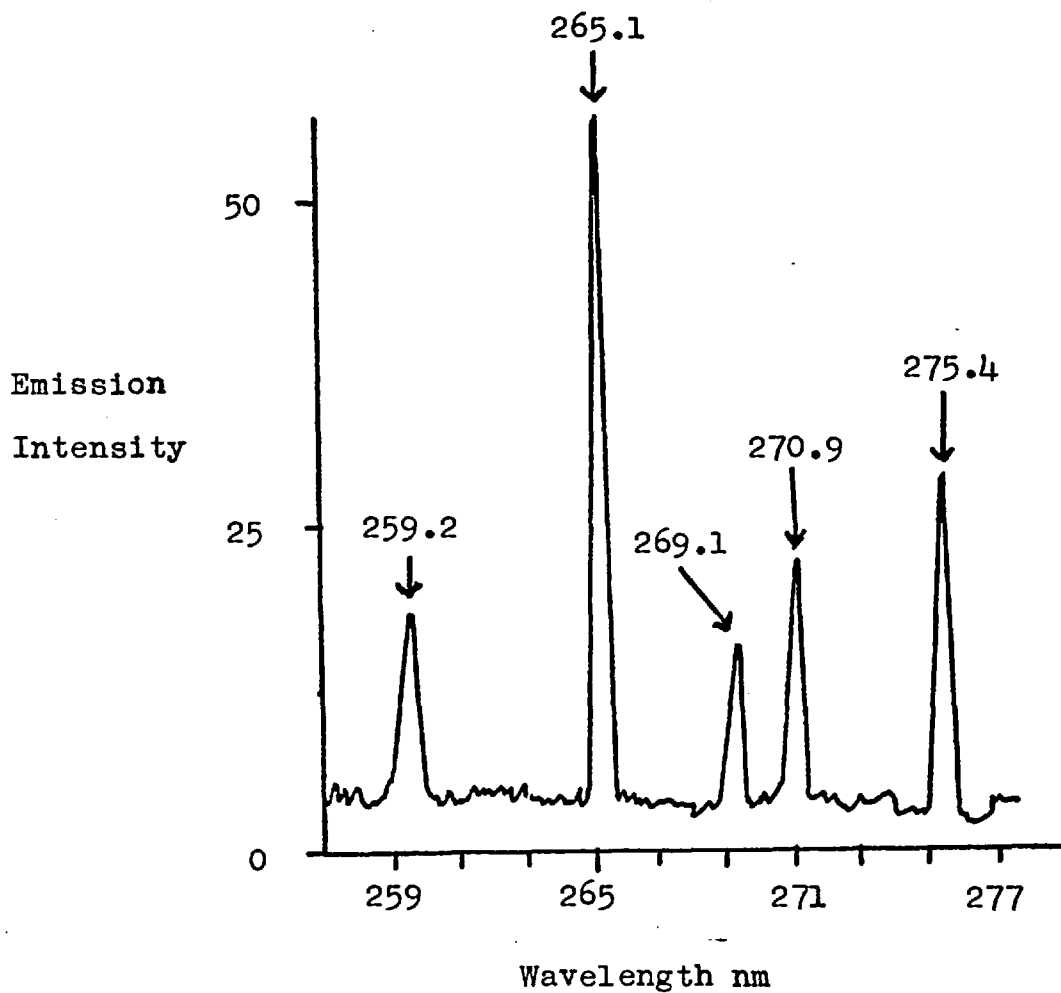


Figure 13: Atomic fluorescence emission spectrum of 10 µg ml⁻¹ germanium solution between 258 and 277 nm, 0.99 spectral band-width, scan speed 1.5 nm minute⁻¹.

obtained with a spectral half-intensity band-width of 0.99 nm. Under these conditions it was the fluorescence radiation from both lines that was observed.

When the atomic absorption sensitivities were determined a spectral band-width of 0.33 nm was employed, and the primary current in the hollow-cathode lamp was 15 milliamps.

3.II.6: Optimum Flame Operating Conditions

The flame and instrumental conditions were chosen to produce the greatest signal:noise ratio for the atomic fluorescence and flame atomic emission. These conditions are summarized in the table below:

	<u>F.A.E.</u>	<u>A.F.S.</u>
Spectral band-width	0.33 nm	0.99 nm
Nitrous oxide flow-rate	5.8 l minute ⁻¹	5.8 l minute ⁻¹
Acetylene flow-rate	3.0 l minute ⁻¹	3.2 l minute ⁻¹
Emission observed at height 3-13 mm above the primary zone		

The variation of emission intensity with acetylene flow-rate that was observed is shown in Figure 14. The optimum flame atomic emission was observed with a slightly leaner flame than that required for the optimum atomic fluorescence. This was probably because the increased temperature of the leaner flame compensated for the

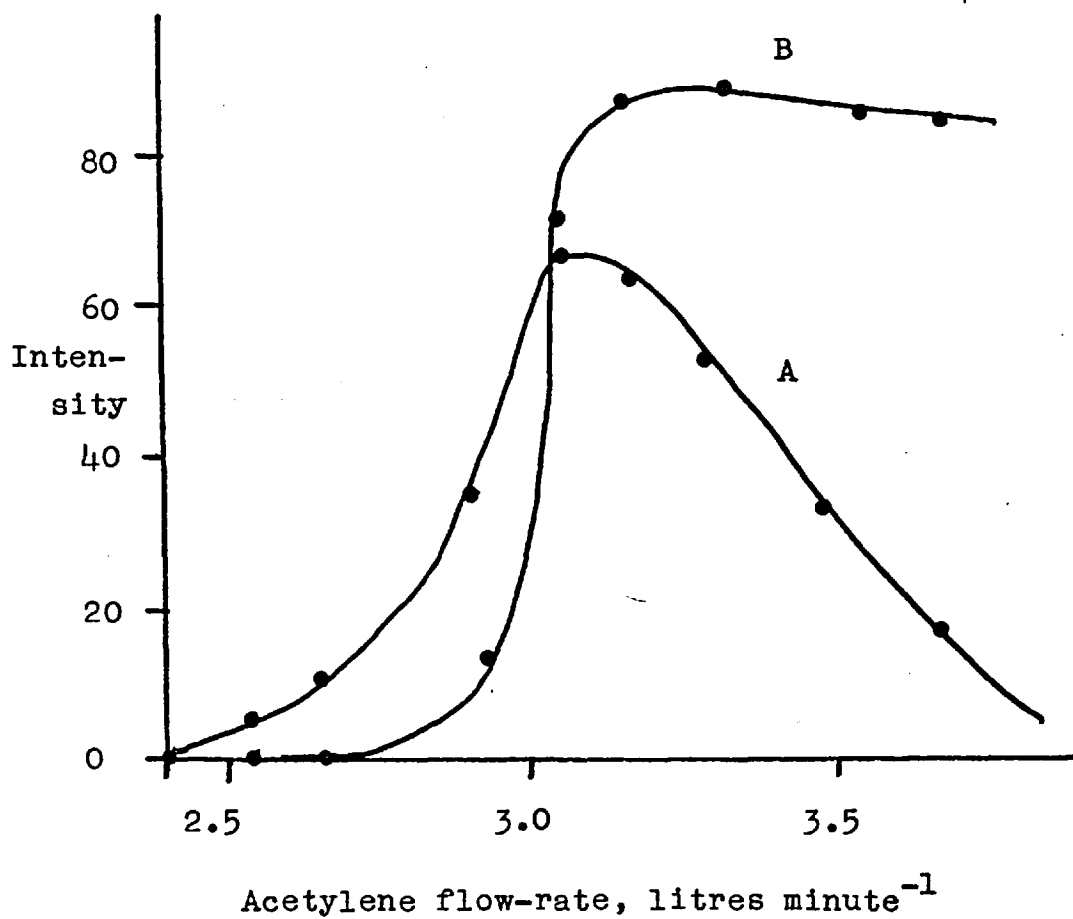


Figure 14: Effect of acetylene flow-rate on A: flame atomic emission intensity of $100 \mu\text{g ml}^{-1}$ germanium at 265.1 nm and B: fluorescence intensity of $100 \mu\text{g ml}^{-1}$ germanium at 265.1 nm . Nitrogen separated flames.

somewhat higher atomic germanium concentration produced in the more fuel-rich flame.

3.II.7: Detection Limits for Germanium by Flame Atomic Spectroscopy

The limits of detection for germanium by atomic fluorescence using the germanium E.D.T. and by flame atomic emission were established for both the separated and conventional flames, under their respective optimum conditions of fuel flow-rate, height of observation and spectral band-width. The detection limits that were determined for each technique are summarized in Table VII. This table also shows the atomic absorption detection limit and sensitivity for 1 per cent absorption which were obtained with a hollow-cathode lamp as source at the Techtron AB 40 50 mm slot burner. A similar sensitivity was obtained when the germanium E.D.T. was employed as the atomic absorption source.

3.II.8: Calibration Graphs and Precision

Linear calibration graphs were obtained for germanium flame atomic emission at 265.1 nm in the nitrogen and argon separated flames over the range 20 to 1,000 $\mu\text{g ml}^{-1}$. For germanium atomic fluorescence with the optimum conditions that have been established for the nitrogen or

TABLE VII

Detection Limits and Sensitivities for Germanium by Flame

Atomic Spectroscopy

Technique	<u>Detection Limit ($\mu\text{g ml}^{-1}$)</u>		
	Conventional	N ₂ sep.	Ar sep.
Flame atomic emission ^a	4	1.3	1.1
Atomic fluorescence ^a	0.2	0.10	0.066
Atomic absorption ^{ab}	2	-	-
Atomic absorption sensitivity ^{ab}	3.5 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron) ^{ab}	2 $\mu\text{g ml}^{-1}$		
^a wavelength 265.1 nm			
^b determined with conventional flame at commercial burner			

argon separated flame, linear calibration graphs were obtained over the range 1 to 1,000 $\mu\text{g ml}^{-1}$.

A standard deviation of 1 per cent was obtained in the germanium atomic emission at 265.1 nm by the repetitive introduction (10 times) of a 200 $\mu\text{g ml}^{-1}$ germanium solution into the separated flames under the optimum conditions used above. A standard deviation of 1.25 per cent was obtained in the germanium atomic fluorescence intensity at 265.1 nm when a 10 $\mu\text{g ml}^{-1}$ germanium solution was employed.

3.II.9: Interference Studies

The effects of 100-fold excesses by weight of a range of cations and anions commonly associated with germanium in ores on the intensity of the atomic emission and atomic fluorescence produced by $100 \mu\text{g ml}^{-1}$ and $10 \mu\text{g ml}^{-1}$ of germanium at 265.1 nm respectively was studied. The effect of each ion is summarized in Table VIII.

The atomic fluorescence of germanium was completely free from any interference by the ions studied, but germanium flame atomic emission exhibited seven interferences. The interferences were assigned as spectral line interferences from the diverse ion solution if a concentrated solution of the diverse ion produced a significant emission signal. Interference from the potassium solution was assumed to be a stray light effect and not an ionisation effect because when sodium was aspirated into the flame, no interference was observed.

3.III: THE DETERMINATION OF ALUMINIUM

Aluminium has been determined by flame atomic emission in the nitrous oxide-acetylene flame (3, 41) and by atomic absorption spectroscopy in the oxy-acetylene (58, 59), premixed oxygen-nitrogen-acetylene (60) and premixed nitrous oxide-acetylene flame (38, 61). There has been

TABLE VIII

Effect of Diverse Ions on Germanium Emission

Element	A.F.S. (10 $\mu\text{g ml}^{-1}$)	F.A.E. (100 $\mu\text{g ml}^{-1}$)
Al (III)	No Interference	+ 570% ^a
Cd	"	No Interference
Co	"	+ 40% ^a
Cr	"	+ 40%
Cu	"	No Interference
Fe (II)	"	"
K	"	+ 30%
Mg	"	No Interference
Mo (VI)	"	+ 130% ^a
Na	"	No Interference
Ni	"	"
Pb	"	"
Si	"	"
Ta	"	"
V (V)	"	+ 240% ^a
W (VI)	"	+ 50% ^a
Zn	"	No Interference
Cl ⁻	"	"
NO ₃ ⁻	"	"
F ⁻	"	"
PO ₄ ³⁻	"	"

^aexistence of some spectral contribution to interference has been experimentally confirmed.

no work on the atomic fluorescence properties of aluminium reported in the literature. In this Section the determination and evaluation of the atomic fluorescence of aluminium is presented. Aluminium electrodeless discharge tubes were employed as the fluorescence emission source after the initial experiments with a high intensity aluminium hollow-cathode lamp proved unsuccessful.

3.III.1: The Preparation of Aluminium Electrodeless Discharge Tubes

The aluminium discharge tubes were produced from the elemental metal and iodine by the same general procedure described for other elements (73). The most satisfactory tubes for use in the three-quarter wave cavity were found to be about 40 mm long, and were sealed at an argon filler-gas pressure of about 4 torr. The optimum tubes contained ca 2 mg of metal and 2 mg of iodine. The tubes were operated at 40 W (reflected power 11 W), with a warm-up period of 10 minutes; at this power they exhibited their greatest intensity and stability. The visible emission was bright blue under these conditions.

3.III.2: Spectral Characteristics of the Discharge Tubes

The emission spectrum from an aluminium E.D.T. was

obtained between 250 and 400 nm by the same procedure as employed for silicon (Section 3.I.3.). The intensities that were obtained under the same instrumental conditions for a Techtron high-intensity hollow-cathode lamp are shown in Table IX with the comparable atomic lines from the discharge tube. The stability of each source is also indicated in the table.

3.III.3: Stock Aluminium Solution, 1,000 $\mu\text{g ml}^{-1}$

1 g of pure aluminium metal foil (Hopkin and Williams Ltd) was dissolved in 20 ml of concentrated hydrochloric acid, cooled and diluted to 1 litre with distilled water.

3.III.4: Atomic Spectroscopy Measurements

The flame emission spectrum and the aluminium flame atomic emission spectrum were obtained over a region spanning the most intense aluminium atomic lines using the nitrogen separated flame. The relative emission intensities that were obtained are shown in Table X. It was not possible to resolve the 309.27-309.284 nm doublet line usually employed for atomic absorption with the instrumentation available. The atomic emission line that was employed in the emission determination was the 396.15 nm line.

TABLE IX

Principal Source Emission Characteristics

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
257.5	$^2D_{3/2} \longrightarrow ^2P_{3/2}^{\circ}$	0.4	1.33
308.2	$^2D_{3/2} \longrightarrow ^2P_{1/2}^{\circ}$	3	34.7
309.27 ^{cd}	$^2D_{3/2} \longrightarrow ^2P_{3/2}^{\circ}$	5	66.6
309.28 ^d	$^2D_{3/2} \longrightarrow ^2P_{1/2}^{\circ}$		
394.4	$^2S_{1/2} \longrightarrow ^2P_{1/2}^{\circ}$	3	77.5
396.2	$^2S_{1/2} \longrightarrow ^2P_{3/2}^{\circ}$	5	100

Line-to-background at 396.2 nm 120:1 150:1

Long period fluctuation over 1 hour $\pm 4\%$ $\pm 2\%$

Instantaneous noise over 1 minute $\pm 1\%$ $\pm 1\%$

^aemission intensities expressed relative to intensity of 396.2 nm line from E.D.T.

^bH.C.L. primary electrodes operated at 8 mA, secondary electrodes at 400 mA.

^cmost sensitive for atomic absorption

^ddoublet cannot be resolved with instrumentation employed

TABLE X

Relative Emission Intensities of the Principal Aluminium

<u>Lines</u>		
Line	Relative Intensity	Relative Intensity
nm	F.A.E. (arbitrary units)	A.F.S. (arbitrary units)
	(100 $\mu\text{g ml}^{-1}$)	(100 $\mu\text{g ml}^{-1}$)
308.21	0	9
309.271 ^{ab}	2	35
309.284		
394.40	61	79
396.15 ^c	100	100

^amost sensitive for atomic absorption

^bdoublet cannot be resolved with apparatus employed

^cmost analytically useful for atomic fluorescence

The arbitrary units in the two columns are not interrelated.

The aluminium atomic fluorescence spectrum was obtained similarly to the flame atomic emission spectrum. The most intense lines that were observed are shown in Table X. The most intense fluorescence was observed at the 396.15 nm line, and not at the line most sensitive for atomic absorption. This is probably because the E.D.T. was significantly more intense at the longer wavelength line (Table IX).

The atomic emission at 396.15 nm was shown to be

atomic fluorescence in the same manner as employed for silicon previously. In this case the aluminium discharge tube was replaced by a titanium discharge source, and no scatter was observed at the Ti 399.9 nm line. The three other experiments also indicated the absence of scatter signals.

When the atomic absorption sensitivities were obtained a spectral band-width of 0.33 nm was employed, and the primary current in the hollow-cathode lamp was 8 mA; the secondary electrodes of the lamp were operated at 400 mA.

3.III.5: Optimum Flame Operating Conditions

The experimental conditions that were employed to obtain the greatest signal:noise ratios for the atomic fluorescence and emission are summarized in the table below:

	<u>F.A.E.</u>	<u>A.F.S.</u>
Spectral band-width	0.33 nm	0.33 nm
Nitrous oxide flow-rate	5.8 l minute ⁻¹	5.8 l minute ⁻¹
Acetylene flow-rate	3.1 l minute ⁻¹	3.2 l minute ⁻¹
Separating gas flow-rate	at least 10 l minute ⁻¹	
Emission observed at height 3-13 mm above the primary zone.		

3.III.6: Detection Limits for Aluminium by Flame Atomic Spectroscopy

The limits of detection for aluminium by atomic spectroscopy were established under the respective optimum conditions for each technique. The limits that were determined are summarized in Table XI. A high-intensity hollow-cathode lamp was employed as source at the Techtron 50 mm high-temperature burner for the 1 per cent atomic absorption sensitivity which was obtained.

3.III.7: Calibration Graphs and Precision

The calibration graphs that were obtained for the atomic fluorescence were linear from 0 to $250 \mu\text{g ml}^{-1}$ with a slight curvature of the graph towards the concentration axis between 250 and $500 \mu\text{g ml}^{-1}$ and appreciable curvature between 500 and $1,000 \mu\text{g ml}^{-1}$. The range of linearity in the atomic emission was 0 to $500 \mu\text{g ml}^{-1}$ with a slight curvature of the graph towards the concentration axis between 500 and $1,000 \mu\text{g ml}^{-1}$. These graphs were obtained in the gas separated flame.

The standard deviation of the atomic fluorescence and atomic emission determinations were obtained as outlined previously. The values obtained are shown in the table

TABLE XI

Detection Limits and Sensitivities for Aluminium by Flame

Atomic Spectroscopy

Technique	<u>Detection Limit ($\mu\text{g ml}^{-1}$)</u>		
	Conventional	N ₂ sep.	Ar sep.
Flame atomic emission ^a	0.1	0.06	0.05
Atomic fluorescence ^a	0.2	0.12	0.1
Atomic absorption ^{bc}	0.8	-	-
Atomic absorption sensitivity ^{bc}	1.7 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron) ^{bc}	1.0 $\mu\text{g ml}^{-1}$		
^a wavelength 396.15 nm			
^b wavelength 309.27 nm			
^c determined with conventional flame at commercial burner			

below:

<u>Atomic Fluorescence</u>		<u>Flame Atomic Emission</u>	
<u>$\mu\text{g ml}^{-1}$</u>	<u>S.D. (%)</u>	<u>$\mu\text{g ml}^{-1}$</u>	<u>S.D. (%)</u>
100	1.15	20	1.3

3.III.8: Interference Studies

The interference studies were conducted using 100-fold excesses by weight of a range of cations and anions on the intensity of the atomic fluorescence and emission of

aluminium. The effect of each ion is shown in Table XII. The atomic fluorescence determination was found to be completely free of any interference effects, but considerable interference was observed in the flame atomic emission determination. Any spectral contribution to the interference is noted in Table XII; these were determined in the manner described previously (Section 3.I.10).

3.IV: THE DETERMINATION OF TITANIUM AND ZIRCONIUM

The determinations of titanium and zirconium are presented together in this Section because of their common Grouping (4b) and, as a result, their similarity of atomic fluorescence determination. Titanium (38, 51, 62) and Zirconium (54, 67) have been determined by atomic absorption spectroscopy in the nitrous oxide-acetylene flame; titanium (3) and zirconium (3) have also been determined by flame atomic emission in this flame. There has been no report of the atomic fluorescence properties of either element in the literature. In this Section the determination of both elements by flame atomic emission using the instrumentation already described is presented; the attempts to observe atomic fluorescence from both elements is also described. Hollow-cathode

TABLE XII

Effect of Diverse Ions on Aluminium Emission

Element	A.F.S. (20 $\mu\text{g ml}^{-1}$)	F.A.E. (20 $\mu\text{g ml}^{-1}$)
As (III)	No Interference	No Interference
Cd	"	"
Co	"	"
Cr	"	+ 11% ^a
Cu	"	No Interference
Fe (III)	"	"
K	"	+ 11%
Mg	"	+ 9% ^a
Mo	"	+ 11% ^a
Na	"	+ 9%
Ni	"	No Interference
Pb	"	"
Si	"	+ 30% ^a
Ta	"	+ 40% ^a
Th	"	+ 10% ^a
V (V)	"	+ 30% ^a
W (VI)	"	+ 22% ^a
Zn	"	No Interference
Cl ⁻	"	"
NO ₃ ⁻	"	"
F ⁻	"	+ 26%
PO ₄ ³⁻	"	No Interference

^aexistence of some spectral contribution to interference has been experimentally confirmed.

lamps were unsuccessful when used to excite fluorescence emission from either element and electrodeless discharge tubes were prepared to provide a more intense source.

3.IV.1: The Preparation of the Electrodeless Discharge Tubes

The preparation of the titanium and zirconium discharge tubes have been described in detail elsewhere (75). The tubes were sealed at an argon filler-gas pressure of about 4 torr and were operated in the three-quarter wave resonant cavity. It was necessary to air-cool the titanium tubes strongly to obtain a stable emission. The titanium tubes were operated at 40 W (reflected power approximately 14 W) and the zirconium tubes also at 40 W (reflected power approximately 13 W); they then exhibited their greatest intensity and stability after a warm-up period of ten and five minutes respectively.

3.IV.2: Spectral Characteristics of the Discharge Tubes

The emission spectrum from each discharge tube was obtained over the range of most intense output by the same procedure as employed for silicon (Section 3.I.3). The intensities obtained under the same instrumental

conditions for the corresponding Techtron hollow-cathode lamps were also investigated as were the relative intensities of each source. The characteristics of each source for both elements are shown in Tables XIII and XIV.

3.IV.3: Stock Reagent Solutions, 1,000 $\mu\text{g ml}^{-1}$

1 g of pure titanium metal sponge (Hopkin and Williams Ltd) was dissolved in 20 ml of concentrated hydrochloric-hy^{dr}ofluoric acids (2:1 mixture by volume) and the solution was cooled and diluted to 1 litre with distilled water. The zirconium solution was prepared by dissolving 3.54 g of zirconyl chloride (B.D.H. Ltd) in distilled water and sufficient hydrochloric acid to give an overall acidity of 2 per cent on dilution to 1 litre.

3.IV.4: Atomic Spectroscopy Measurements

The flame background and emission spectra for each element were scanned, and the relative intensities for each line were obtained using the nitrogen separated nitrous oxide-acetylene flame. The relative emission intensities for each significant line for both elements are shown in Tables XV and XVI. The lines that were most suitable for flame atomic emission in this flame

TABLE XIII

Principal Source Emission Characteristics for Titanium

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
334.19	x ${}^3G_3^o \longrightarrow a {}^3F_2$	5	31
336.13	w ${}^3D_3^o \longrightarrow a {}^3F_3$	3	48
337.15	w ${}^3G_5^o \longrightarrow a {}^3F_4$	3	30
363.55	y ${}^3G_3^o \longrightarrow a {}^3F_2$	7	66
364.27 ^c	y ${}^3G_4^o \longrightarrow a {}^3F_2$	7	64
365.35	y ${}^3G_5^o \longrightarrow a {}^3F_4$	8	81
375.29	x ${}^3F_4^o \longrightarrow a {}^3F_4$	6	70
394.87	y ${}^3D_1^o \longrightarrow a {}^3F_2$	5	55
395.63	y ${}^3D_2^o \longrightarrow a {}^3F_3$	6	54
395.82	y ${}^3D_3^o \longrightarrow a {}^3F_4$	6	68
398.18	y ${}^3F_2^o \longrightarrow a {}^3F_2$	9	83
398.98	y ${}^3F_3^o \longrightarrow a {}^3F_3$	8	75
399.86	y ${}^3F_4^o \longrightarrow a {}^3F_4$	9	100

Line-to-background ratio at 399.86 nm 140:1 140:1

Long period fluctuation over 1 hour $\pm 1\%$ $\pm 2\%$

Instantaneous noise over 1 minute $\pm 1\%$ $\pm 1\%$

^aemission intensities expressed relative to intensity of 399.86 nm line from E.D.T.

^bH.C.L. electrodes operated at 20 mA.

^cmost sensitive for atomic absorption

TABLE XIV

Principal Source Emission Characteristics for Zirconium

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
351.96	x $^3G_3^o \longrightarrow a^3F_2$	3	50
354.77	x $^3G_4^o \longrightarrow a^3F_3$	4	55
360.12 ^c	x $^3G_5^o \longrightarrow a^3F_4$	6.5	82
362.39	w $^3F_3^o \longrightarrow a^3F_3$	1	10
383.59	x $^3F_2^o \longrightarrow a^3F_2$	4	58
389.03	x $^3F_4^o \longrightarrow a^3F_4$	5	100
407.27	x $^5D_3^o \longrightarrow a^5F_4$	3	29
408.12	x $^5D_4^o \longrightarrow a^5F_5$	3	41
422.78	y $^5F_5^o \longrightarrow a^5F_5$	4	40
423.93	y $^5F_4^o \longrightarrow a^5F_5$	3	45
468.78	y $^5G_6^o \longrightarrow a^3F_5$	12	74

Line-to-background ratio at 360.12 nm 83:1 90:1

Long period fluctuation over 1 hour $\pm 1\%$ $\pm 3\%$

Instantaneous noise over 1 minute $\pm 1\%$ $\pm 1\%$

^aemission intensities expressed relative to intensity of 389.03 nm line from E.D.T.

^bH.C.L. electrodes operated at 15 mA.

^cmost sensitive for atomic absorption

TABLE XV

Relative Emission Intensities of the Principal Titanium

<u>Lines</u>		
Line	Relative Intensity	Relative Intensity
nm	F.A.E. (arbitrary units) (100 $\mu\text{g ml}^{-1}$)	A.F.S. (arbitrary units) (100 and 1,000 $\mu\text{g ml}^{-1}$)
363.55	41	-
364.27 ^a	45	-
365.35	54	-
375.29	50	-
394.87	43	-
395.63	91	-
395.82	16	-
398.18	61	-
398.98	73	-
399.86	100	-

^amost sensitive for atomic absorption

(i.e. exhibit the best signal:noise ratios) were 399.86 nm for titanium and 468.78 nm for zirconium.

It was found that no definable atomic fluorescence was observed for either titanium or zirconium even when a discharge tube was employed as the fluorescence source. This was surprising as good atomic absorption sensitivities

TABLE XVI

Relative Emission Intensities of the Principal Zirconium

<u>Lines</u>		
Line	Relative Intensity	Relative Intensity
nm	F.A.E. (arbitrary units)	A.F.S. (arbitrary units)
	(100 $\mu\text{g ml}^{-1}$)	(100 and 1,000 $\mu\text{g ml}^{-1}$)
351.96	100	-
360.12 ^a	65	-
407.27	59	-
408.12	83	-
468.78	94	-
473.95	51	-
477.20	100	-

^amost sensitive for atomic absorption

for each element were obtained, as were good detection limits by atomic emission. It was therefore decided (see Conclusion 3.VI) that the sources available were probably not sufficiently intense to excite fluorescence emission.

When the atomic absorption sensitivities and detection limits were obtained a spectral band-width of 0.08 nm was employed for the titanium and for the zirconium determination. The titanium hollow-cathode

lamp was operated at 20 milliamp and 15 milliamp was used in the zirconium lamp.

3.IV.5: Optimum Flame Operating Conditions

The experimental conditions that were chosen to produce the most intense (i.e. greatest signal:noise ratio) flame atomic emission signals are shown in the table below:

	<u>Titanium</u>	<u>Zirconium</u>
Spectral band-width	0.33 nm	0.33 nm
Nitrous oxide flow-rate	5.8 l minute ⁻¹	5.8 l minute ⁻¹
Acetylene flow-rate	3.2 l minute ⁻¹	3.2 l minute ⁻¹
Separating gas flow-rate at least	10 l minute ⁻¹	
Emission observed at height 3-13 mm above the primary zone.		

3.IV.6: Detection Limits for Titanium and Zirconium

The limits of detection for titanium and zirconium at their respective wavelengths were established by atomic emission for the separated and conventional flames. The detection limit for atomic absorption was determined at the conventional 50 mm slot burner for each element. The limits and the 1 per cent atomic absorption sensitivities that were obtained are shown in Table XVII.

TABLE XVII

Detection Limits and Sensitivities for Titanium and Zirconium
by Atomic Emission and Atomic Absorption Spectroscopy

Technique	Detection Limit ($\mu\text{g ml}^{-1}$)		
	Conventional	N ₂ sep.	Ar sep.
<u>Titanium</u>			
Flame atomic emission ^a	0.71	0.23	0.2
Atomic absorption ^{be}	1.2	-	-
Atomic absorption sensitivity ^{be}	4.4 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron) ^{be}	2.6 $\mu\text{g ml}^{-1}$		
<u>Zirconium</u>			
Flame atomic emission ^c	7.1	1.13	1.05
Atomic absorption ^{de}	8	-	-
Atomic absorption sensitivity ^{de}	17.5 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron) ^{de}	12 $\mu\text{g ml}^{-1}$		
^a wavelength 399.86 nm			
^b wavelength 364.27 nm			
^c wavelength 468.78 nm			
^d wavelength 360.12 nm			
^e determined with conventional flame at commercial burner			

3.IV.7: Calibration Graphs and Precision

A range of linearity of 0 to 1,000 $\mu\text{g ml}^{-1}$ was obtained for titanium atomic emission. However, over the range 0 to 1,000 $\mu\text{g ml}^{-1}$ any series of concentrations produced a graph with a pronounced curvature towards the intensity axis for the zirconium atomic emission determination.

The standard deviations of the titanium and zirconium flame atomic emission determinations were obtained as outlined previously. The values which were obtained are shown in the table below:

<u>Titanium</u>		<u>Zirconium</u>	
<u>$\mu\text{g ml}^{-1}$</u>	<u>S.D. (%)</u>	<u>$\mu\text{g ml}^{-1}$</u>	<u>S.D. (%)</u>
10	2.6	100	3.1

3.IV.8: Interference Studies

The effects of 100-fold excesses by weight of a range of cations and anions on the intensity of the atomic emission produced by an appropriate concentration of each of the elements at their respective wavelengths are investigated. The interferences which were found are shown in Table XVIII. Both determinations were subject to a considerable number of interferences, and where these have been shown to be spectral in part they are noted in the table.

TABLE XVIII

Effect of Diverse Ions on Titanium and Zirconium Emission

Element	Titanium (10 $\mu\text{g ml}^{-1}$)	Zirconium (100 $\mu\text{g ml}^{-1}$)
Al	+ 90%	- 44%
As	No Interference	Precipitated ^b
Cd	"	- 78%
Co	+ 37% ^a	+ 15%
Cr	No Interference	+ 34%
Cu	"	- 80%
Fe (III)	"	- 68%
K	+ 35%	- 79%
Mg	+ 35% ^a	- 87%
Mn	-	- 53%
Mo	+ 140% ^a	+ 1400% ^b
Na	No Interference	- 69%
Ni	"	- 60%
Pb	"	-
Ta	+ 140%	+ 150%
Th	+ 225% ^a	+ 270%
V (V)	+ 225% ^a	+ 270% ^a
W (VI)	+ 320% ^a	+ 54%
Zn	No Interference	- 70%
Cl ⁻	"	No Interference
NO ₃ ⁻	"	"
F ⁻	"	- 16%
PO ₄ ³⁻	"	Precipitated ^b

^aexistence of some spectral contribution to interference has been experimentally confirmed.

^belements with a tendency to form insoluble zirconates

3.V: THE DETERMINATION OF MOLYBDENUM AND VANADIUM

The atomic fluorescence characteristics of molybdenum and vanadium have been investigated and compared with their respective flame atomic emission characteristics. The results of these studies for both elements are presented together in this section owing to the similarity in their A.F.S. properties with regard to interferences.

Molybdenum has been determined by atomic absorption spectroscopy in the air-acetylene (64, 65) and the nitrous oxide-acetylene flames (66, 67), and by flame atomic emission in the nitrous oxide-acetylene flame (3). Similarly, vanadium has been determined in the nitrous oxide-acetylene (38, 68, 69) and fuel-rich oxy-acetylene flames (59, 70) by atomic absorption, and by flame atomic emission in the nitrous oxide-acetylene flame (3).

The fluorescence studies reported here employed electrodeless discharge tubes as the sources of radiation; initial experiments with hollow-cathode lamps (high-intensity in the molybdenum case) were unsuccessful.

3.V.1: The Preparation of Electrodeless Discharge Tubes

The molybdenum discharge tubes were prepared by the reaction of elemental molybdenum and chlorine. The

chloride was formed by heating the metal in an atmosphere of chlorine gas. The preparation of the vanadium tubes has been described elsewhere (75). The molybdenum tubes were sealed at an argon filler-gas pressure of ca 4 torr and the vanadium tubes at a pressure of ca 7 torr. The molybdenum tubes were prepared from about 2 mg of the metal, and required a bulb length of ca 40 mm.

All the tubes were operated in the three-quarter wave resonant cavity, but it was necessary to air-cool the molybdenum tubes strongly to obtain a stable emission. The molybdenum tubes produced their greatest stability and intensity when operated at 90 W (reflected power approximately 17 W, warm-up period about 5 minutes) and the vanadium tubes when operated at 25 W (reflected power approximately 9 W, warm-up period about 5 minutes).

3.V.2: Spectral Characteristics of the Discharge Tubes

The emission spectrum from each discharge tube was scanned over the region of its greatest intensity by the same procedure as that employed previously (Section 3.I.3). The relative intensities of the most important lines were obtained, as were the intensities at the same lines for the respective hollow-cathode lamps. The characteristics of each source are shown in Tables XIX and XX.

TABLE XIX

Principal Source Emission Characteristics for Molybdenum

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
313.26 ^c	$y \ ^3P_4 \longrightarrow a \ ^3S_3$	6	100
315.81	$z \ ^3D_3 \longrightarrow a \ ^3S_3$	3.5	26
317.04	$y \ ^3P_3 \longrightarrow a \ ^3S_3$	4.5	63
319.39	$y \ ^3P_2 \longrightarrow a \ ^3S_3$	4	58
379.83	$z \ ^3P_2 \longrightarrow a \ ^3S_3$	25	80
386.41	$z \ ^3P_1 \longrightarrow a \ ^3S_3$	32	67
390.29	$z \ ^3P_1 \longrightarrow a \ ^3S_3$	25	54
Line-to-background ratio at 313.26 nm		60:1	85:1
Long period fluctuation over 1 hour		$\pm 2\%$	$\pm 2\%$
Instantaneous noise over 1 minute		$\pm 1\%$	$\pm 1\%$
^a emission intensities expressed relative to intensity of 313.26 nm line from E.D.T.			
^b H.C.L. primary electrodes operated at 10 mA, secondary electrodes at 400 mA.			
^c most sensitive for atomic absorption			

TABLE XX

Principal Source Emission Characteristics for Vanadium

Line nm	Transition	Relative Emission Intensity ^a	
		H.C.L. ^b	E.D.T.
306.64	w $^4F_{7/2}^{\circ} \longrightarrow a \ ^4F_{7/2}$	18	30
318.40 ^c	x $^4G_{9/2}^{\circ} \longrightarrow a \ ^4F_{5/2}$	2	100
	x $^4G_{7/2}^{\circ} \longrightarrow a \ ^4F_{5/2}$		
318.54	x $^4G_{7/2}^{\circ} \longrightarrow a \ ^4F_{7/2}$	1	52
370.36	y $^6P_{7/2}^{\circ} \longrightarrow a \ ^6D_{7/2}$	1	32
384.08	y $^4D_{5/2}^{\circ} \longrightarrow a \ ^4F_{5/2}$	1	48
385.59	y $^4D_{3/2}^{\circ} \longrightarrow a \ ^4F_{7/2}$	2	60
409.98	y $^4D_{3/2}^{\circ} \longrightarrow a \ ^4D_{5/2}$	0.5	46
411.18	y $^4D_{5/2}^{\circ} \longrightarrow a \ ^4D_{7/2}$	0.5	17
411.52	y $^4D_{3/2}^{\circ} \longrightarrow a \ ^4D_{7/2}$	1	46
437.92	y $^4F_{5/2}^{\circ} \longrightarrow a \ ^4D_{7/2}$	3	88
438.47	y $^4F_{7/2}^{\circ} \longrightarrow a \ ^4D_{3/2}$	3	62
438.99	y $^4F_{7/2}^{\circ} \longrightarrow a \ ^4D_{5/2}$	2	38
439.52	y $^4F_{5/2}^{\circ} \longrightarrow a \ ^4D_{7/2}$	1	24
440.82	y $^4F_{5/2}^{\circ} \longrightarrow a \ ^4D_{5/2}$		
440.85	y $^4F_{5/2}^{\circ} \longrightarrow a \ ^4D_{3/2}$	2	59
	y $^4F_{7/2}^{\circ} \longrightarrow a \ ^4D_{3/2}$		

Line-to-background ratio at 318.40 nm 79:1 100:1

Long period fluctuation over 1 hour $\pm 2\%$ $\pm 1.5\%$

Instantaneous noise over 1 minute $\pm 1\%$ $\pm 1\%$

^aemission intensities expressed relative to intensity of 318.40 nm line from E.D.T.

^bH.C.L. electrodes operated at 20 mA.

^cmost sensitive for atomic absorption

3.V.3: Stock Reagent Solutions, 1,000 $\mu\text{g ml}^{-1}$

The molybdenum solution was prepared by dissolving 1.84 g of AnalaR ammonium molybdate (Hopkin and Williams Ltd) in distilled water and making to 1 litre. The vanadium solution was prepared by dissolving 1 g of pure vanadium metal powder (Hopkin and Williams Ltd) in 20 ml of concentrated hydrochloric/nitric acid (2:1 ratio by volume) and was diluted to 1 litre when cool.

3.V.4: Atomic Spectroscopy Measurements

The flame atomic emission spectra for each element, and the flame background over the same region, were obtained. The relative intensities for each line were obtained and these are shown for each element in Tables XXI and XXII. The lines which exhibited the best signal:noise ratio in the nitrogen separated flame, and so were most suitable for atomic emission were 313.26 nm for molybdenum and 437.92 nm for vanadium. The 379.83, 386.41 and 390.29 nm lines of molybdenum are very much more intense than the shorter wavelength lines but are unsuitable for flame atomic emission in the nitrous oxide-acetylene flame because of the very intense flame background emission present (mainly from the blue CN band systems).

TABLE XXI

Relative Emission Intensities of the Principal Molybdenum

<u>Lines</u>		
Line	Relative Intensity	Relative Intensity
nm	F.A.E. (arbitrary units)	A.F.S. (arbitrary units)
	(100 $\mu\text{g ml}^{-1}$)	(100 $\mu\text{g ml}^{-1}$)
313.26 ^{ab}	0.42	100
315.81	0.13	13
317.04	0.32	59
319.39	0.29	46
379.83	100 ^c	35
386.41	30 ^c	25
390.29	14 ^c	7

^amost sensitive for atomic absorption

^bmost analytically useful for atomic fluorescence

^cparticularly poor signal:noise and signal:background ratios

The arbitrary units in the two columns are not interrelated.

The atomic fluorescence spectrum for each element was obtained in the same manner as the flame atomic emission spectrum. The most intense lines that were observed in each case are also shown in Tables XXI and XXII. The optimum wavelengths that were used to excite

TABLE XXII

Relative Emission Intensities of the Principal Vanadium

<u>Lines</u>		
Line	Relative Intensity	Relative Intensity
nm	F.A.E. (arbitrary units)	A.F.S. (arbitrary units)
	(100 $\mu\text{g ml}^{-1}$)	(100 $\mu\text{g ml}^{-1}$)
306.64	8	8
318.40 ^{ab}	32	100
437.92	100	0
438.47	74	0
438.99	48	0
439.52	29	0
440.82 ^c	99	0
440.85		

^amost sensitive for atomic absorption

^bmost analytically useful for atomic fluorescence

^cdoublet cannot be resolved with apparatus employed

The arbitrary units in the two columns are not interrelated.

the fluorescence radiation were found to be 313.26 nm and 318.40 nm for molybdenum and vanadium respectively. The atomic emission from each line was confirmed as atomic fluorescence and not scatter in the same manner as used for silicon previously. In this case no scattered

bismuth radiation at 306.7 nm was observed when the molybdenum or vanadium discharge sources were replaced by an intense bismuth discharge tube and a $1,000 \mu\text{g ml}^{-1}$ solution of either element was aspirated into the flame. The other experiments also indicated the absence of scatter signals, although there appeared to be an anomalously high number of interferences observed in the case of molybdenum atomic fluorescence.

When the atomic absorption sensitivities and detection limits were obtained a spectral band-width of 0.33 nm was employed for both the molybdenum and vanadium determinations. The primary electrodes of the molybdenum lamp were run at 10 mA and the secondary at 400 mA, while the vanadium electrodes were run at 20 mA.

3.V.5: Optimum Flame Operating Conditions

The instrumental conditions that were chosen to produce the most intense (greatest signal:noise ratios) atomic fluorescence and flame emission signals with the minimum background and noise are shown in the table below,

<u>Atomic Fluorescence</u>	<u>Molybdenum</u>	<u>Vanadium</u>
Spectral band-width	0.99 nm	0.99 nm
Nitrous oxide flow-rate	$5.8 \text{ l minute}^{-1}$	$5.8 \text{ l minute}^{-1}$
Acetylene flow-rate	$3.2 \text{ l minute}^{-1}$	$3.2 \text{ l minute}^{-1}$

<u>Atomic Emission</u>	<u>Molybdenum</u>	<u>Vanadium</u>
Spectral band-width	0.33 nm	0.33 nm
Nitrous oxide flow-rate	5.8 l minute ⁻¹	5.8 l minute ⁻¹
Acetylene flow-rate	3.0 l minute ⁻¹	3.1 l minute ⁻¹

Separating gas flow-rate was at least 10 l minute⁻¹ and the emission was observed at height 3-13 mm above the primary zone in each technique.

3.V.6: Detection Limits for Molybdenum and Vanadium

The limits of detection for molybdenum and vanadium were established by atomic fluorescence, absorption and emission at the respective wavelength and under the optimum conditions for each technique. The sensitivity of the atomic absorption determination was also found and this, and the detection limits, are shown in Table XXIII.

3.V.7: Calibration Graphs and Precision

The range of linearity for the molybdenum atomic fluorescence determination was 0 to 50 $\mu\text{g ml}^{-1}$, with a marked curvature of the graph towards the concentration axis between 100 and 1,000 $\mu\text{g ml}^{-1}$. The vanadium atomic fluorescence determination exhibited a range of linearity between 0 and 250 $\mu\text{g ml}^{-1}$ with a slight curvature towards the concentration axis over the range

TABLE XXIII

Detection Limits and Sensitivities for Molybdenum and
Vanadium by Atomic Spectroscopy

Technique	<u>Detection Limit ($\mu\text{g ml}^{-1}$)</u>		
	Conventional	N ₂ sep.	Ar sep.
<u>Molybdenum</u>			
Flame atomic emission ^a	0.71	0.23	0.2
Atomic fluorescence ^a	10.2	0.75	0.46
Atomic absorption ^{ad}	1.0	-	-
Atomic absorption sensitivity ^{ad}	1.3 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron)	0.4 $\mu\text{g ml}^{-1}$		
<u>Vanadium</u>			
Flame atomic emission ^b	0.1	0.044	0.037
Atomic fluorescence ^c	1.2	0.088	0.07
Atomic absorption ^{cd}	1.0	-	-
Atomic absorption sensitivity ^{cd}	3.1 $\mu\text{g ml}^{-1}$		
Specified atomic absorption sensitivity (Techtron)	1.5 $\mu\text{g ml}^{-1}$		
^a wavelength 313.26 nm			
^b wavelength 437.93 nm			
^c wavelength 318.40 nm			
^d determined with conventional flame at commercial burner			

250 to 1,000 $\mu\text{g ml}^{-1}$. Both the molybdenum and vanadium atomic emission determinations exhibited a range of linearity between 0 and 500 $\mu\text{g ml}^{-1}$ and a slight curvature of the plot towards the concentration axis between 500 and 1,000 $\mu\text{g ml}^{-1}$.

The standard deviations in the atomic emission and fluorescence signals were obtained as outlined previously. The values which were obtained are shown in the table below,

	<u>A.F.S.</u>		<u>F.A.E.</u>	
	<u>$\mu\text{g ml}^{-1}$</u>	<u>S.D. (%)</u>	<u>$\mu\text{g ml}^{-1}$</u>	<u>S.D. (%)</u>
Molybdenum	20	1.95	20	1.9
Vanadium	25	1.75	25	1.85

3.V.8: Interference Studies

The effects of 100-fold excesses by weight of various cations and anions on the intensity of the atomic fluorescence and emission of molybdenum and vanadium were studied. The effects of each ion which were observed are shown in Table XXIV.

TABLE XXIV

Effect of Diverse Ions of Molybdenum and Vanadium Emission

Element	Molybdenum (20 $\mu\text{g ml}^{-1}$)		Vanadium (25 $\mu\text{g ml}^{-1}$)	
	A.F.S.	F.A.E.	A.F.S.	F.A.E.
Al	+ 34%	+ 100% ^a	+ 18%	+ 30%
As	+ 25%	+ 53%	N.I.	+ 20%
Cd	+ 18%	+ 56%	"	+ 12%
Co	N.I.	- 16%	- 11%	N.I.
Cr	+ 31%	+ 72% ^a	N.I.	+ 19% ^a
Cu	+ 33%	+ 58%	"	N.I.
Fe (III)	N.I.	+ 60%	"	+ 47% ^a
K	+ 63%	+ 55%	"	+ 19%
Mg	+ 20%	+ 58%	-	+ 13%
Mn	-	-	N.I.	+ 17%
Mo	-	-	"	+ 32% ^a
Na	- 44%	- 40%	"	+ 12%
Ni	+ 10%	+ 2900% ^a	"	N.I.
Pb	+ 29%	+ 57%	"	+ 10%
Ta	+ 27%	+ 54% ^a	"	+ 60%
Th	N.I.	-	"	+ 27%
V (V)	+ 27%	+ 485% ^a	-	-
W (VI)	N.I.	+ 23 ^a	+ 14%	+ 43% ^a
Zn	+ 26%	+ 52%	N.I.	+ 7%
Cl ⁻	N.I.	N.I.	"	N.I.
NO ₃ ⁻	"	"	"	"
F ⁻	"	- 7%	"	"
PO ₄ ³⁻	"	N.I.	"	"

N.I. : no interference

^aexistence of some spectral contribution to interference has been experimentally confirmed.

3.VI: CONCLUSION

The advantages of the nitrous oxide-acetylene flame as an atom reservoir have been presented previously in this thesis (pp 31) as have the advantages to be obtained upon inert-gas separation of that flame (pp 32). A substantial increase in the detection limits was observed in the atomic emission and atomic fluorescence determinations for each element upon inert-gas separation. This was the result of (a) an increase in signal intensity as the result of the maintenance of a substantially greater population of free ground state atoms of the elements than was obtained in a conventional nitrous oxide-acetylene flame supported at the same burner (6) and (b) from the reduction of the background thermal noise of the flame which was seen by the photomultiplier.

The atomisation of each element requires very hot and very reducing flames. The fuel-rich nitrous oxide-acetylene flame was able to fulfil both these requirements. Different fuel:support gas stoichiometries were required for each element (see text); the flame had to be luminous rather than showing the red interconal zone to obtain effective atomisation of the silicon solutions when it was used in the conventional mode. Separation of the flame enabled the very fuel-rich flame to be supported with greater facility at the round burner and

with a reduction in the rate of carbon deposition on the burner. This effect was more noticeable when the flame was separated by argon rather than nitrogen as the inert gas.

The high temperature permitted effective excitation of the principal resonance lines of all the elements, so that good sensitivity was obtained by flame atomic emission. The determination of silicon and germanium in this way was also relatively free from physical and chemical interference effects. The study showed that the sensitivity of flame atomic emission is very considerably improved by the use of the separated flame.

The determination of silicon, germanium, aluminium and vanadium by atomic fluorescence was either completely or relatively free from interference effects, while considerable interferences were observed in the flame atomic emission determination of the latter two elements. These interferences were not only spectral but also have a chemical (or physical) origin, as the aspiration of the interfering solution into the flame in the absence of the element to be determined produced no significant emission in many instances.

The addition of excess diverse ion appeared to

enhance the production of free ground state molybdenum atoms; this was shown by the increase of the atomic fluorescence emission in many instances. Similarly an increased population of thermally excited molybdenum atoms must also have been produced.

No atomic fluorescence was observed in this study for zirconium and titanium. These elements have a multiplicity of lines with very similar oscillator strengths. The photo-excited atom has, as a result, many pathways available for the dissipation of its acquired energy. A fluorescence signal will only therefore be observed with an extremely intense line source. In the instance of zirconium an additional factor is the very refractory nature of the zirconium oxide species which prevents production of a significant population of ground state atoms (c.f. the poor atomic absorption sensitivity).

The atomic fluorescence determination of vanadium, silicon, germanium and aluminium was about one order of magnitude more sensitive than their respective determination by atomic absorption. The sensitivity is dependent upon the line intensity and source noise, but is high even with the simple tubes used in this work. The atomic fluorescence signals were not critically

dependent upon burner height which suggests that the flame provided a population of ground-state atoms of each element that extended well above the primary reaction zone.

Both emission techniques gave linear calibrations over a wide range of concentrations for most of the elements, molybdenum being the exception. Similarly it was found that both gave high precisions in the replicate analysis studies in every case.

The relative sensitivities of flame atomic emission and atomic fluorescence were found to be dependent upon wavelength. Consideration of all the determinations suggested that for elements with principal resonance lines below 300 nm atomic fluorescence is the more sensitive technique. For the range 300 to 350 nm the two techniques have an approximately equal sensitivity, but for wavelengths longer than 350 nm flame atomic emission tends to be the more sensitive technique. The virtue of atomic fluorescence spectroscopy, however, lies in its relatively high freedom from interference effects, and this is generally the more decisive factor for practical analytical problems. The preliminary work on a determination of silicon in steels (76) supports this view.

CHAPTER 4. THE DETERMINATION OF FLAME TEMPERATURE PROFILES

4.I: Introduction

The premixed laminar flame, which has been employed throughout the work presented in this thesis, offers several advantages in the study of the chemical and physical processes (77-90) within the flame over the turbulent diffusion flame. These advantages are the unidimensional flow, a clear distinction between the reaction zone and the outer cone of the flame and a homogeneous distribution of temperature and species across the flame (91). The interconal zone of the premixed flame, when burning at atmospheric pressure, has been shown to be in thermal equilibrium (77-83), but deviations from thermal and thermodynamic equilibrium are known to occur within the reaction zones of the flame. The kinetics of the flame processes within this region have likewise been studied (84-88). Any departures from equilibrium would particularly affect the amount of ionisation of a species in this region: Belcher and Sugden (89, 90) have reported thermal equilibrium deviations just above the primary zone of a Bunsen-type flame.

The thermal energy of a flame is distributed as

different types of energy between the particles within the flame: each of these may possess different translational, rotational, vibrational, electronic or ionisation energies. When the population temperatures for all the flame species and types of energy are in close agreement the part of the flame in which the measurements are made may be said to be in thermal equilibrium and possess that temperature.

There are two principal types of methods for temperature measurements; thermometric and optical. When a thermometric method is employed a metallic wire or thermocouple is introduced into a specific area of the flame, and the temperature of the wire is determined. However, although thermometric methods have advantages, particularly the small size of the probes, they suffer from heat loss in the wire probes and the softening and melting points of the metals that may be used as the probes impose an upper limit for the temperature of the flames studied. Optical methods have an advantage over the thermometric methods as the flame is not disturbed. However, the point study of a region in the flame is seldom possible because the mean value along the optical light path is usually obtained. These methods are not limited by any temperature considerations and may

therefore be employed when high temperature flames are studied. The range of methods available have been extensively reviewed by Mavrodineanu and Boiteux (9), Gaydon and Wolfhard (49) and Gaydon (92).

In each of the optical methods that may be employed for the flame temperature measurement a specific characteristic of a species within the flame is observed. Thus the population temperature derived from the distribution of the atoms or molecules in different translational, rotational, vibrational, electronic or ionisation states may be determined as the corresponding population temperature for that species. However, this temperature is only characteristic of that species and type of energy. Although the spectrum-line reversal method is most commonly employed as the means of determining the flame temperature it is not realistic to define this as the 'true' flame temperature: it is the effective electronic excitation temperature for the element used. Other methods may give the effective population temperature of the other types of energy for the other species present.

When thermal equilibrium conditions are to be tested within a particular region of a flame, it is logical to study the temperature for that type of energy which takes

longest to equilibrate. It has been reported (9) that the ionisation of a species takes the greatest time, i.e. requires the greatest number of collisions, to equilibrate (see table below).

<u>State</u>	<u>Number of Collisions for Equilibration</u>
Translation	10
Rotation	10^3
Vibration	10^5
Excitation and dissociation	10^7
Ionisation	10^9

If a precise and reproducible flame temperature is obtained from an ionisation method, and if this value agrees well with the maximum temperature calculated for the fuel-oxidant mixture employed, it may be assumed that thermal equilibrium prevails in that area of the flame, and that other methods of measurement will yield similar results.

In this chapter a method for determining the percentage ionisation contours of an element within a flame is presented. The percentage ionisation of an element is proportional to the concentration of that element and the electron concentration within the flame, and to the temperature of the system that is observed. If the percentage ionisation can be accurately related to

the temperature, an effective ionisation temperature profile for the flame may be determined from the ionisation contours that were observed. The equilibrium constant for the ionisation of an element may be calculated from the atomic properties of the element (ionisation potential, atomic partition functions and/or the statistical weights of the atomic and ionic levels of the element) and the temperature, and without any consideration of a concentration term. This calculation follows from the Saha equation, which is the fundamental ionisation equation. The equilibrium constant may also be obtained in conventional concentration terms, i.e. for the system,



the ionisation equilibrium constant, K , is given by,

$$K = \frac{[A^+][e]}{[A]} \quad -$$

The value of the degree of ionisation of an element which was observed may be expressed as $[A^+]/([A] + [A^+])$, and provided $[e]$ was large and constant, a change in $[A^+]/([A] + [A^+])$ could be directly related to a change in temperature.

The values of the degree of ionisation were obtained by evaluating the emission intensities for an atomic line

of an element (i) when there was natural ionisation present and (ii) when this ionisation had been suppressed to at most 1 per cent by the addition of an excess of potassium to the solution. The ratio of these intensities may then be taken and used to express the degree of ionisation. This method should be relatively free from self-absorption effects as the same atomic emission line was observed in each case.

4.II: Theory

4.II.1: Atomic-Ionic Line Intensity Ratio Method

The only previously reported ionisation temperature method for analytically useful flames has employed a method using the ratio of the intensities of the atomic and ionic lines for the alkaline earth elements (91). This method, the theory of which is outlined below, has been applied to turbulent flames, and not to premixed laminar flames. A flame electron concentration was also obtained and this determination has also been applied to these studies.

Local thermal equilibrium may be assumed to exist in a flame if, in addition to the previously mentioned criteria, the same temperature is common to,

(1) Maxwell's equation for the velocity distribution of

the particles.

(ii) Boltzmann's equation for the population distribution over the electronically, vibrationally and rotationally excited energy levels, and

(iii) Saha's equation for the ionisation of a species within the flame.

It has been suggested that significant deviation from thermal equilibrium does not result from the flame not radiating as a black-body (24, 93).

The emission intensity from a particular transition (subscripted t for that transition) is given by,

$$I_t = \frac{A_t \cdot n_a}{Z} \cdot \exp (-E_t/kT) \quad [4.1]$$

where

A_t is a generalised transition probability,

n_a is the concentration of the species (in number of particles per cm^3),

Z is the partition function,

k is the Boltzmann constant (in appropriate units),

E_t is the excitation energy of the upper level and

T is the temperature.

The ionisation equilibrium between atoms and ions of one species is given by the Saha equation, which is

shown in its most general form below,

$$\frac{n_i \cdot n_e}{n_a} = \left[\frac{2\pi m k T}{h^2} \right]^{3/2} \cdot \frac{2Z_i}{Z_a} \cdot \exp (-V_i/kT) \quad [4.2]$$

where

The ion and atom are denoted by the subscripts i and a respectively,

h is Planck's constant,

m is the mass of the electron,

n_e is the electron concentration in the flame, in cm^{-3} ,

V_i is the ionisation potential of the species, in cm^{-1} .

Equations [4.1] and [4.2] may be combined to give, with all the energies in cm^{-1} ,

$$\log (I_a/A_a) - \log (I_i/A_i) = \log n_e - 1.5 \log T - 15.68 + (0.625/T)(V_i + E_i - E_a)$$

where

I_a is the intensity of the atomic line,

I_i is the intensity of the ionic line,

A_a is the atomic line transition probability,

A_i is the ionic line transition probability,

E_i is the excitation level of the ionic line upper level,

E_a is the excitation level of the atomic line upper level.

All the energies are in cm^{-1} .

If the intensities of the atomic and ionic resonance lines are determined, then values of $\log (I_a/A_a) - \log (I_i/A_i)$ for an element may be plotted against the corresponding values of $(V_i + E_i - E_a)$ for that element. Suitable elements that may be employed in flames with this method are the alkaline earths, calcium, barium and strontium. If the values obtained for these three elements produce a straight line plot then thermal equilibrium conditions are indicated for that part of the flame. The ionisation temperature and the electron concentration in that part of the flame may be calculated from the gradient and intercept of the plot.

4.II.2: Atomic Line Suppression Method

The natural ionisation of an element may be suppressed by the addition of another more easily ionised element (e.g. sodium or potassium). The percentage ionisation can be obtained by evaluating the ratio of the emission intensities of the atomic line of the element with and without a suppressing agent present. The percentage ionisation which is obtained can be related to the temperature of the system and the concentrations of the elements present in the following manner:

The ionisation of an atom to its positive ion and a free electron may be represented as,



and treated as a simple dissociation process. The ionisation equilibrium constant for this process is given by the ratio of the concentrations (expressed as partial pressures),

$$K = \frac{[A^+][e]}{[A]}$$

The ionisation equilibrium constant may also be predicted from the Saha equation, a rigid and precise form of which has been given previously (equation [4.2]). The equation may also be expressed logarithmically (49) as,

$$\log K = - \frac{U}{4.573 T} + 2.5 \log T - 6.49 + \log (g_{A^+} \cdot g_e / g_A) \quad [4.3]$$

where

U is the ionisation potential of A expressed in calories per mole. $U = 23053 V$, where V is the ionisation potential expressed in electron volts (eV),

T is the temperature in $^{\circ}K$,

g_{A^+} is the statistical weight of the ionised atom,

g_A is the statistical weight of the neutral atom and

g_e is the statistical weight of the electron.

This equation may be applied to atoms and ions having a simple electronic structure, such as the alkali metals, the alkaline earths and copper, silver, gold, zinc and mercury, where the statistical weight of the ground level is virtually equal to the atomic partition function. For more complex elements the statistical weight term may be replaced by,

$$\log (Z_i/Z_a)$$

where Z_i and Z_a are the atomic partition functions for the ion and atom. These values are well documented in the literature for different elements at different temperatures (94, 95). Although atomic partition functions are temperature dependent, Boumans (96) has demonstrated that this dependence may be compensated for when applying the Saha equation to high temperature systems. He suggests that the atomic partition function term in the Saha equation (when expressed logarithmically) may be replaced by putting

$$\log (Z_i/Z_a) = - (5040/T)\delta$$

where δ (expressed in electron volts) is taken as constant over a given temperature range. For that temperature range an apparent ionisation potential may be defined as

$$V_{app} = V + \delta$$

This term may be substituted into the Saha equation (equation [4.3]) to give,

$$\log K = - (5040 V_{\text{app}}/T) + 2.5 \log T - 6.49 \quad [4.4]$$

The values of the true and apparent ionisation potentials reproduced from Bouman's data, which have been used in the work presented in this thesis, are shown in Table XXV. The apparent ionisation potential values have been employed when the predicted degrees of ionisation of the elements were calculated.

This simple treatment may be extended to more complex systems, such as when there is more than one ionisable atom and where there is an additional source of electrons present. Such a system is present within a flame when two ionisable elements (such as potassium and sodium) are introduced, and where there is an appreciable concentration of natural flame electrons. There will be additional equilibria and equations to consider in such a system, i.e. for two elements, A and B, in a flame, with a natural flame electron concentration n_f the following equations may be written,

$$K_A = \frac{[A^+][n_e]}{[A]} \quad [4.5]$$

TABLE XXV

True Ionisation Potentials and Apparent Ionisation Potentials at Different Temperatures for the Various Elements Employed (96)

Element	V (eV)	Apparent Ionisation Potential (eV)			
		1500- 2000°K	2000- 2500°K	2500- 3000°K	3000 3600°K
Ag	7.57	7.67	7.70	7.73	7.77
Ba	5.21	5.10	5.05	5.01	4.98
Ca	6.11	6.01	5.98	5.95	5.91
Cr	6.76	6.78	6.80	6.81	6.83
Cs	3.89	3.99	4.02	4.06	4.10
K	4.34	4.44	4.47	4.50	4.54
Mg	7.64	7.54	7.51	7.48	7.44
Na	5.14	5.24	5.27	5.30	5.34
Sr	5.69	5.59	5.56	5.53	5.50

V is the true ionisation potential

$$K_B = \frac{[B^+][n_e]}{[B]} \quad [4.6]$$

$$[n_e] = [n_f] + [A^+] + [B^+] \quad [4.7]$$

where K_A and K_B are the ionisation equilibrium constants for the elements A and B, and $[n_e]$ is the total electron concentration in the flame from all sources. The value

of $[n_f]$ would be expected to be small as the ionisation potentials are very high for all common equilibrium flame gas species; the values are generally between 12 and 16 eV. The only stable gas with a lower ionisation potential is nitric oxide, NO, which has a value of 9.23 eV. However, it has been found in real flames (49) that there is a significant contribution to the overall flame electron concentration from the natural flame ions.

Equations [4.5] and [4.7] may be rearranged and combined to give:

$$K_A = \frac{([n_e] - [n_f] - [B^+])[n_e]}{[A]} \quad [4.8]$$

n_e may be expressed in terms of K_B , $[B^+]$ and $[B]$ from equation [4.6] and substituted in equation [4.8] to give,

$$K_A = \frac{((K_B[B]/[B^+]) - [n_f] - [B^+])(K_B[B]/[B^+])}{[A]} \quad [4.9]$$

Equation [4.9] expands and simplifies to give:

$$K_A[A] = \frac{K_B^2 [B]^2}{[B^+]^2} - [n_f] \cdot \frac{(K_B[B])}{[B^+]} - K_B[B] \quad [4.10]$$

The concentration of element A was determined from equation [4.10] such that a predetermined degree of ionisation of element B would be obtained. This was achieved by assuming that element B was to be 1 per cent

ionised. This enabled the partial pressure ratio $[B]/[B^+]$ to be expressed numerically.

i.e. for 1% ionisation, $[B]/[B^+] = [99]/[1] = 99$

for 5% ionisation, $[B]/[B^+] = [95]/[5] = 19$

These partial pressures only relate to the concentration of B in the atomic and ionic form in the flame at the moment when ionisation occurs, and not to the original concentration of the element B which reaches the flame. This initial concentration, $[B_t]$, may be related to either the atomic or ionic concentrations of B in the flame by,

$$[B_t] = [B] + [B^+]$$

so, for 1 per cent ionisation of the element B,

$$[B^+] = 0.01 [B_t]$$

and $[B] = 0.99 [B_t]$

The ratio $[B]/[B^+]$ was substituted by 99 in equation [4.10] as was $[B]$ by $0.99 [B_t]$ to give equation [4.11],

$$K_A[A] = K_B^2[99.0]^2 - [n_f][K_B][99.0] - [0.99][B_t] \quad [4.11]$$

The concentration of element A in atomic form (i.e. $[A]$) which was required to give a 1 per cent ionisation of element B was determined from the above equation. All the terms may be evaluated---- $[B_t]$ from the original concentrations of element B which reaches the flame, K_A and K_B from the Saha equation and $[n_f]$ by

assumption or experimental determination.

The value obtained from the evaluation of equation [4.11] gives the partial pressure of element A in its atomic form in the flame. This concentration, $[A]$, has an associated concentration of element A in its ionic form. This can be determined, and hence the total concentration of element A that is aspirated into the flame. The initial concentration of element A to be introduced into the flame $[A_t]$, was given by,

$$[A_t] = [A] + [A^+]$$

If equation [4.7] is substituted into equation [4.5], then,

$$K_A = \frac{[A^+]([n_f] + [B^+] + [A^+])}{[A]}$$

$$[A]K_A = [A^+]^2 + [A^+][B^+] + [A^+][n_f] \quad [4.12]$$

Rearranging as a quadratic equation,

$$[A^+]^2 + [A^+]([B^+] + [n_f]) - K_A[A] = 0 \quad [4.13]$$

$[A^+]$ may be evaluated by solving for the roots of the quadratic equation in the conventional manner. The terms $[A]$, $[n_f]$, $[B]$ and $[B^+]$ have all been previously determined. The concentration of the element A which was required to be aspirated into the flame to produce a 1 per cent ionisation of element B can be determined

by the addition of $[A]$ and $[A^+]$.

In a practical example the element with the lower ionisation potential is the suppressing agent, i.e. potassium (4.33 eV) suppresses sodium ionisation (5.14 eV) to one per cent. Other percentage values may readily be obtained by simple numeric substitutions for the ratio $[B^+]/[B]$.

4.III: Evaluation of Partial Pressures and Computer Calculation

The partial pressure of any particular species in the flame may be evaluated in terms of the total number of particles of that species in the flame per cm^3 , and the total number of individual molecular and atomic particles of all different species (which would arise principally from the flame gases) within the flame per cm^3 . The latter value, for the total number of every molecular and atomic particles arising mainly from the combustion of the flame gases, is obtained from the ideal gas law, where,

$$N_{\text{tot}} = P_{\text{tot}}/kT$$

where,

N_{tot} is the total number of molecular and atomic particles per cm^3 in the flame which have arisen from every source,

k is the Boltzmann constant in suitable units,

T is the absolute temperature and

P_{tot} is the pressure in mm of mercury of the foreign gas particles.

As the flame burns at atmospheric pressure, P_{tot} is 760 (mm of mercury) and the value of k is in the corresponding units,

$$\text{i.e.} \quad N_{tot} = (9.74 \times 10^{18} \times 760)/T$$

The total number of atoms of an element present in the flame, without regard to their state of combination and ionisation state, can be calculated from the flame and solution parameters (97) by,

$$n_{at} = \frac{CV_1A}{MV_v}$$

where,

n_{at} is the total number of atoms of an element present in the flame per cm^3 ,

C is the concentration of the aspirated element in the sample solution, expressed in $\mu\text{g ml}^{-1}$,

V_1 is the volume of the sample solution reaching the flame in ml minute^{-1} . This is dependent upon the flow-rate of gases, nebulizer efficiency etc.

A is the Avogadro number, 6.027×10^{23} ,

M is the atomic weight of the aspirated element, expressed in $\mu\text{g mole}^{-1}$ and

V_v is the volume of the combusted gas at the flame temperature. This is derived by assuming the ideal gas law, and correcting for temperature,

i.e.

$$V_v = \frac{V_g \cdot T}{T_r}$$

where,

V_g is the volume of gases before combustion at room temperature,

T is the temperature of the flame ($^{\circ}\text{K}$) and

T_r is the room temperature ($^{\circ}\text{K}$).

The value of the nitrous oxide volume contribution to V_v , when the nitrous oxide-acetylene flame was employed, must be multiplied by 3/2 to take account of the change in stoichiometry as the gases were burnt.

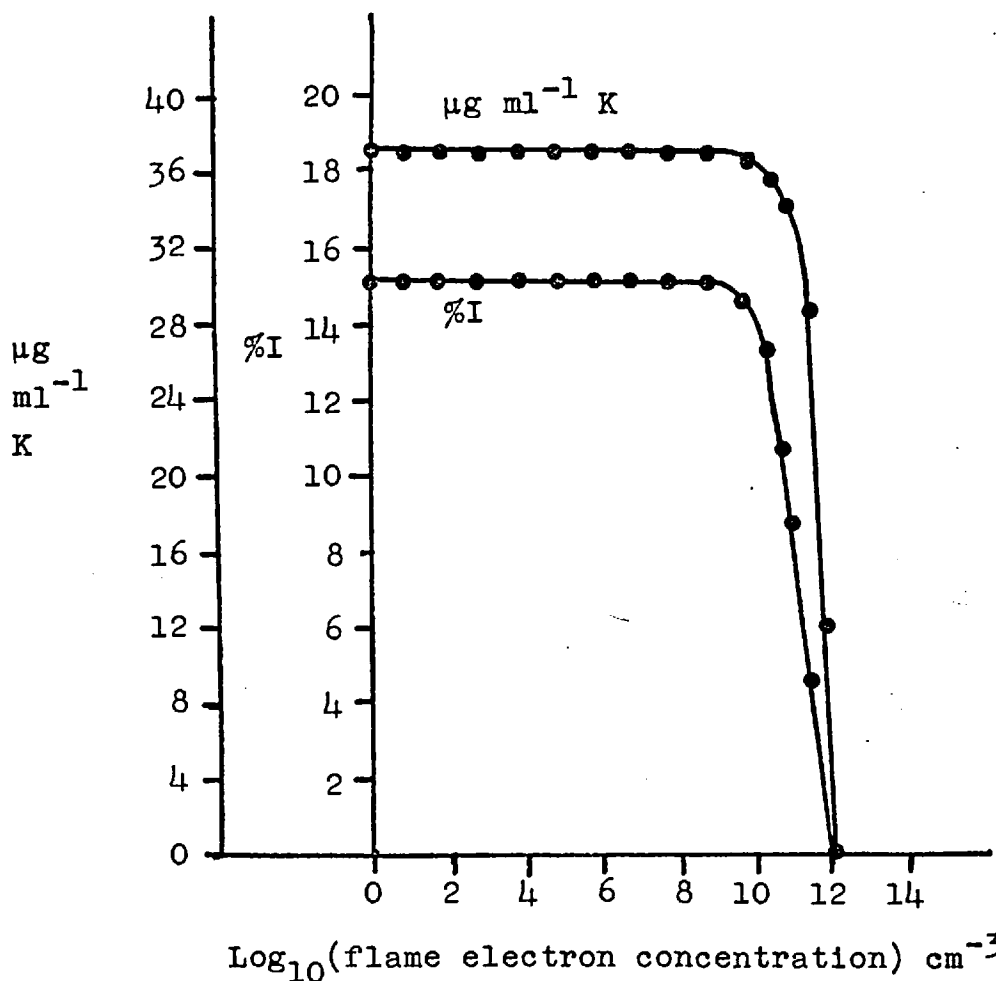
The nebulisation efficiency is determined from the aspiration of a known volume of water into the flame. All the waste water from the drain pipe and nebulizer chamber was collected and measured. The volumes of water are most easily determined by weighing. The efficiency of nebulisation is then determined from,

$$\text{efficiency} = \frac{\text{Water (aspirated)} - \text{water (collected)}}{\text{water (aspirated)}}$$

The efficiency determination was repeated utilizing 1,000 $\mu\text{g ml}^{-1}$ potassium as the aspirated solution.

This corrected value was employed when the concentrated potassium solutions were nebulized.

The flame electron concentration, arising from the natural flame gas species, was also evaluated as a partial pressure. The total number of flame gas ions in a premixed laminar air-acetylene flame has been reported to be 10^{10} to 10^{11} ions per cm^3 (98). The average value, $5 \times 10^{10} \text{ cm}^{-3}$ flame ions, was assumed initially when the air-acetylene flame was employed. When the nitrous oxide-acetylene flame was employed, the concentration was determined with more accuracy using the atomic-ionic line intensity ratio method outlined previously. The predicted effect of the variation in the flame ion concentration upon the natural ionisation of a $2.5 \mu\text{g ml}^{-1}$ sodium solution is shown in Figure 15, as is the concentration of potassium that is required to suppress that ionisation to one per cent. The natural degree of ionisation of the sodium remains at a constant value of 14.9% while the flame ion concentration varies over the range 0 to 10^9 ions cm^{-3} , at a temperature of $2,500^\circ\text{K}$. Similarly the concentration of potassium required to suppress the ionisation to one per cent is unchanged. However, over the range 10^9 to 10^{11} ions cm^{-3} , the natural ionisation of the sodium is markedly



$\mu\text{g ml}^{-1} \text{ K}$: concentration of potassium in $\mu\text{g ml}^{-1}$ required to suppress sodium ionisation to 1 per cent.

%I: percentage ionisation of sodium.

Figure 15: Plot of the predicted variation in the ionisation of $2.5 \mu\text{g ml}^{-1}$ sodium and the concentration of potassium required to suppress ionisation to 1 per cent with flame electron concentration. Temperature $2,500^{\circ}\text{K}$ in a conventional air-acetylene flame.

dependent upon the flame ion concentration, but the curve for the potassium concentration does not change so rapidly. This indicates that it should be possible to predict the minimum concentrations of potassium required as a suppressing agent with a reasonable precision.

Calculation

The calculation of the equilibrium constants, degrees of ionisation and concentrations of one easily ionised element required to produce a predetermined percentage ionisation in a second less easily ionised element was aided by the use of an IBM 7094 electronic digital computer. A programme was written and compiled in Fortran IV language and operated by the Purdue University Fast Fortran Translator system (PUFFT). An example of the programme is given subsequently; the two elements employed are sodium and potassium. The Namelist for the terms used in the programme is given below.

Namelist

FLAME; the concentration of the natural flame ions, cm^{-3} .

TEMP; the temperature, $^{\circ}\text{K}$.

CKINNA; the initial concentration of sodium, $\mu\text{g ml}^{-1}$.

DGONNA; the degree of ionisation of the sodium solution.

DGONK; the degree of ionisation of the potassium solution.

PPM K; the concentration of potassium required to suppress the sodium ionisation to 1 per cent, $\mu\text{g ml}^{-1}$.

PARPRS; the concentration of the sodium solution, expressed as a partial pressure.

TTPART; the total number of flame particles (atomic, ionic and molecular), cm^{-3} .

TTPTNA; the total number of sodium particles in the flame, from the sodium solution, in cm^{-3} .

TTPTLM; the total number of sodium particles in the flame from a 1 M sodium solution, in cm^{-3} .

FIINA; the final concentration of the sodium solution, $\mu\text{g ml}^{-1}$.

PRPSLM; the concentration of a 1M sodium solution, expressed as a partial pressure.

FLAMON; the concentration of the natural flame gas ions, expressed as a partial pressure.

EQCTNA; the Saha ionisation equilibrium constant for the reaction $\text{Na} \rightleftharpoons \text{Na}^+ + \text{e}$.

EQCTK; the Saha ionisation equilibrium constant for the reaction $\text{K} \rightleftharpoons \text{K}^+ + \text{e}$.

ATOMK; the concentration of potassium atoms in the flame to give 1 per cent ionisation of sodium solution.

POSITK; the concentration of potassium ions in association with ATOMK, expressed as a partial pressure.

CONCK; ATOMK + POSITK expressed in molarity of potassium solution to be nebulized.

DGONTK; the degree of ionisation of a potassium solution of concentration PPM K in $\mu\text{g ml}^{-1}$.

```

C  CALCULATION PPM K REQUIRED TO GIVE 1 PER CENT IONIZATION OF SODIUM
C  CONCENTRATION FLAME IONS 5*10**10 PER C.C.
    READ (5,10C0) FLAME
1000 FORMAT (E12.2)
C
    WRITE (6,2000)
2000 FORMAT (1H1, 5X, 4HTEMP, 3X, 6HCKINNA, 7X, 6HGDONNA, 7X, 5HGDONK,
19X, 6HPPM K, 9X, 6HPRPRS, 8X, 6HTTPART, 8X, 6HTTPTNA)
C
    CKINNA = 2.5/2.0
    FIINNA = CKINNA*(2.0**2.0)
C
15  CKINNA = 2.0*CKINNA
    IF (CKINNA.GT.FIINNA) GO TO 30
    TEMP = 1990.0
C
C  START OF LOOP FOR EACH TEMPERATURE
10  TEMP = TEMP + 10.0
    IF (TEMP.GT.3300.0) GO TO 15
    TTPART = (9.74E+18*760.0)/TEMP
    TTPTNA = (CKINNA*0.395*6.027E+23*293.0)/(22.99E+09*6.27*TEMP)
    PRPRS = TTPTNA/TTPART
C
    TTPT1M = (0.395*6.027E+23*293.0)/(TEMP*6.27E+06)
    PRPS1M = TTPT1M/TTPART
    FLAMON = (FLAME*2450.0)/(9.74E+18*760.0)
C
    B = (2.5*ALOG10(TEMP)) - 6.49 - ((23053.0*5.14)/(4.573*TEMP))
    EQCTNA = 10.0**B
    C = (2.5*ALOG10(TEMP)) - 6.49 - ((23053.0*4.33)/(4.573*TEMP))
    EQCTK = 10.0**C
C

```

C CALCULATION DEGREE OF IONIZATION FOR INITIAL CONCENTRATION NA
 $DGONNA = 0.5 * (SQRT((EQCTNA * EQCTNA + 2.0 * FLAMON * EQCTNA + FLAMON * 1FLAMON + 4.0 * EQCTNA * PARPRS) / (PARPRS * PARPRS)))$
 $1- (EQCTNA + FLAMON) / (2.0 * PARPRS)$

C
 C CALCULATION DEGREE OF IONIZATION FOR EQUIVALENT CONCENTRATION K
 $DGONK = 0.5 * (SQRT((EQCTK * EQCTK + 2.0 * FLAMON * EQCTK + 1FLAMON * FLAMON + 4.0 * EQCTK * PARPRS) / (PARPRS * PARPRS)))$
 $1- (EQCTK + FLAMON) / (2.0 * PARPRS)$

C
 C PARTIAL PRESSURE K ATOMS TO GIVE REQUIRED NA IONIZATION
 $ATOMK = (EQCTNA * EQCTNA * 99.0 * 99.0 - 0.99 * EQCTNA * PARPRS$
 $1- 99.0 * EQCTNA * FLAMON) / EQCTK$

C PARTIAL PRESSURE OF K IONS ASSOCIATED WITH K ATOMS IN EQUILIBRIUM
 $POSITK = (SQRT((PARPRS / 100.0 + FLAMON) ** 2.0 + 4.0 * ATOMK * EQCTK)$
 $1- PARPRS / 100.0 - FLAMON) / 2.0$
 $ZMOLK = ATOMK + POSITK$

C
 C CONCENTRATION IN M OF ZMOLK
 $CONCK = ZMOLK / PRPS1M$
 $PPMK = 39100.0 * CONCK$

C DEGREE OF IONIZATION OF TOTAL K INTRODUCED INTO FLAME
 $DGONTK = POSITK / ZMOLK$

C
 WRITE (6,3000) TEMP, CKINNA, DGONNA, DGONK, PPMK, PARPRS, TTPART,
 1TTPTNA
 3000 FORMAT (1X, 2X, F6.1, 3X, F6.1, 3X, E12.5, 2X, E12.5, 2X, E12.5,

12X, E12.5, 2X, E12.5, 2X, E12.5)

GO TO 10

30 STOP

END

4.IV: Experimental

The instrument used throughout the flame temperature profile studies was a Techtron AA4 flame spectrophotometer, which has been described in Chapter 2. A Honeywell Electronik Continuous Balance recorder was employed to determine the signal values. The spectrophotometer was employed in the emission mode with the cylindrical air-acetylene and nitrous oxide-acetylene burners or the long path (50 mm) nitrous oxide-acetylene atomic absorption burner.

The analytical emission signal was obtained by consideration of the total integrated signal over a predetermined time, usually one minute. It was found that of the three recording systems available (integrating recorder, and the direct reading from either recorder paper or spectrophotometer meter) the greatest precision was obtained when the integrated signal technique was used. The standard deviations in the determination of the same atomic emission signal from a standard chromium solution, using the nitrous oxide-acetylene flame and the integrating recorder, recorder chart or amplifier meter direct reading were 0.5, 0.8 and 1.0 per cent respectively.

The flame profile was scanned by an optical pin-hole technique. The emission from the flame was focussed onto a pin-hole, and then refocussed onto the monochromator entrance slit. The system that was employed is shown diagrammatically in Figure 16. The advantage of using this arrangement was that the primary image of the flame could be enlarged, and hence greater spacial resolution could be obtained when the pin-hole was employed. The flame was well shielded from any extraneous draughts and, with the experimental arrangement described above, was sufficiently distant from the photomultiplier housing to cause no signal drift.

The response of the detection system, which was dependent upon the photomultiplier characteristics and monochromator blazing variations, was calibrated with respect to wavelength by observing the emission from a standard source. This should, ideally, be a perfect black-body but, in reality, a standard tungsten ribbon-filament lamp was employed. The intensity of emission from a black-body is given by Wien's Law,

$$I_{\lambda} = 2E_{\lambda}Ac_1\lambda^{-5} \exp (-c_2/\lambda T) d\lambda$$

where

I_{λ} is the intensity in watts (ergs sec⁻¹) per unit solid angle, normal to the surface,

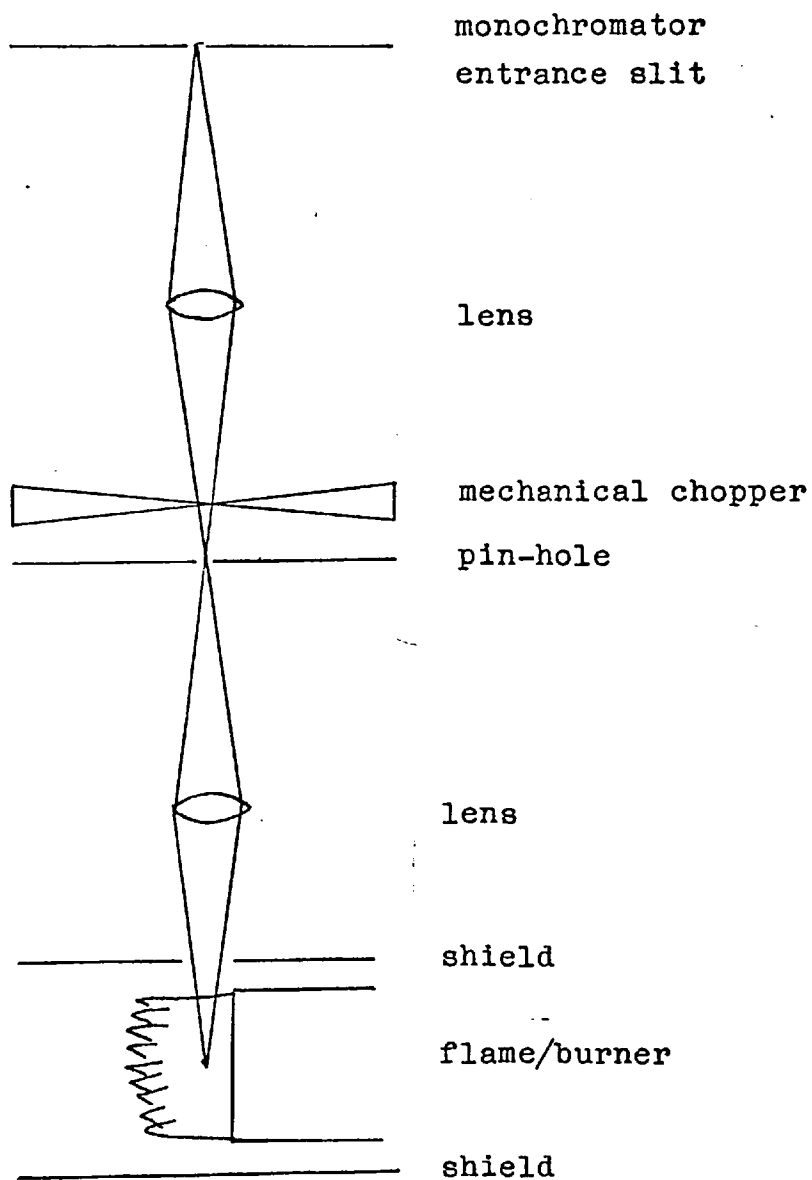


Figure 16: Optical arrangement employed for the flame temperature profile studies.

E_λ is the emissivity of the body at wavelength λ .

A is the area of the emitting body, in cm^2 ,

c_1 is the first radiation constant, and has the value $0.588 \times 10^{-5} \text{ erg cm}^{-2} \text{ sec}^{-1}$ or $0.588 \times 10^{-12} \text{ watts cm}^2$ and

c_2 is the second radiation constant, and has the value $1.438 \text{ cm deg}^{-1}$.

For a black-body the emissivity, E_λ , is equal to one at all wavelengths, and for a grey-body the emissivity is constant, but less than one, at all wavelengths. The temperature of the tungsten ribbon filament lamp, which was used as the source, was determined by comparison with a perfect black-body (i.e. by determination with an optical pyrometer). This temperature was subject to correction as the calibration determined the brightness temperature in the red (the optical pyrometer was calibrated at a mean wavelength of 655.0 nm); this was the temperature a black-body would have to be to have given the same light intensity at that wavelength. The true temperature (which was substituted in the Wien's Law expression) of the tungsten lamp was higher than this temperature. The emissivity of tungsten at different wavelengths has been reported by de Vos (99), and by using these values, and the correction to the brightness temperature suggested by Gaydon and Wolfhard (49)

it was possible to predict the variation in the intensity of emission of the lamp with respect to wavelength, over the range 300 to 700 nm. This is shown in Figure 17. The experimentally determined responses to this emission is also shown on the same Figure. From these two plots it was possible to calibrate the detection system responses at any two wavelengths. The tungsten ribbon-filament was encased in a glass envelope so it was not possible to determine the 'black-body emission' at wavelengths shorter than about 370 nm.

4.V: The Air-Acetylene Flame

The percentage ionisation of sodium in the air-acetylene flame was determined with different concentrations of potassium as the suppressing agent. A flame electron concentration was assumed and the temperature relating to the percentage ionisation which was observed was calculated. The flame electron concentration was determined by a successive approximation procedure employing the percentage ionisation of the sodium and the minimum concentration of potassium required to produce that ionisation. The spectrophotometer was employed without a pin-hole in the emission light-path and the emission from the flame 2-12 mm above the

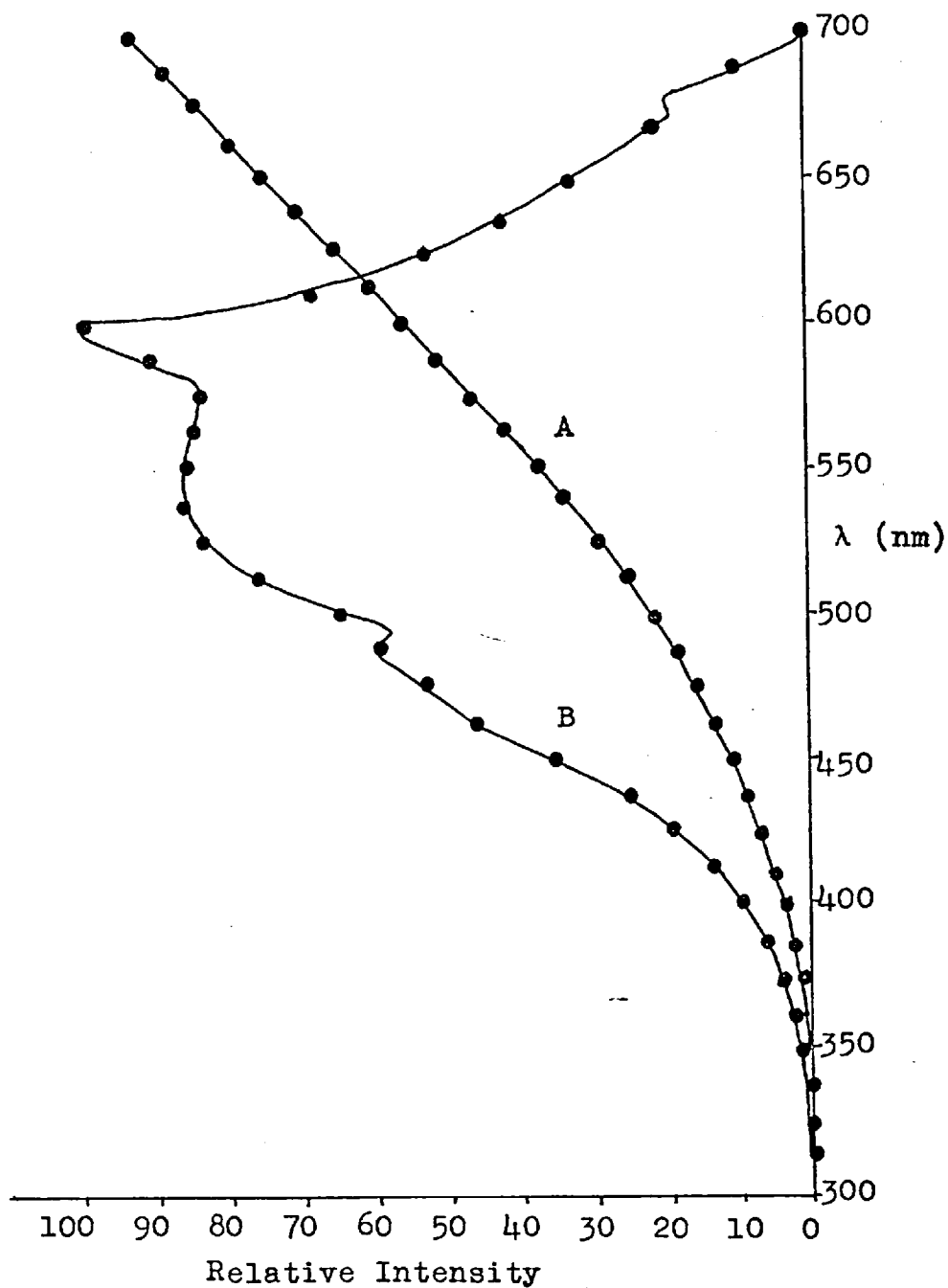


Figure 17: Emission of tungsten ribbon-filament lamp source (A) and the detection system response to the emission (B) over the wavelengths 300 to 700 nm.

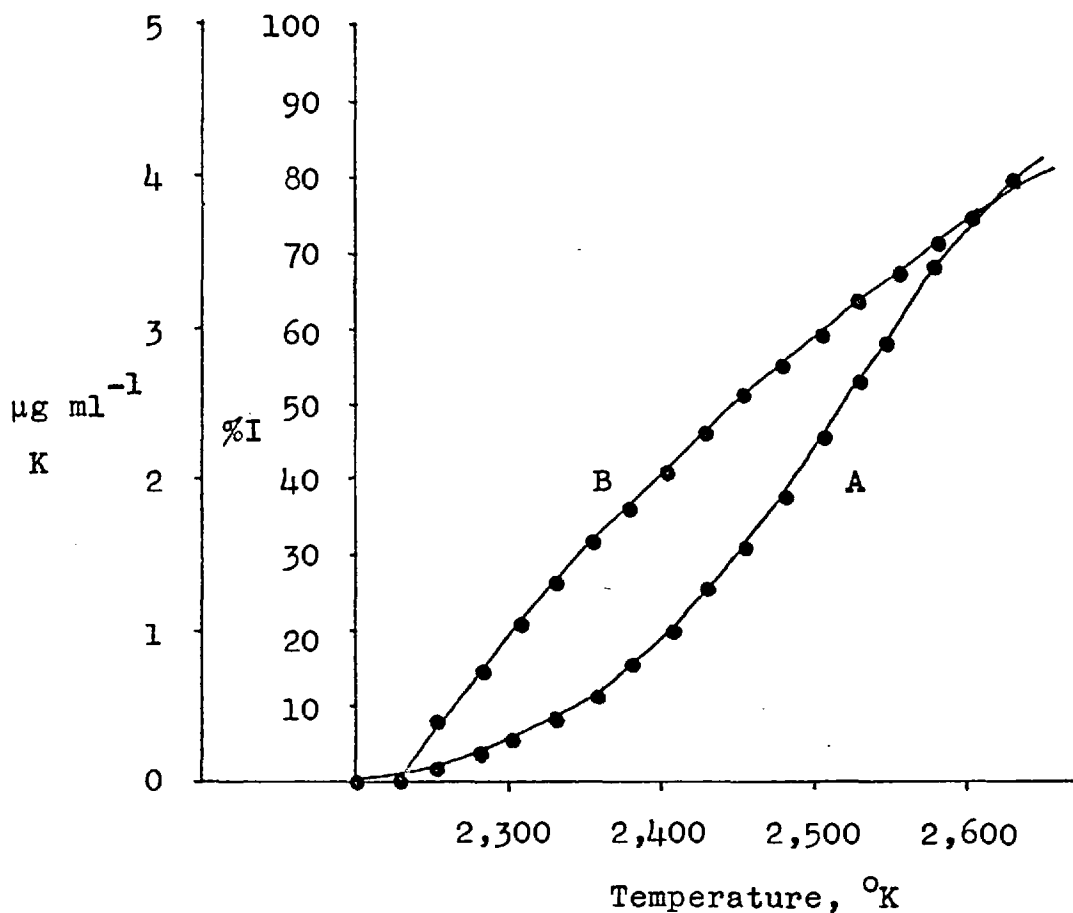
primary cone of the flame was observed in all cases.

4.V.1: Choice of the Element Pair

The element whose atomic emission was to be observed had to satisfy certain requirements. Firstly the element that was nebulized into the flame must be present in the flame in atomic or ionic rather than molecular form. This would occur when the free atom fraction (β value) was unity. These values have been reported by Koirttyohann and Pickett (97) and de Galan and Winefordner (100) for several elements in different flames. It has been reported that both sodium and potassium exhibit negligible compound formation within the flame, while the other alkali metals, lithium and caesium, give rise to some compound formation. The compounds which could be formed in the flame have been characterised by Herrmann and Alkemade (7). Secondly the predicted rate of change of ionisation with temperature should be large over the flame temperature region to be investigated. The first criteria also applied to the element which was to be used as the suppressing agent, but as this would be either sodium or potassium, no compound formation would occur.

The predicted variation in the ionisation of 2.5 $\mu\text{g ml}^{-1}$ sodium with change in temperature is shown in Figure 18; this was determined assuming 5×10^{10} natural flame electrons cm^{-3} . Figure 18 also shows the plot of concentration of potassium that was required to suppress the ionisation to one per cent at each temperature. The greatest rate of change in ionisation occurs over the range 2,400 to 2,600^oK, which is also the temperature range of interest in the air-acetylene flame. Potassium was employed as the suppressing agent because the concentrations that were required were not unreasonable, i.e. the concentrations were not sufficiently great to cause excessive 'clogging' of the burner. If concentrations greater than 10,000 $\mu\text{g ml}^{-1}$ were employed it was found that rapid 'clogging' resulted; this effect was even more noticable with the nitrous oxide-acetylene burner.

The other element with a lower ionisation potential than sodium, caesium (3.96 eV), and which could be employed as the suppressor element, was not satisfactory because, although the molarity of the solutions was less than if potassium were used, the final solution concentrations in $\mu\text{g ml}^{-1}$ were greater. There was also the greater possibility of compound formation if caesium were employed.



%I: percentage ionisation of sodium

$\mu\text{g ml}^{-1} \text{ K}$: $\log_{10}$ (concentration of potassium) in $\mu\text{g ml}^{-1}$ required to suppress sodium ionisation to 1%

Figure 18: Plot of the predicted variation in the ionisation of $2.5 \mu\text{g ml}^{-1}$ sodium (A) and the concentration of potassium required to suppress that ionisation to 1 per cent (B) with change in temperature, assuming a natural flame electron concentration of $5 \times 10^{10} \text{ cm}^{-3}$.

4.V.2: Experimental

A series of solutions containing $2.5 \mu\text{g ml}^{-1}$ sodium and various concentrations of potassium were prepared, as well as a series of potassium blanks. The solutions were sequentially aspirated into the air-acetylene flame, and the emission at 589.6 nm was measured. The percentage ionisation of the sodium solutions were determined by,

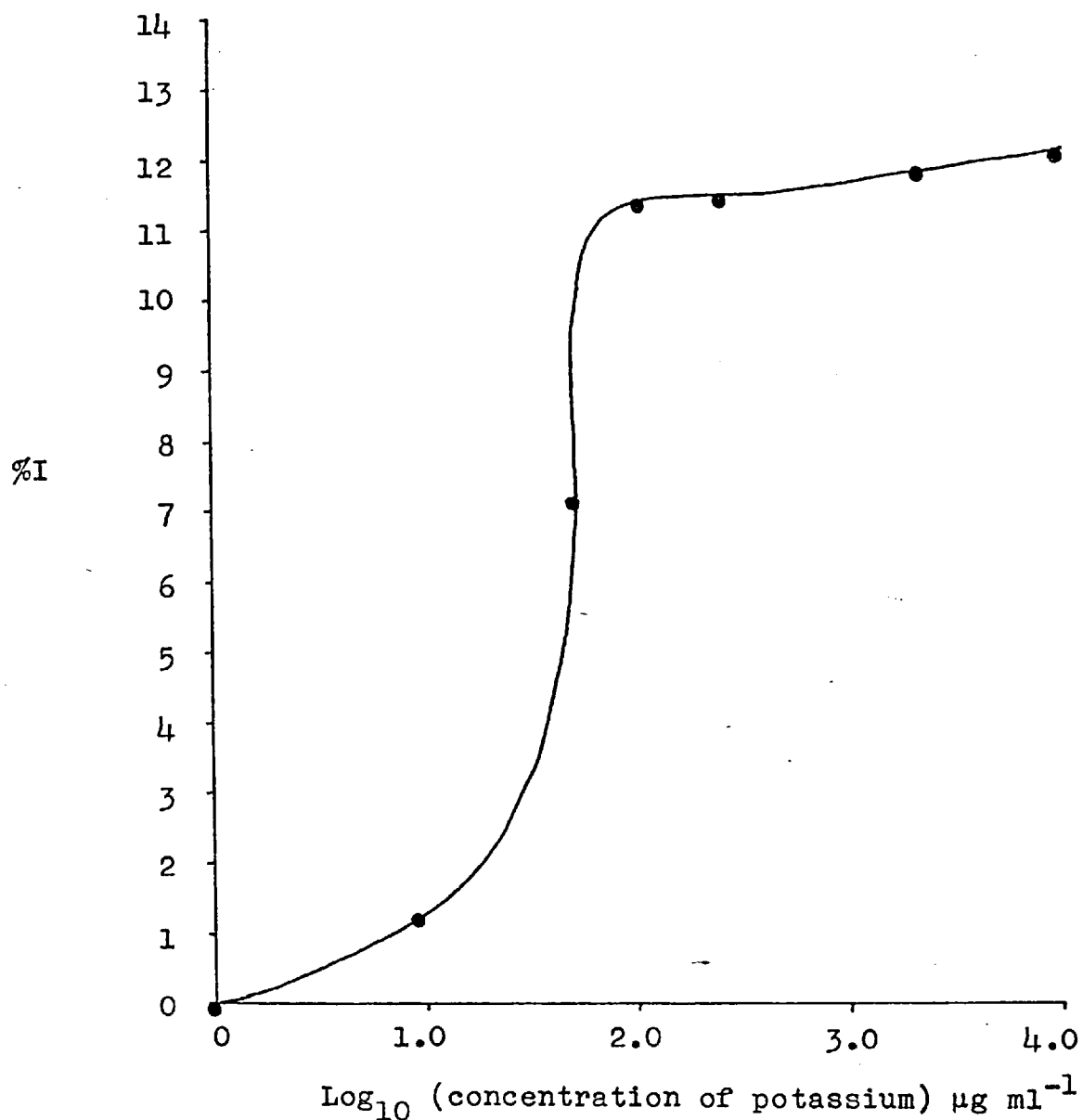
$$\frac{I_1 - I_2}{I_1} \times 100 = \text{percentage ionisation}$$

where,

I_1 is the (atomic emission of the sodium and potassium solution - emission of the potassium blank) and

I_2 is the (atomic emission of sodium solution - emission of the water blank).

The E.H.T. to the photomultiplier was maintained constant when the solutions corresponding to a particular potassium concentration were aspirated. The monochromator entrance slit viewed the flame 2-12 mm above the primary cone of the flame; the spectral band-width employed was 0.33 nm. The plot of percentage ionisation against potassium concentration is shown in Figure 19. The maximum percentage ionisation that was observed was 11.5%; this was obtained when potassium solutions of



%I: percentage ionisation of sodium.

Figure 19: Plot of the percentage ionisation of $2.5 \mu\text{g ml}^{-1}$ sodium experimentally determined at various potassium concentrations.

greater concentration than $70 \mu\text{g ml}^{-1}$ were employed. It was therefore assumed that $70 \mu\text{g ml}^{-1}$ of potassium was the minimum concentration that was required to suppress the ionisation to one per cent, and that the natural degree of ionisation of $2.5 \mu\text{g ml}^{-1}$ sodium was 11.5 per cent in an air-acetylene flame.

This degree of ionisation was predicted to occur with a temperature of $2,510^{\circ}\text{K}$ and would require $40 \mu\text{g ml}^{-1}$ of potassium to suppress the ionisation to one per cent, assuming a flame ion concentration of $5 \times 10^{10} \text{ cm}^{-3}$. By changing the assumption of the flame ion concentration it was found that the predicted and experimentally determined potassium concentrations (required to give one per cent ionisation) coincided. This was found when $9 \times 10^{10} \text{ ions cm}^{-3}$ was assumed. The temperature corresponding to the sodium ionisation of 11.5 per cent was then found to be $2,540^{\circ}\text{K}$. It was therefore suggested that the air-acetylene flame of the stoichiometry studied was burning at an effective ionisation temperature of $2,540^{\circ}\text{K}$, and exhibited a flame ion concentration of $9 \times 10^{10} \text{ natural flame ions cm}^{-3}$.

4.VI: The Air-Propane Flame

A similar procedure to that used to determine the air-acetylene flame temperature was employed to obtain the effective ionisation temperature of the air-propane flame. The elements sodium and potassium were prepared in solution as described in Section 4.V, and aspirated into the flame. It was found that at all potassium concentrations the effective ionisation of the sodium was zero. This indicated that the temperature of the air-propane flame was less than $2,220^{\circ}\text{K}$, assuming 5×10^{10} flame ions per cm^3 . The air-propane flame has been reported to have a temperature of $2,208^{\circ}\text{K}$ (19). The ionisation method used, and presented in this thesis, would not seem to produce anomalously high flame ionisation temperatures, and also indicated that thermal equilibrium had been achieved in the flames studied.

4.VII: The Nitrous Oxide-Acetylene Flame

The determination of the percentage ionisation of an element within the nitrous oxide-acetylene flame was undertaken by a procedure similar to that employed for the air-acetylene flame. The optical arrangement of the spectrophotometer incorporated the pin-hole system

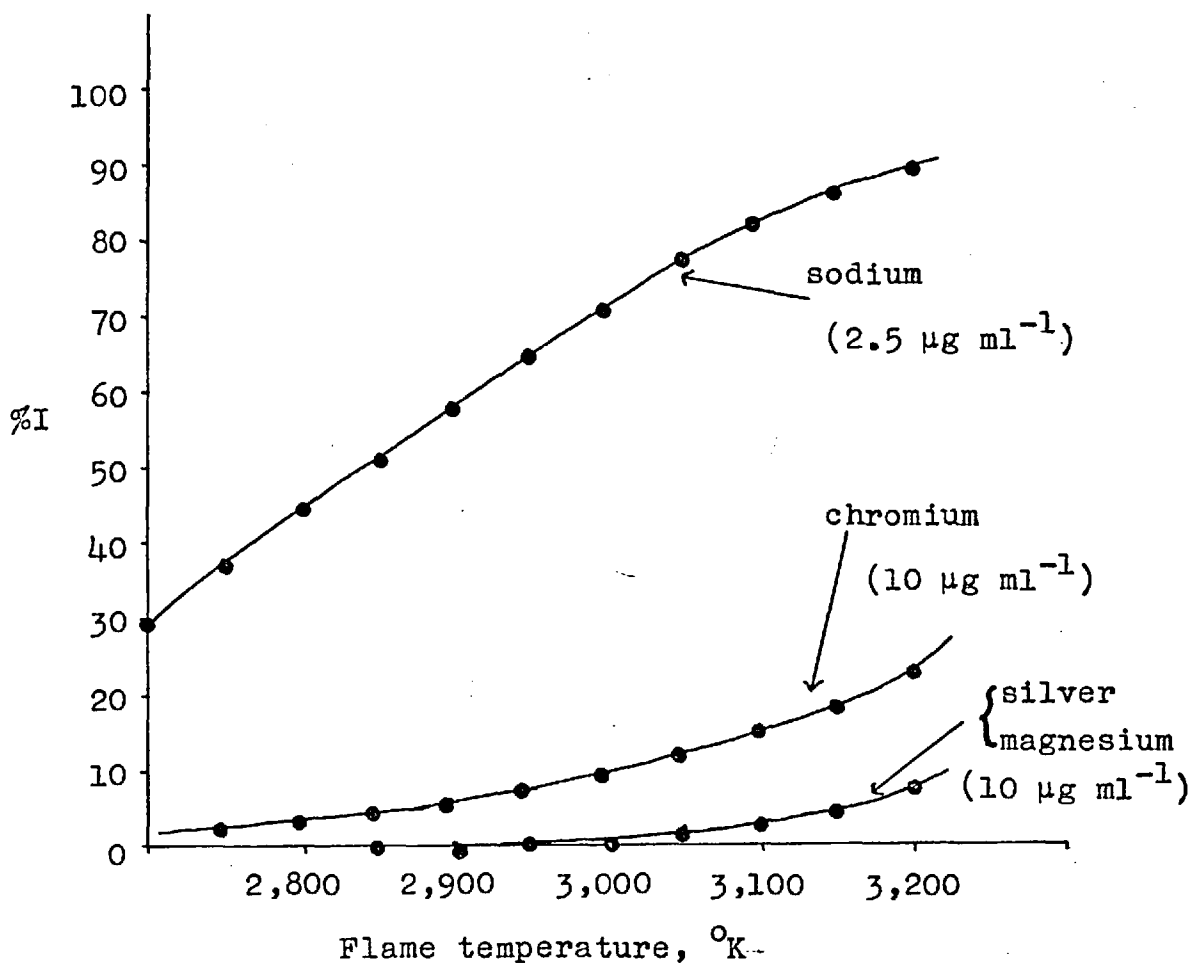
described previously (pp 141). This enabled ionisation contours of an element within the flame to be determined. The contours so obtained were related to flame temperature profiles by assuming a flame electron concentration. This value of the flame electron concentration was experimentally determined by the Atomic-Ionic line intensity ratio method, the theory of which has been outlined previously. Although the natural flame electron concentration would change in different parts of the flame a constant value had to be employed in the calculations. In spite of this approximation it will be seen that the profiles which were obtained are very similar to those which have been determined previously by other workers (101, 102), who have used other methods for the flame temperature determination.

Previously recorded temperature determinations (101, 102) for the nitrous oxide-acetylene flame have suggested that a flame temperature in the region 3,000 to 3,100°K would be expected; the maximum theoretically calculated thermodynamic temperature is 3,228°K (103), but this is rarely achieved practically (102). The sodium-potassium system that was employed previously was unsatisfactory with temperatures of this order because the natural degree of ionisation of the sodium in this flame is so

great that small differences in temperature show only a minimal effect, and the concentration of potassium required to suppress the sodium ionisation to one per cent is impractically high (about $10,000 \mu\text{g ml}^{-1}$).

An element with a greater ionisation potential than sodium was required in order that an appreciable rate of change of ionisation with temperature could be obtained. Most elements with an ionisation potential greater than 5 eV form compounds readily within the flame. However, the free atom fractions of silver, chromium and magnesium are almost unity in the nitrous oxide-acetylene flame (97), and so could be employed. The predicted rate of ionisation for each over the range $3,000$ to $3,200^\circ\text{K}$ is shown in Figure 20. The greatest rate of change was exhibited by chromium (the element with the lowest ionisation potential, 6.76 eV; the ionisation of silver is 7.57 eV, and of magnesium is 7.64 eV), and it was therefore employed for the temperature determinations.

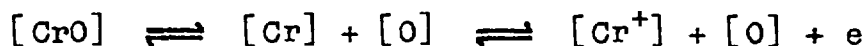
The chromium flame atomic emission which was observed was from the most intense atomic emission line, i.e. 425.4 nm. The emission from the CrO species could only be detected at maximum E.H.T. gain and instrumental slit-width, and with no pin-hole in the



%I: percentage ionisation of the element

Figure 20: Predicted rate of change of ionisation with temperature for various elements, assuming a natural flame electron concentration of $5 \times 10^{10} \text{ cm}^{-3}$.

optical system. The emission from the CrO species did not significantly alter when (a) the flame was made fuel lean or (b) potassium was added to the chromium solution which was employed. The emission could not be detected when the flame became fuel-rich because of the increased flame background emission. The chromium equilibrium system present within the flame may be represented as,



The addition of potassium to the system causes no increase in the CrO emission. This suggests that although the [Cr] concentration has increased, the rate of the reaction $[\text{Cr}] + [\text{O}] \rightarrow [\text{CrO}]$ is sufficiently low that comparatively small changes in [Cr] does not affect the [CrO] concentration in this flame system. This also means that even when the free atom fraction of chromium is not unity any variation in the oxide concentration will be negligible and will not invalidate any calculations.

It was necessary to determine the partial pressure of the natural flame electrons before calculating a flame temperature from an observed degree of ionisation of chromium in the nitrous oxide-acetylene flame. This was obtained by use of the Atomic-Ionic line intensity ratio method. Standard 30 and 0.3 $\mu\text{g ml}^{-1}$ solutions

containing equi-weight portions of calcium, strontium and barium were prepared and aspirated into the unseparated nitrous oxide-acetylene flame. The spectrophotometer was employed in the conventional emission mode, with the monochromator entrance slit viewing the emission 3-13 mm above the primary zone. This region of the flame was selected to give an 'average' value of the flame electron concentration. The wavelength and the excitation energies of the alkaline earth elements' atomic and ionic lines which were observed are shown in Table XXVI; also shown in the table are the detector system response corrections necessary to compare the intensities of the lines. A plot of $\log (I_a/A_a) - \log (I_i/A_i)$ against $(V_i + E_i - E_a)$ was constructed for the flame. This is shown in Figure 21. The three points corresponding to the calcium, strontium and barium energies for the flame formed a straight line, and so it was assumed that thermal equilibrium prevailed within the flame. From the intercept of the plot a value of the total electron concentration within the flame could be calculated. This was employed to assess the free electron concentration present when chromium was aspirated by making some allowance for the contribution from ionisation of the alkaline earth metals. As the

TABLE XXVI

Atomic-Ionic Line Intensity Ratio Method for Flame Electron Concentrations (91)

Transition (nm)	Oscillator Strength	Excitation Energy (cm^{-1})	$(V_1 + E_1 - E_a)$ (cm^{-1})	$\log(A_a/A_1)$
Ca I 422.7	1.55	23,652	51,067	-0.127
Ca II 393.3	0.84	25,414		
Sr I 460.7	1.55	21,698	48,745	-0.151
Sr II 407.7	0.76	24,517		
Ba I 553.5	1.45	18,060	45,925	-0.214
Ba II 455.4	0.66	21,952		

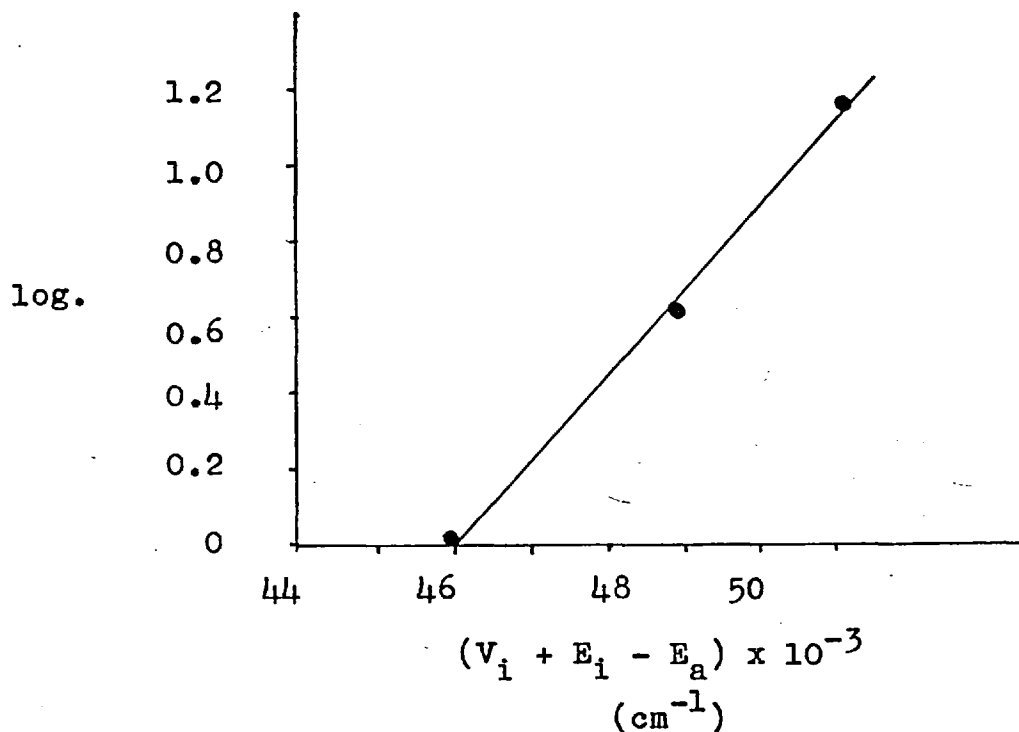
Detector System Response Corrections

Ca I/Ca II Multiply Ca I intensity by 0.632

Sr I/Sr II Multiply Sr I intensity by 0.65

Ba I/Ba II Multiply Ba I intensity by 1.76

overall concentration which was aspirated was small ($0.3 \mu\text{g ml}^{-1}$) the result which was obtained could be assumed to approximate to the natural flame ion concentration. The experimentally determined flame electron concentration was $5 \times 10^{10} \text{ cm}^{-3}$ of which the expected contribution from the alkaline earths in their ionised form was $1 \times 10^{10} \text{ cm}^{-3}$. This variation in the natural flame electron concentration produced minimal



$$\log.: \log (I_a/A_a) - \log (I_i/A_i)$$

Figure 21: Plot of $\log (I_a/A_a) - \log (I_i/A_i)$ against $(V_i + E_i - E_a)$ for the nitrous oxide-acetylene flame (unseparated) supported at the long path burner using a $0.3 \mu\text{g ml}^{-1}$ equi-weight solution of calcium, barium and strontium.

differences in the final flame temperatures.

4.VII.1: Slightly Fuel-Rich Flame Supported at Emission Burner

The ionisation contours, and hence the flame temperature profile of the slightly fuel-rich nitrous oxide-acetylene flame ($6.5 \text{ l minute}^{-1}$ nitrous oxide, $3.9 \text{ l minute}^{-1}$ acetylene, stoichiometry nitrous oxide to acetylene is 1.65:1) which was supported at the round emission burner (described previously pp 37) was investigated initially. The fuel flow-rate was determined by using that flow-rate which gave a conventional non-luminous red feather appearance upon nitrogen separation at a support gas flow-rate of $6.5 \text{ l minute}^{-1}$. When the conventional flame was studied the acetylene flow-rate was not increased.

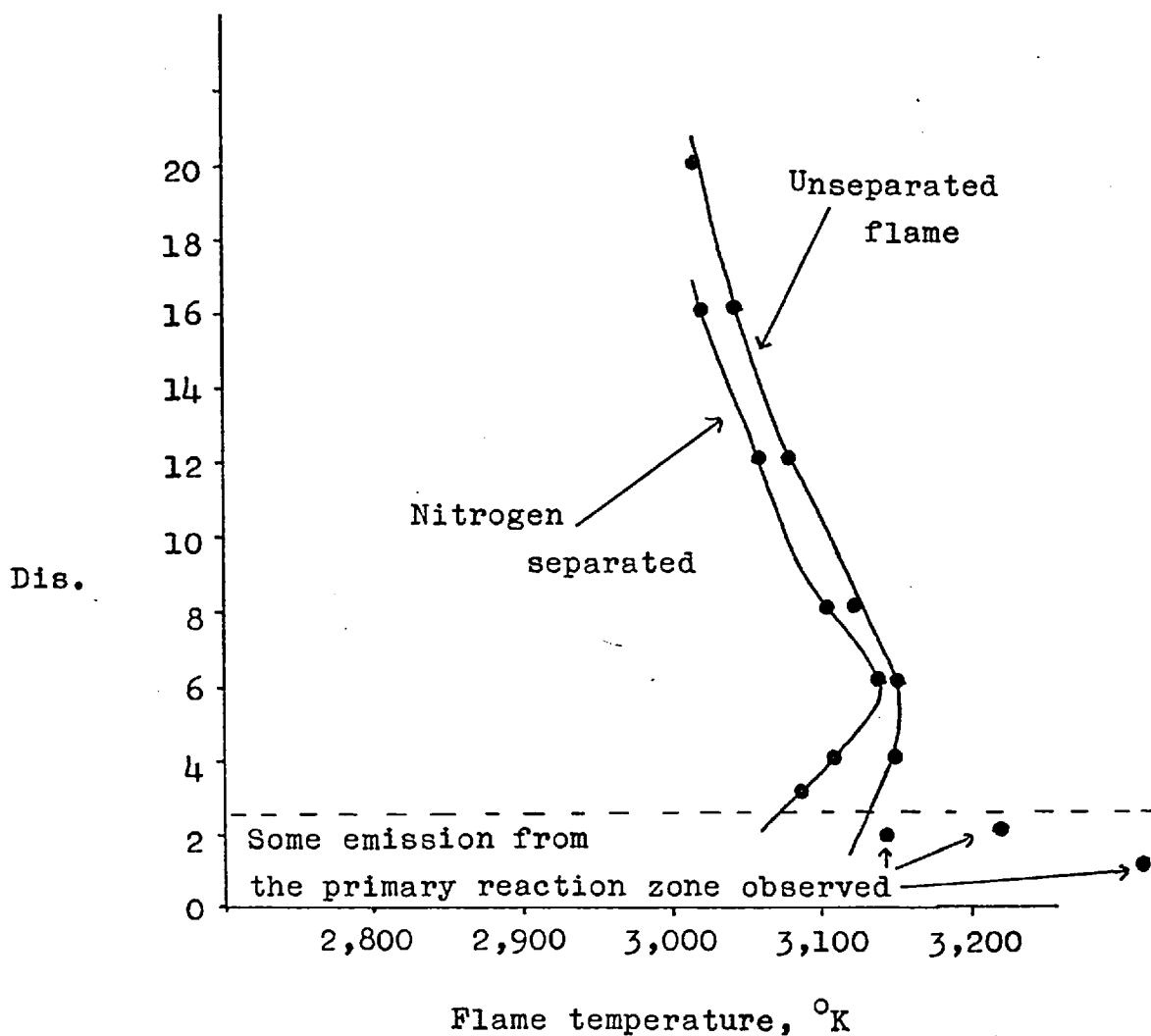
The reference point for the height profile was taken at the maximum continuum emission from the primary zone of the flames. This emission was always very intense at the chromium wavelength employed, and so was distinguished from any conventional chromium atomic emission without difficulty. The chromium atomic emission was optically scanned in two millimetre steps, up to a maximum of 24 mm above the primary zone, by lowering the

burner assembly vertically to the focussed light-path. The maximum chromium emission at any height was always observed, i.e. the emission from the centre of the flame.

The profiles which were obtained for both the conventional and nitrogen separated flames are shown in Figure 22. There were some 'random' percentage ionisation values (and hence flame temperatures) obtained at one and two millimetres above the primary zone. It was possible that the upper region of the primary zone was observed by the monochromator at these heights and that these anomalous flame temperatures (which were not reproducible at these heights) were caused by either some of the intense emission from the primary zone being observed or that thermal equilibrium had not been established within the flame at the very small distances above the primary reaction zone.

4.VII.2: Flames Supported at the Long-Path Burner

A more systematic study was attempted at a long-path (5 mm x 0.457 mm) high-temperature atomic absorption burner. This burner could be water-cooled, and was provided with inert gas separation facilities. It was selected because a similar flame temperature study was being completed at the time of presentation of this



Dis.: height above the primary reaction zone of flame

Figure 22: Height profiles for the slightly fuel-rich (1.65:1) nitrous oxide-acetylene flame supported at the cylindrical emission burner.

thesis with the same burner using the iron two-line method for flame temperature determinations (104) and it was hoped that a comparison of the profiles that were obtained by each method could be made.

The nitrous oxide flow-rate was maintained constant at $6.5 \text{ l minute}^{-1}$ throughout all the determinations. The flame temperatures were studied with three different acetylene flow-rates corresponding to the very fuel-rich (acetylene $4.5 \text{ l minute}^{-1}$, nitrous oxide:acetylene ratio 1.45:1), the slightly fuel-rich (acetylene $3.9 \text{ l minute}^{-1}$, nitrous oxide:acetylene ratio 1.65:1) and the fuel-lean or 'stoichiometric' flame (acetylene $3.25 \text{ l minute}^{-1}$, nitrous oxide:acetylene ratio 2:1). The stoichiometry ratios were obtained by controlling the gas input volumes, and no account of air-entrainment into the flame was considered. The fuel-lean or 'stoichiometric' flame was defined from the reaction,



The fuel-flows were selected to give flames that were (a) luminous and could not be nitrogen separated, (b) a red non-luminous 'feather' upon nitrogen separation and (c) a 'stoichiometric' mixture. The nitrogen separating gas flow-rate was maintained constant at 13 l minute^{-1} and the argon at 15 l minute^{-1} .

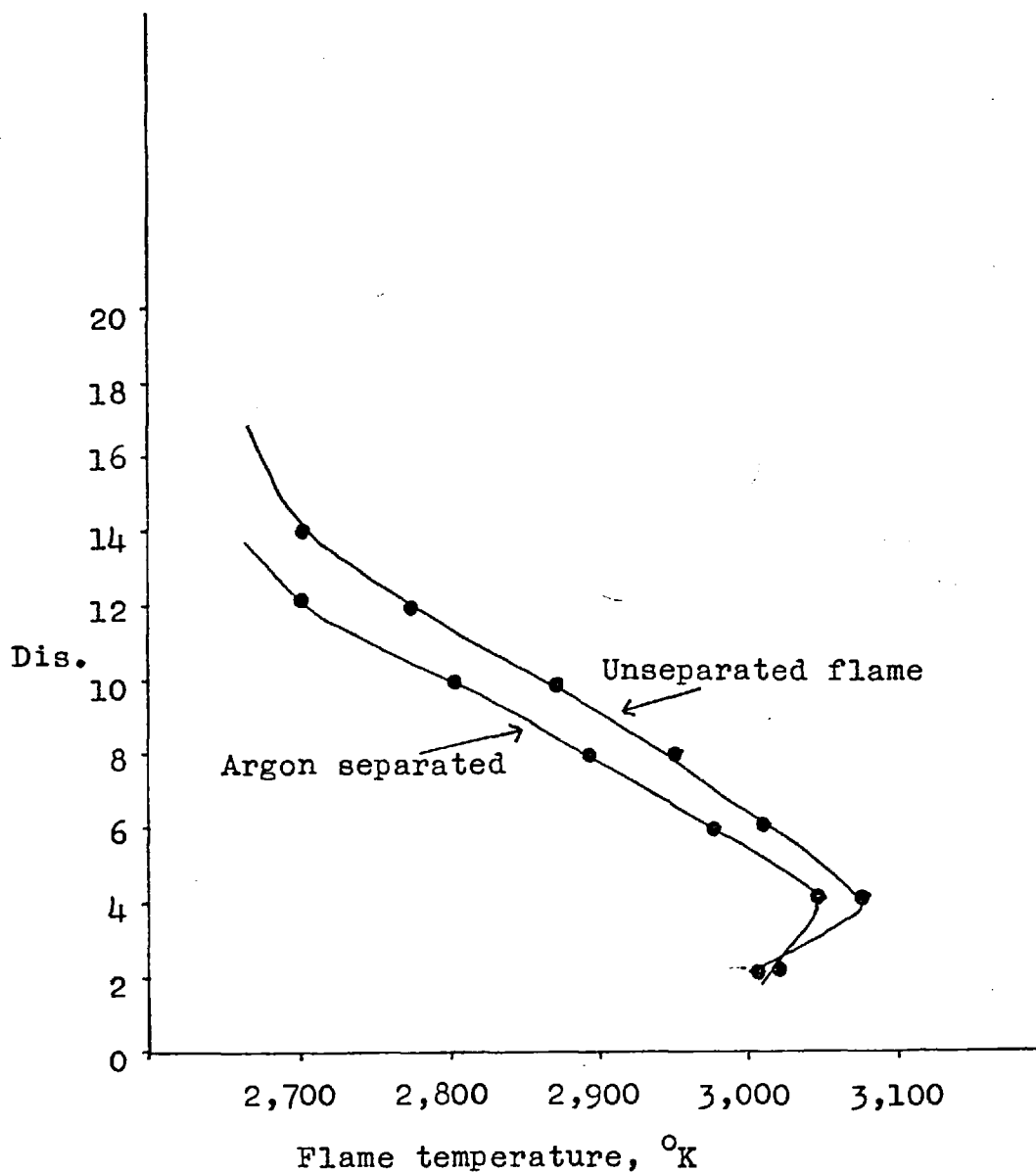
a. Height Profiles

The centre of the long-path flame was focussed onto the pin-hole and monochromator entrance slit, and the maximum chromium emission from the flame was obtained at each height. The height reference point was at the position of maximum emission from the primary reaction zone (as was employed for the studies with the round burner). The height profiles for the separated and unseparated flames at each fuel flow-rate are shown in Figures 23 to 25. Figure 23 refers to the very fuel-rich (1.45:1) flame, Figure 24 to the slightly fuel-rich (1.65:1) flame and Figure 25 to the stoichiometric (2:1) flame.

b. Width Profiles

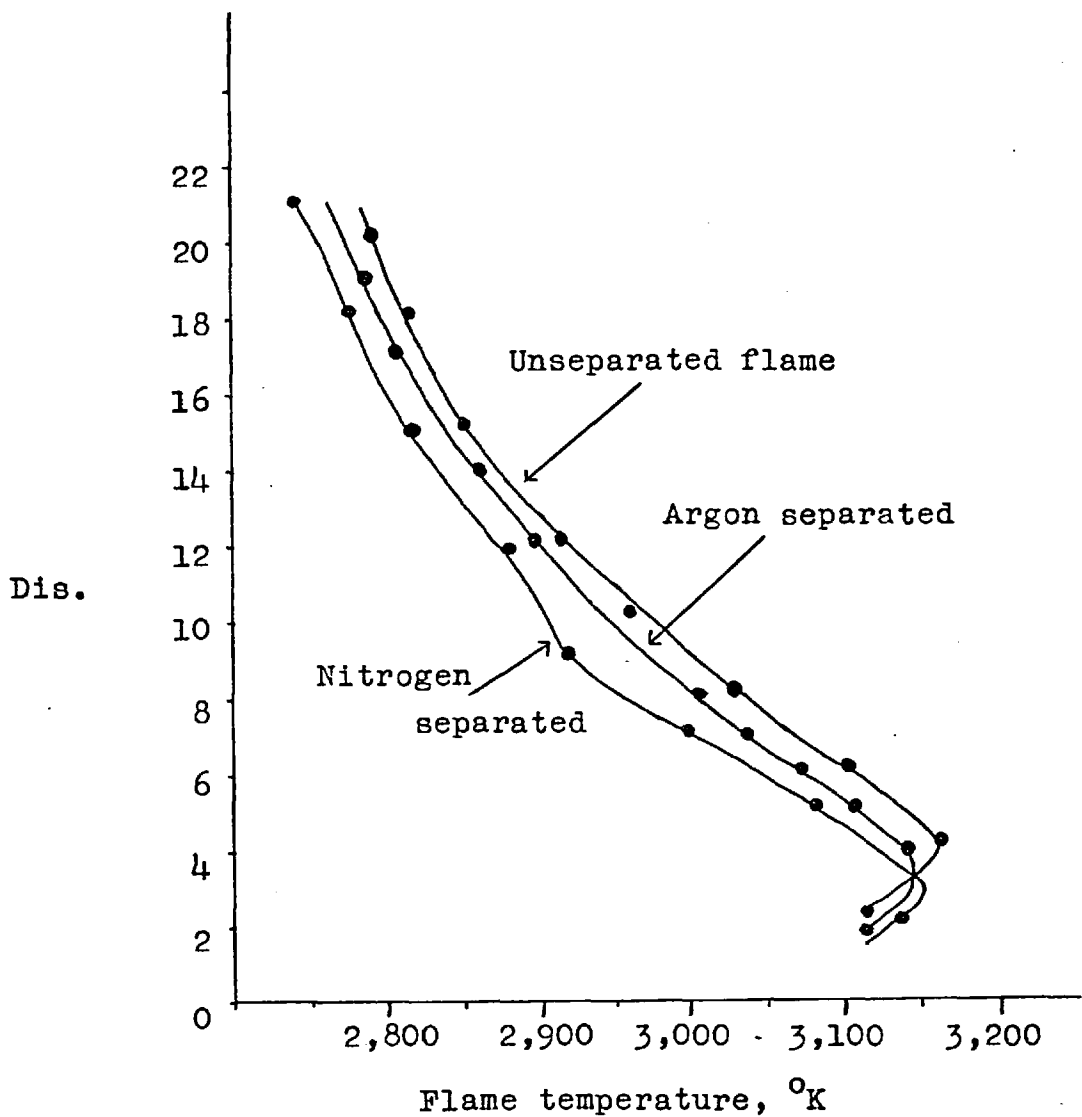
The width profile of a flame could be obtained in a similar manner as that employed to determine the height profiles. The chromium emission was maximised to a particular previously chosen height. This corresponded to the emission from the centre of the flame. The burner assembly was moved horizontally out of the line of focus at 1 mm intervals. An ionisation determination was obtained at each interval.

The plot of the slightly fuel-rich (1.65:1) and



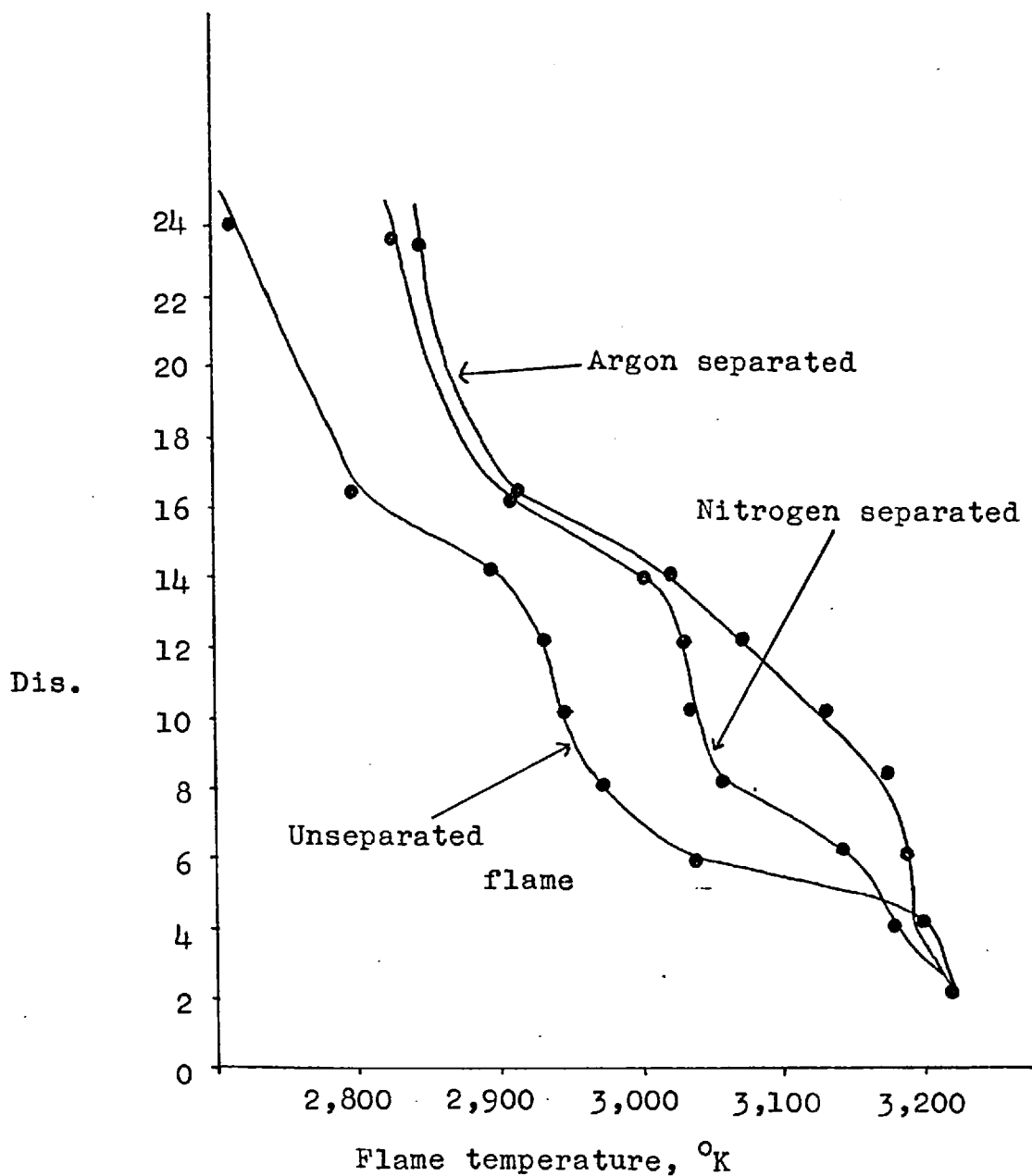
Dis.: height above the primary reaction zone of flame

Figure 23: Height profiles for the fuel-rich (1.45:1) nitrous oxide-acetylene flame supported at the long path burner.



Dis.: height above the primary reaction zone of flame

Figure 24: Height profiles for the slightly fuel-rich (1.65:1) nitrous oxide-acetylene flame supported at the long path burner.



Dis.: height above the primary reaction zone of flame

Figure 25: Height profiles for the 'stoichiometric' (2.00:1) nitrous oxide-acetylene flame supported at the long path burner.

stoichiometric (2.0:1) flames at a height of 10 mm above the primary zone is shown in Figure 26 for the conventional, the nitrogen and the argon separated flames. The precision of each value is considerably less than that obtained with the height profiles as the emission intensity from the chromium was reduced and the background flame emission showed more variations because it was more susceptible to extraneous draughts.

4.VIII: Conclusion

The air-acetylene and nitrous oxide-acetylene ionisation profiles have been examined in some detail. From the ionisation contours flame temperature profiles have been calculated by determining a natural flame electron (or ion) concentration. This concentration could not be accurately determined in these studies and an 'average' value for all parts of the flame has been employed. However, the profiles that were obtained are very similar, with one exception, to those which have been previously reported in the literature (101, 102) and this suggests that this method is useful in giving profiles of temperature variation in flames, if not their absolute values.

The previously reported values of the air-acetylene

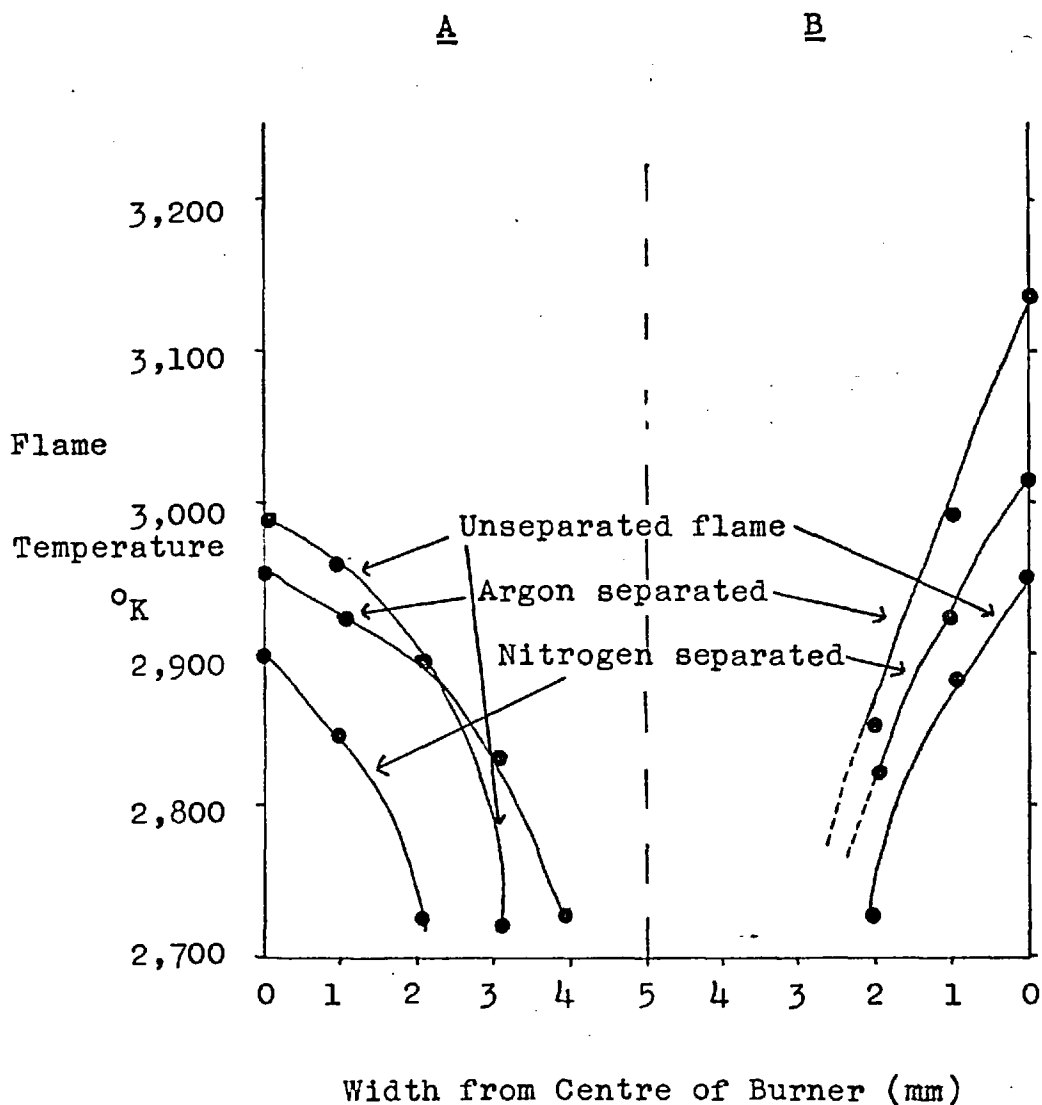


Figure 26: Width profiles at 10 mm above the primary zone for A: 1.65:1 and B: 2.00:1 stoichiometry nitrous oxide-acetylene flames supported at the long path burner.

flame temperature are $2,398^{\circ}\text{K}$ (19) and $2,598^{\circ}\text{K}$ (9).

The value which has been obtained by the ionisation method employed in these studies was $2,540^{\circ}\text{K}$. This was substantially higher than the other determinations, and approaches the theoretically calculated maximum thermodynamic value ($2,598^{\circ}\text{K}$ (9)).

A similar pattern was repeated in the nitrous oxide-acetylene flame determinations. Previously reported temperature determinations are (at an adjusted height of 10 mm above the primary zone),

<u>Method</u>	<u>Stoichiometry</u>	<u>Temp.</u>	<u>Reference</u>
Line reversal	1.60:1	$2,860^{\circ}\text{K}$	102
"	2.98:1	$2,970^{\circ}\text{K}$	102
"	4.96:1	$2,870^{\circ}\text{K}$	102
Iron 2-line	2.15:1	$2,850^{\circ}\text{K}$	101
"	1.87:1	$2,830^{\circ}\text{K}$	101
"	1.51:1 (12 mm)	$2,855^{\circ}\text{K}$	101
Ionisation	1.45:1	$2,870^{\circ}\text{K}$	Text
"	1.65:1	$2,990^{\circ}\text{K}$	"
"	2.00:1	$3,040^{\circ}\text{K}$	"

All flames are unseparated.

The effective ionisation temperatures are about 150°K greater than the highest reported effective electronic

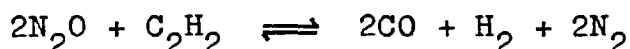
temperatures. The temperature that was obtained was very dependent upon the natural flame electron concentration and the difficulty in determining this quantity (and the accuracy of the determination) relates to the final accuracy of the temperature determinations. The quantitative values of the flame temperatures must, therefore be regarded with some reservations. However, the method does give the temperature gradients within the flame with accuracy because the variation of ionisation could easily be obtained. The percentage ionisation at any height was found to be reproducible over long time intervals. The precision of the technique (pp 140) indicates a temperature variation of $\pm 20^{\circ}\text{K}$ about any mean value.

Both height and width profiles were obtained for the nitrous oxide-acetylene flames. It was found that because the precision of individual readings in the width profiles was low only a brief study at one height was undertaken. The results of this study (Figure 26) were treated with some reservation because of the lack of precision. However, it is felt that if the flame were to be effectively shielded satisfactory width profiles would be obtained. Improvements in the shielding of the flame from draughts would also improve the precision of the height profiles.

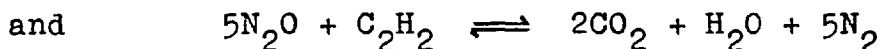
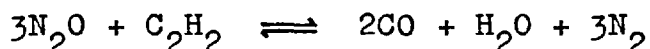
The nitrous oxide-acetylene flame temperature profiles for the fuel-rich flame exhibit a maximum temperature corresponding to the top of the red interconal zone, which then progressively falls with height. This pattern was not repeated by the stoichiometric flame (Figure 25), in which the red zone was not formed. The profiles of the flame supported at the round emission burner maintained higher temperatures at the same height compared to the long-path burner. The maximum temperature occurred at 8 mm above the primary zone, while for the long-path burner it occurred at 4 mm above the primary zone. The measured heights of the red zones were (a) about 8 mm for the long-path burner (unseparated flame) and (b) about 20 mm for the emission burner (unseparated flame). The different height profiles obtained for the two burners were as expected as the red interconal zone was much larger for the emission burner.

Ionisation measurements can only be made in those areas of the flame in which measurable ionisation takes place. The percentage ionisation of an element decreases with increasing height in the flame and it was not possible to make measurements above about 22 mm in the nitrous oxide-acetylene flame; at this height no ionisation of the chromium is observed.

From free energy considerations the maximum theoretical temperature of the nitrous oxide-acetylene flame is obtained with a stoichiometric 2:1 support to fuel-gas ratio. This corresponds to the reaction



The temperature decreases as the fuel flow-rate is increased or decreased. Fassel and co-workers (102) have investigated the temperature of the nitrous oxide-acetylene flame at the stoichiometries 1.60:1, 2.98:1 and 4.96:1. The latter two correspond to the reactions



It would be expected that the temperature of a flame decreases upon separation by an inert gas. The degree of cooling is proportional to the thermal capacity of the separating gas, and so is less for monatomic argon than diatomic nitrogen. This effect was exhibited by the slightly fuel-rich flame (Figure 24) where the greatest temperature at any height was observed when the unseparated flame was employed and the lowest temperature when the flame was nitrogen separated. A similar pattern was shown by the very fuel-rich flame (Figure 23) in which the argon separated flame temperatures at any height

were lower than the unseparated flame temperatures. However, the pattern was not repeated with the (2:1) stoichiometric flame, where the temperature appeared to increase upon separation of the flame. It was decided that at the 2:1 stoichiometry there were two factors to consider, (a) the cooling effect described above and (b) air-entrainment into the flame. The stoichiometry of the flame was determined from the input gas volumes with no consideration of air-entrainment into the flame. The stoichiometry of the flame would, taking account of air-entrainment, be greater than that determined from the gas input volumes. When a fuel-rich flame was employed separation effectively increased the fuel-flow to the flame by decreasing the air-entrainment, but only brought the support to fuel-gas ratios to those expected. This separation would, for the fuel-rich flames (a) lower the temperature by increasing the effective fuel-flow and (b) lower the temperature from the cooling effect. However, for the 2:1 stoichiometry flame separation would (a) lower the temperature from the cooling effect, but (b) raise the temperature by bringing the stoichiometry to the maximum value expected. Because the temperature was increased upon separation it was assumed that effect (b) was more important than

effect (a). The difference between the separated and unseparated flames increased with height (Figure 25) because air-entrainment would become greater further from the primary reaction zone.

The spectrophotometer receives the emission from the centre of the flame as a result of the optical pin-hole system employed. It would therefore be expected that the emission observed would not be affected by the cooling of the flame, and so the effect of air-entrainment would predominate.

The maximum absolute temperature was obtained with the separated 'stoichiometric' flame and a decreasing temperature was observed as the fuel-flow was increased. The maximum temperature, about $3,200^{\circ}\text{K}$, was observed just above the primary reaction zone of the 'stoichiometric' flame. This very high value may have a contribution from the primary reaction zone emission because of insufficient resolution of the optical system. An 'f-value' of at least 5 is required to obtain good spacial resolution with sharp focus of the flame when an optical system such as that employed in these studies is used. The 'f-value' of the standard Techtron lens, when employed at full aperture within the experimental arrangement described previously

(pp 140), is 4.5. It was hoped that this would prove sufficient if the maximum aperture were employed when low intensity emission was being observed. The maximum temperatures of the slightly fuel-rich flames supported at both burners were comparable at about $3,150^{\circ}\text{K}$. The maximum temperature for the very fuel-rich flame was found to be about $3,075^{\circ}\text{K}$, which is very much higher than that observed previously. However, all the temperatures from each flame have been in their expected order, even though the absolute values are much higher than have been previously reported. This suggests that the method for flame temperature determinations presented in this thesis gives good relative temperature values in different parts of the flame. The absolute values determined by this method are generally too high because of the difficulty in determining the flame electron concentration accurately and because the percentage ionisation values experimentally found appear to be systematically high. This probably results from complete ionisation equilibrium conditions not prevailing within the flames.

CHAPTER 5. CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

The conclusions for the work which has been presented in this thesis have been written at the end of the relevant chapters. However, general comments may be made about the work in the form of suggestions for possible future extensions of the studies.

Several interesting observations may be made and conclusions drawn from the determination of the refractory elements. The relative sensitivities of the spectroscopic techniques are proportional to the wavelengths of the principal resonance lines employed, as has been theoretically predicted (1, 2). Where two elements are in the same Group of the Periodic Table (silicon and germanium in Group IVb, titanium and zirconium in Group IVa) their atomic fluorescence characteristics are very similar, i.e. silicon and germanium both gave very sensitive atomic fluorescence determinations, each superior to either their respective atomic emission or atomic absorption determinations, but titanium and zirconium both gave no appreciable fluorescence. It is suggested that it would be interesting to extend the comparisons further and to compare the hafnium determination with titanium and zirconium. It would be

hoped that this would give a similar pattern by also exhibiting no fluorescence radiation.

The most interesting observation which may be seen in the atomic fluorescence studies is the susceptibility of some elements to interference from diverse ions. The element which suffered most in this respect was molybdenum, where most of the diverse ions exhibited some interference in the element's determination. There was no diverse ion which exhibited an interference in the molybdenum atomic fluorescence determination without exhibiting an interference in the flame atomic emission determination. If a solution of the diverse ion alone was aspirated into the flame and a positive emission signal was obtained it was assumed that a spectral contribution to the atomic emission interference was present. There were no spectral interferences in the atomic fluorescence studies, and the presence of scatter was experimentally discounted (pp 104). A list of the ions which caused chemical or physical interferences in the molybdenum atomic fluorescence determination and also caused a chemical or physical contribution to the atomic emission interferences could be obtained. It was found that the average enhancement to the atomic fluorescence signal was about 27 per cent and to the atomic emission

signal about 54 per cent. All the elements which clearly exhibited non-spectral interferences gave enhancements very similar to the above averages. This suggested that a range of (cationic) diverse ions would cause interference in the flame spectroscopic determination of molybdenum, and that the extent of the interferences would be very similar. Previous to these studies there has been discussion in the literature on the interferences in the determination of molybdenum by atomic absorption spectroscopy (64-66), as well as the suggested use of ammonium or aluminium chloride to suppress the observed enhancements. When a suppressing agent was added in the determination of molybdenum by atomic fluorescence no suppression was observed. It is therefore suggested that a thorough study should be undertaken of the complete mechanism and causes of non-spectral interferences in the determination of molybdenum by atomic spectroscopy. If a satisfactory suppressing agent for the interferences were to be obtained, effective practical analysis of molybdenum by atomic fluorescence would become a possibility.

It was found that there were many non-spectral interferences in the determination of vanadium and aluminium by atomic emission, but that the magnitude of the enhancement which was observed was much less than that

observed in the case of molybdenum. It is suggested that any study on interferences should also include these two metals in order to determine if similar phenomena occur.

The determination of flame temperature profiles could be further investigated by (a) extending the range of flames to be studied and (b) improving the technique. The flames which are of interest to the flame spectroscopist are worthy of future study. All should be able to be determined by this ionisation method provided that they have a sufficiently high temperature to excite the principal atomic lines of the element which is selected as suitable for the temperature range to be investigated.

The two most useful improvements to the technique would be (a) complete shielding of the flame to be investigated from extraneous draughts and (b) determination of the flame electron concentration with accuracy. Belcher and Sugden (89, 90) have determined the flame electron concentration from the observed attenuation of microwaves and have, from this, determined the temperature of some cool flames. This method could be further modified and extended to include the analytically useful flames. An absolute flame temperature could be

determined by this means as could definite evidence of the establishment, or not, of thermal equilibrium within the flame.

It is hoped that, with further understanding of the reactions of atomic populations in relation to their environment within flames, flame atomic spectroscopy may be developed and extended, and that the three techniques will be seen to be complementary to each other in the analysis of most routine analytical problems.

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