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THE DETERMINATION OF TRACE CONSTITUENTS IN
REFRACTORY METALS BY ATOMIC ABSORPTION SPECTROSCOPY.

By

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ABSTRACT.

Atomic absorption spectroscopy has been applied to the determination of traces of copper and molybdenum in refractory matrices. Copper is extracted into ethyl acetate at pH 4.5 as its 8-hydroxyquinolate, before aspirating into air-propane or air-acetylene flames for absorption measurements.

Molybdenum is extracted as its 8-hydroxyquinolate into n-butanol at pH 4.5. Absorbance measurements are made within the red 'feather' region of the nitrous oxide-acetylene flame. Interferences from other ions is prevented by the addition of E.D.T.A.

The causes of the effectiveness of the nitrous oxide-acetylene flame for the determination of refractory elements is investigated, and a mechanism is postulated for the production and protection of ground state metal atoms by the CN and NH species present in large quantities in the red 'feather' region of the flame.

Temperature profiles for the nitrous oxide - acetylene flame under different fuel : support gas ratios have been obtained.

An investigation into the analytical utility of other premixed gas flames is described, and their properties for atomic absorption spectroscopy compared with more usual flames.

In the final chapter some suggestions for increasing the sensitivity and extending the scope of the method are made.

ACKNOWLEDGEMENTS.

The work described in this thesis is entirely original except where due reference is made. No part of this work has been submitted previously for any other degree. The work was performed in the Analytical Chemistry Department of Imperial College between October 1964 and July 1967.

I wish to thank my supervisors Professor T.S.West and Dr.G.F.Kirkbright, for their invaluable help and guidance throughout this project, and to my colleagues for helpful discussions.

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INTRODUCTION.

In the nineteenth century Kirchhoff ⁽¹⁾ and Bunsen ⁽²⁾ clearly demonstrated the great power of atomic emission spectroscopy and its scope as an investigative tool in chemistry and physics. Several elements (e.g. indium, caesium, rubidium and gallium) were discovered by observation of their atomic emission spectra, and qualitative and semi-quantitative spectrography rapidly evolved as a useful tool in chemical analysis. During the past half-century many improvements in monochromator and photo-electric detectors have been made to exploit the potentially high sensitivity and selectivity of emission spectroscopy in inorganic analysis. These developments have resulted in the emergence of direct reading instruments whose general utility for inorganic analysis cannot be challenged by any other technique.

In 1800, **Fraunhofer** ⁽³⁾ observed dark absorption lines in the spectrum of the sun, and Bunsen ⁽²⁾ and Kirchhoff ⁽¹⁾ demonstrated that the positions of these dark lines corresponded with those in the emission spectra of certain elements. Observation of such line spectra, produced by the discretely quantised absorption by atoms of radiation from a continuum background source, thus has permitted the chemical analysis of stellar atmospheres. With the exception of its utilisation in astro-physics,

however, atomic absorption spectroscopy found little application in inorganic analysis in the laboratory until 1955.

Workers (4,5) researching into the physical aspects of atomic structure use the technique appreciably, but apart from isolated applications, e.g. the determination of mercury vapour (6) in laboratory atmospheres, it was unknown as an analytical method of importance. The principal experimental difficulty which delayed the application of the technique to inorganic analysis was the unsuitable nature of most available background sources. When a continuum source is employed the integrated absorption over a finite bandwidth must be measured. Measurement of the absorption line profile is experimentally difficult, and imprecise. In 1953 Walsh (7) proposed that the absorption coefficient be measured at the wavelength of maximum absorption by the use of a stable sharp-line background source of high intensity. He proposed the use of hollow cathode lamps which emit sharp-line spectra of the element of the cathode and permit absorption measurements to be made accurately. It was the introduction of these intense and stable sources which enabled the potential of atomic absorption spectroscopy in inorganic analytical chemistry to be realised. Walsh devised a simple flame spectrophotometer which could be applied to the analysis of solutions of a wide range of elements by this absorption technique.

The first publications on atomic absorption spectroscopy appeared in 1955, when Walsh ⁽⁷⁾, Alkemade and Milatz ⁽⁸⁾ independently applied the technique to chemical analysis. The first monograph on this subject was written by W.T.Elwell and J.A.F.Gidley ⁽⁹⁾ and was published in 1961, this book is now in its second edition. During the past decade atomic absorption spectroscopy has been applied to an increasingly wide variety of problems, and the advantages of this method over emission methods shown emphatically for many elements. Three of its principal advantages are, that the sensitivity of the technique for flame sources is independent of the excitation potential of the transition involved, that the sensitivity is less subject to interference from temperature variation and extraneous radiation or inter-element effects.

Thermal Emission Spectroscopy.

In emission spectroscopy methods the sample for analysis is atomised and excited. The emitted radiation is then dispersed and the intensities of the selected atomic lines measured. If self-absorption and induced emission are neglected, the integrated intensity of emission of a line is given by,

$$\int I_{\nu} d\nu = C N_j f \quad (1)$$

where N_j = The number of atoms in the excited state involved in the transition responsible for the line.

f = The oscillator strength - a measure of the average number of electrons/atom capable of transition.

C = A constant depending 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,

$$N_j = N_0 \frac{P_j}{P_0} e^{-E_j/KT} \quad (2)$$

N_0 = Number of atoms in the ground state.

K = Boltzmann Constant.

P_j and P_0 = The statistical weights for the excited and ground states respectively (For the atom $P = 2J + 1$ where J is the quantum no. for total angular momentum of the electron for the ground state).

From equations (1) and (2) it is evident that the number of atoms in the excited state and hence 'I' the emission intensity, depends on T and E_j (which for resonance lines is inversely proportional to the wavelength).

Emission of high intensity requires a high temperature and low excitation potential. Examples of the variation of N_j/N_0 with T and E for several elements are given in Table 1. Even for the alkali metals with low excitation potentials the number of atoms in the first excited state is small compared with the number in the ground state. Generally

N_0 is $10^4 - 10^{16}$ times greater than N_j . N_0 is virtually constant over a wide range of temperatures, whereas N_j varies exponentially with temperature.

TABLE 1.

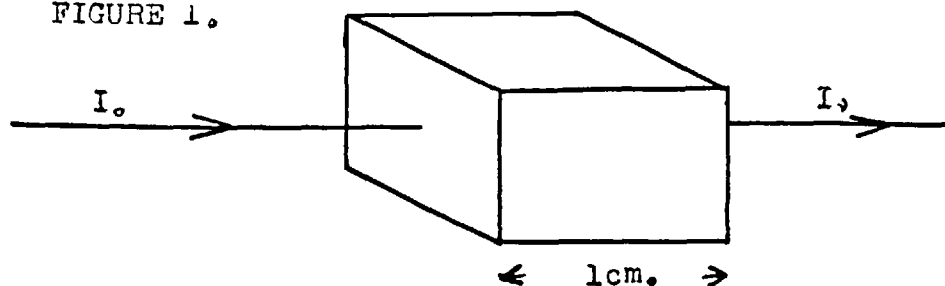
Resonance Line (Å)	Transition	P_j/P_0	N_j/N_0			
			T=2000°K	T=3000°K	T=4000°K	T=5000°K
Cs 8521	$2S_{1/2} - 2P_{3/2}$	2	4.44×10^{-4}	7.24×10^{-3}	2.98×10^{-2}	6.82×10^{-2}
Na 5890	$2S_{1/2} - 2P_{3/2}$	2	9.86×10^{-6}	5.88×10^{-4}	4.44×10^{-3}	1.51×10^{-2}
Ca 4227	$1S_0 - 1P_1$	3	1.21×10^{-7}	3.69×10^{-5}	6.03×10^{-4}	3.33×10^{-3}
Zn 2139	$1S_0 - 1P_1$	3	7.29×10^{-15}	5.58×10^{-10}	1.48×10^{-7}	4.32×10^{-6}

(after Elwell and Gidley).

Atomic Absorption Spectroscopy.

Consider a parallel beam of radiation of intensity ' I_0 ' and frequency ' ν ' incident on an atomic gas or vapour of thickness 1 cm.

FIGURE 1.



Then if I_ν is the intensity of the transmitted radiation, the absorption coefficient K of the vapour at frequency ' ν ' is defined by

$$I_\nu = I_0 e^{-K.l} \quad (3)$$

According to classical dispersion theory the relationship between integrated absorption and concentration is given by,

$$\int K.d\nu = \frac{\pi e^2}{mc} \cdot N_\nu \cdot f \quad (4)$$

where,

e = electronic charge

m = electronic mass

c = velocity of light

N_ν = number of atoms/cm³ capable of absorption in the range $\nu + d\nu$ to ν .

Equation (4) assumes a refractive index of 1 over the breadth of the absorption line and is not applicable to strong absorption lines.

For a resonance line due to a transition from a ground state which is well separated from the lowest excited state, N_ν can be considered equal to N , the total number of atoms/cm³. If, however, the transition does not originate in the ground state, then the number of atoms capable of absorbing is given by,

$$N_\nu = N \cdot \frac{P_i e^{-E_i/KT}}{\sum_j P_j e^{-E_j/KT}} \quad (5)$$

where 'i' denotes the initial state involved in the

transition, and the summation in the denominator extends over all possible energy states. In practice the summation can be restricted to the low lying levels.

Putting equation (4) in terms of transition probabilities we obtain,

$$\int K d\nu = \frac{\lambda^2 P_j}{8\pi P_i} \cdot N_\nu A_{ji} \left[1 - \frac{P_i N_j}{P_j N_i} \right] \quad (6)$$

where λ is the wavelength at the centre of the absorption line,

P_i and P_j are the statistical weights,

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

In the general case where $N_\nu \gg N_j$ eq. (6) reduces to the well known equation,

$$\int K d\nu = \frac{\lambda^2 P_j}{8\pi P_i} \cdot N_\nu A_{ji} \quad (7)$$

N_ν is generally given by equation (5) but for resonance lines is equal to N . Similarly if the transition from the j^{th} to i^{th} state is the only one which can occur (as is the case for resonance lines) $A_{ji} = 1/\tau$, where ' τ ' is the average lifetime of an atom in the excited state ' j '.

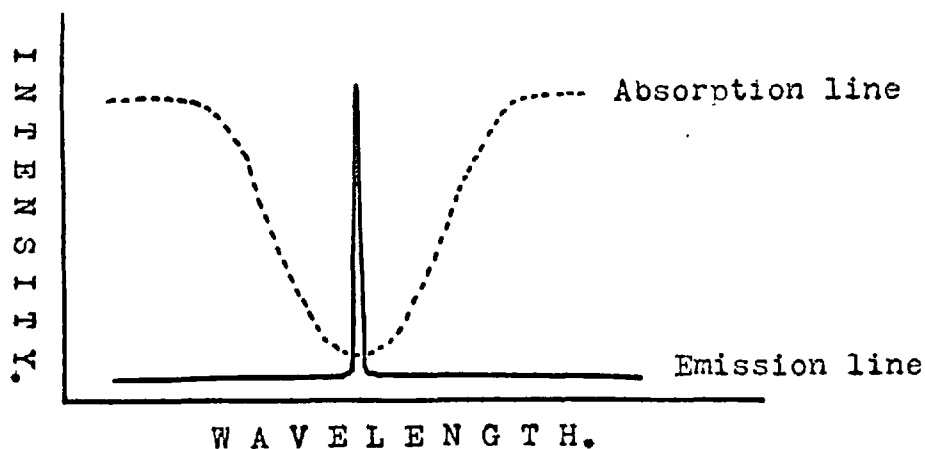
The most difficult problem lies in the measurement of the integrated absorption. In flames at temperatures between 2,000°K and 3,500°K the width of the absorption line is of the order of 0.02 Å. The width of an absorption

line depends on

- (1) the natural line width - due to the finite time an atom is in the excited state;
- (2) Doppler broadening - due to the thermal motions of the atoms;
- (3) Lorentz broadening - due to collisions with foreign gases;
- (4) Holtzmark broadening - due to collisions with atoms of the same kind;
- (5) Stark broadening - due to electric fields, either internal (ions or electrons) or external.

The natural width of the line, ca. 10^{-4} Å may be neglected in relation to other factors, of these Doppler, Lorentz and Holtzmark broadening contribute significantly to the line width at low partial pressures of an element in ordinary flames or furnaces, Doppler broadening probably predominates.

To measure the profile of an absorption line accurately, and thereby obtain the integrated absorption, it is necessary to use an instrument with resolution of 500,000, which is beyond the capabilities of most spectrographs. However, the method of measurement suggested by Walsh⁽⁷⁾ is simple and effective and eliminates the need for a high resolution instrument. By using a sharp-line source which emits lines with a much smaller half-width than the absorption line, the absorption coefficient at the centre of the line can be measured.



Doppler broadening produces an absorption line width of the order of $0.01 \text{ \AA}$ at $2,000^\circ\text{K}$ and is given by the expression,

$$D_\lambda = 1.67 \frac{\lambda}{c} \sqrt{\frac{2RT}{M}} \quad (8)$$

λ = wavelength, R = Gas constant, M = atomic weight.

TABLE 2.

Values of Doppler widths at various temperatures.

Element	λ	M	D_λ		
			$1,000^\circ\text{K}$	$2,000^\circ\text{K}$	3000°K
Na	5890	22.3	0.028 A	0.039 A	0.048 A
Cu	3247	63.6	0.0092A	0.013 A	0.016 A
Zn	2139	65.4	0.0060A	0.0085A	0.010 A

The same factors as well as self-absorption govern the width of the emission line from the source and the absorption line in the flame. For maximum sensitivity the emission source must be operated at as low a temperature as possible, and the path-length of light through non-emitting

regions of the source must be minimised as this is where self-absorption can occur.

If the half-width of the emission line is negligible compared with that of the absorption line, and if the shape of the latter is determined solely by Doppler broadening, the relationship between $K_{\max}$ (absorption coefficient) and concentration is,

$$K_{\max} = \frac{2 \lambda^2}{D_{\lambda}} \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\pi e^2}{m c^2} \cdot N f \quad (9)$$

From equation (8) $D_{\lambda} \propto T^{\frac{1}{2}}$ and this shows that the absorption coefficient is independent of quite large fluctuations in temperature. Equation (9) implies a linear relationship between $K_{\max}$ and N . This in practice occurs only at low atomic concentration. At high concentration the other broadening factors compete seriously with Doppler broadening for control of the width of the absorption line.

Since the most convenient method of atomisation is a flame, pressure broadening will be caused by the presence of gases other than the atomic vapour. This is a constant factor and is independent of sample concentration, and therefore causes a constant lowering of $K_{\max}$. The linearity between the absorption coefficient and concentration is maintained but the sensitivity is reduced. When the sample concentration is increased, the increase

in the partial pressure of the atomic vapour causes resonance broadening which results in the lowering of the absorbance. This is not a linear function of the atomic vapour concentration and hence destroys the linearity between $K_{\max}$ and N , and the growth curve of absorbance for the element concerned bends towards the concentration axis.

It is necessary to know whether suitable absorption lines lie in the regions of the spectrum which are amenable to measurement. In terms of sensitivity it is obviously desirable to use the strongest resonance lines, and in general these will correspond to the strongest emission lines (10). All elements have their most sensitive lines in the region 2,000 - 9,000 Å, therefore the lines of all the common elements lie in a region of the spectrum where measurement is easily made.

The oscillator strengths of certain elements have been calculated and are listed in Table 3. Theoretical calculation is possible for atoms having simple electronic structures, but this has not been carried out yet for the heavy atoms having complex structures. For those elements with known oscillator strengths the atomic concentration can be determined from the integrated absorption coefficient using equation (4).

TABLE 3.

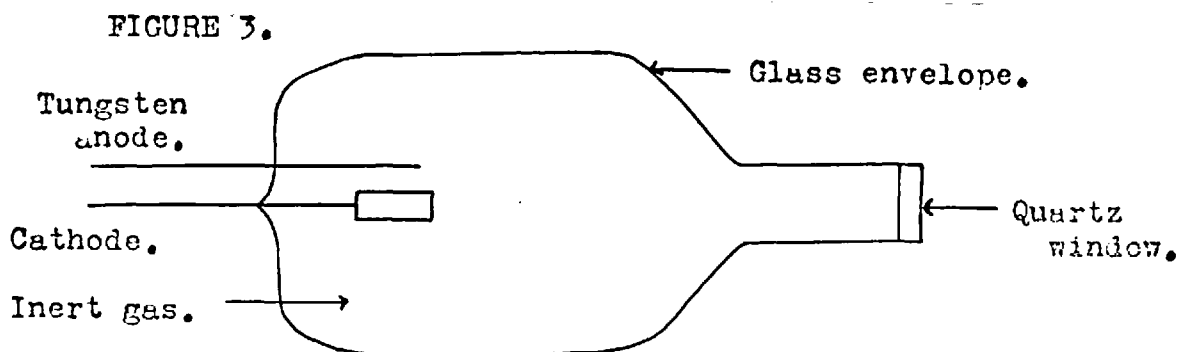
Resonance Line $\text{\AA}$		Transition	Oscillator Strength (f)
Li	6708	$2s_{1/2} - 2p_{3/2}$	0.50
Na	5890	$2s_{1/2} - 2p_{3/2}$	0.70
K	7665	$2s_{1/2} - 2p_{3/2}$	0.64
Cu	3247	$2s_{1/2} - 2p_{3/2}$	0.62
Cs	8521	$2s_{1/2} - 2p_{3/2}$	0.66
Be	2349	$1s_0 - 1p_1$	1.82 *
Mg	2852	$1s_0 - 1p_1$	1.74 *
Ca	4227	$1s_0 - 1p_1$	2.28 *
Cd	2288	$1s_0 - 1p_1$	1.20
Ba	5535	$1s_0 - 1p_1$	2.10
Hg	1849	$1s_0 - 1p_1$	1.19
Tl	2769	$2p_{1/2} - 2d_{3/2}$	0.20
Cr	4254	$7s_3 - 7p_4^0$	0.084
Ni	3415	$3d_3 - 3f_4^0$	0.02
Fe	3720	$5d_4 - 5f_5$	0.013

* Uncorrected values, for method of correction see Trefftz (11).

If a sharp-line source is used it is no longer necessary to use a spectral band width of the same order as the half width of the absorption line. The requirement now is solely the ability to separate and isolate a

selected line from other lines emitted by the source. Thus spectrometers having the same resolution as those used for conventional emission methods are adequate, and in some cases it is possible to use filters.

There are various forms of sharp-line background sources but the most common source is a hollow cathode lamp ^{12,13)}. These were used in all the studies undertaken by the author and found to be very suitable.



The necessity for the emission line to be narrower than the absorption line and for a narrow line source free from self-reversal eliminates the use of conventional sources such as arcs and flames. Fortunately the hollow cathode lamps fulfil most of the requirements.

These lamps comprise a gas discharge tube in which the cathode is a hollow cylinder open at one or both ends, the exact shape being unimportant. The gas pressure

in the tube is adjusted so that the "negative glow" at the cathode is confined almost entirely to the interior of the cathode. Under these conditions the potential gradient is found to be a maximum near the cathode surface, indeed almost all the potential applied to the tube is found across a distance of about 1 mm from the cathode. Positive ions from the filler gas are accelerated through this intense field and bombard the cathode causing sputtering of the cathode material. The 'sputtered atoms' become excited by further collisions, so that in the glow within the cathode the spectrum of the cathode material is seen, in addition to that of the carrier gas. If helium is the carrier gas (Ionisation potential 19.7 eV.) the cathode material spectrum is due largely to ions. Arc lines, due to the atom, are more prevalent when argon (I.P. 1568 eV) is used as the carrier gas. This is preferred as the resonance lines of the cathode material are enhanced.

The emission lines obtained in this way are narrow because the potential gradient in the negative glow itself is small so there is little tendency for Stark broadening, while the low pressures (1 - 2 mm of mercury) at which this type of discharge occurs ensures that pressure broadening is insignificant. Nearly all the power is dissipated at the cathode and even a comparatively heavy metal cathode rapidly becomes hot, therefore Doppler broadening is more serious. However, the effective gas temperature is always

considerably lower than that in the population of absorbing atoms in the flame so that the emission line is always much narrower than the absorption line.

A difficulty in practice arises from the vaporisation of sample producing emission at exactly the same wavelength where absorption measurement is being made. This difficulty can be overcome by modulation of the incident radiation before it reaches the atomic vapour, and so tuning the detector and amplification system, that any unmodulated radiation emitted by the vapour does not produce a signal at the amplifier output.

Apparatus.

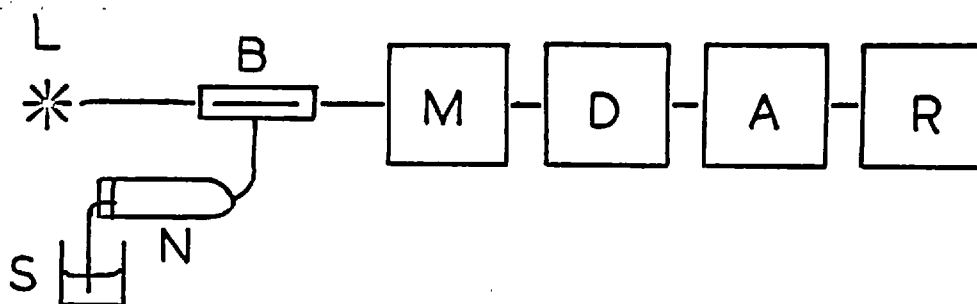
The apparatus generally used in atomic absorption spectroscopy comprises :

- (1) a suitable light source, emitting the line spectrum of an element to be determined ;
- (2) a means of vaporising the sample;
- (3) a monochromator for line isolation; and
- (4) a photocell or photomultiplier detection and amplification system.

The detector is placed to receive only the resonance line of the element from the light source, measurement can be made of the absorption of this resonance line radiation after passage through the atomised sample. The magnitude of this absorption bears a direct relationship

to the concentration of free ground state atoms of the element in the vapour and when referred to a calibration curve, provides a means of determining the concentration of the element in the sample solution. A typical experimental arrangement is shown below in figure 4.

FIGURE 4.



L = Hollow cathode lamp

B = Burner

M = Monochromator

D = Detector

A = Amplifier

R = Recorder

N = Nebuliser

S = Sample

The instruments used by the author were, firstly a Hilger and Watts Uvispek (H700) and the unmodulated atomic absorption attachment (H 1100) with lamp (FL 165), secondly a Unicam SP.900A.

As previously stated, hollow cathode lamps are the most commonly used sources. Multi-element lamps may be produced by using either an alloy for the cathode or several pure metal cathodes. These are of limited use since one metal tends to sputter from the cathode more easily than another and hence one line spectrum is obtained preferentially. In the application of atomic absorption

spectroscopy to chemical analysis both smoothed direct current (7,14,15,16) and half- or full-wave rectified A.C. (17,18,19) have been used to supply these lamps. The use of rectified A.C. or smoothed D.C. and a mechanical chopper (7,8,14) in the light path results in an alternating signal from the detector. If this signal is measured by using an A.C. amplifier tuned to the frequency of the signal, the system is specific to the measurement of light emitted from the hollow cathode lamp.

The double-beam system used by Russell, Shelton and Walsh (14) **requires no** stabilisation of the voltage supplied to the spectral lamps. In single beam instruments (15,20), stabilisation is necessary to enable the blank, standard and unknown solutions to be measured under identical conditions.

Other usable light sources are discharge tubes (9), for the more volatile elements, microwave tubes (21), plasmas (22), continua (23,24), hydrogen lamps (25) and xenon arcs (23). Although flames are well known sources of line spectra, their use as sources for atomic absorption spectroscopy is less satisfactory than other methods, due to line broadening by high operating temperature and pressure. They are also unable to excite lines of high excitation potential and their output over long periods of time is very unstable.

Walsh suggested that if spectral continua were used as light sources, then monochromators of resolution of 500,000 would be required. He also questioned whether there would be sufficient energy available in the $0.01 \text{ \AA}$ to $0.003 \text{ \AA}$ interval of continuum to give an acceptable signal to noise ratio. He concluded that the peak absorption rather than the absorption profile was experimentally more attractive.

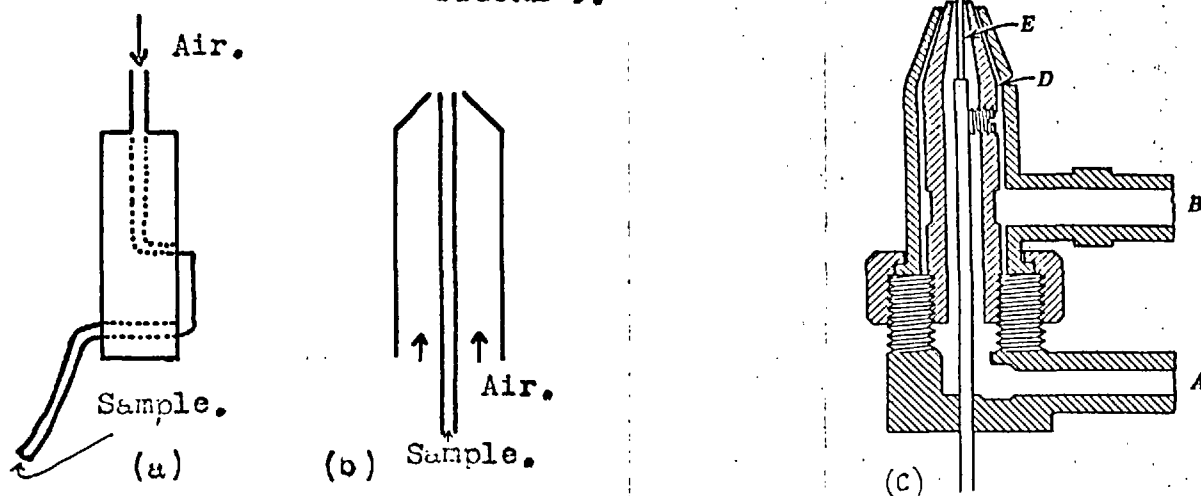
Fassell (23) has used a continuum successfully, especially for the determination of the rare earth elements. Here one lamp provides a light source for all elements and hence is a great practical and economic advantage.

Introduction of sample into the flame.

The substance to be analysed must appear in the flame as atomic vapour. To achieve this the sample solution must first be carried to the flame by means of a nebuliser and spray chamber, and passed into the flame as a fine mist or aerosol. This aerosol must be converted into atomic vapour in which dissociation and ionisation play an important part. The nebulisers carry the samples via a jet of carrier gas which is generally the supporting gas of the flame.

There are three main types of nebuliser :

FIGURE 5.



Nebulisation converts the sample solution to fine droplets which are carried to the flame directly as in the total consumption or direct burner (5c) or indirectly via a spray chamber in (5a) and (5b). In the spray chamber the larger drops separate, either being too big to be carried further or they are broken into smaller drops. The solvent evaporates partly in the spray chamber and tubes to the burner and finally in the flame.

If all the sample solution aspirated by the nebuliser appeared in the flame as vapour and was therefore subsequently atomised, this process of nebulisation would be very straightforward. Unfortunately various losses occur. In the spray chamber large droplets separate and do not get into the flame. If they do pass into the flame which is the case with the total consumption burner, the drops are too big and give rise to incomplete vaporisation. Thus a large proportion of the sample

fails to reach the flame and this reduces the detection limits and sensitivity of the method. The magnitude of these losses is governed largely by the drop-size distribution of the mist, and the production of a large proportion of droplets below a certain critical size gives rise to the best nebuliser efficiency.

The actual rate of uptake of sample depends solely on the viscosity of the solution and the flow rate of the carrier gas. The difference in levels between the sample and atomiser tip does not affect the suction rate. If it did as the level fell the signal would also fall and variation in density and surface tension would cause large errors.

The liquid emerging from the capillary forms into spherical drops due to the action of surface tension forces. The drops can be made into smaller drops by collisions with walls or being torn apart by the gas stream. A dynamic pressure of wV^2 is set up, due to the friction of the gas. w is the density of the gas in gm/cm^3 and V is the relative velocity of the air with respect to the drop. These forces oppose the forces of viscosity and surface tension which keep the drop together. At high relative speeds viscosity can be neglected, and the drop shatters when the dynamic pressure exceeds the pressure of surface tension by at least a factor of 3. Under these conditions the critical radius is given by:

$$wv^2 = \left(\frac{2S}{r}\right)^3 = \frac{6S}{r} \quad (10)$$

and the maximum droplet diameter $2r$ possible during atomisation can be calculated and is of the order of 10μ . This is difficult to calculate and is not strictly accurate. It also does not give a measure of the drop-size distribution. For a measure of the drop-size distribution it is necessary to use empirical formulae which apply to given nebulisers under specific conditions. The following is one such formula for the mean drop diameter D_0 valid only for subsonic velocities and aqueous solutions with concentric atomisers (26).

$$D_0 = 586 \frac{\sqrt{sd}}{v} + 597 \left(\frac{f}{\sqrt{sd}}\right)^{0.5} \left(1000 \frac{Q_1}{Q_2}\right)^{3/2} \quad (11)$$

S = surface tension (dynes/cm); v = velocity of compressed air at orifice (metres/sec.); d = density of liquid (gm/cm^3); f = viscosity (dynes.sec./ cm^2); Q_1 = liquid flow ($\text{cm}^3/\text{sec.}$); Q_2 = air flow ($\text{cm}^3/\text{sec.}$). D_0 is the diameter of the average drop in μ . This is an average value and hence this drop has the same volume/surface ratio as the entire liquid mist, it is also true that the mass of all drops of diameter less than D_0 is about half the total mass.

This formula is valid for the limits :
 $0.8 < d < 1.2$; $30 < s < 73$; and $0.01 < f < 0.3$. For economical nebulisation $Q_2/Q_1 > 3,000$ and in this case the last term in equation (11) can be ignored. The size of the spray drops

depends almost entirely on s , d and V , while the effect of the viscosity, f , vanishes. This conclusion is in accord with the earlier equation (10) for the critical diameter in which viscosity again plays no part. Both equations show that a finer mist is produced if the carrier gas velocity, V , is increased and the surface tension, s , is decreased.

Recombination of small drops occurs as well as the shattering of large drops and the recombination affects the mean drop-size appreciably when $Q_2/Q_1 < 5,000$ and so cannot really be ignored.

Vaporisation of solvent obviously affects the size distribution of the drops reaching the flame. The effect of vaporisation can be estimated by considering the loss by evaporation per unit time from a stationary spherical droplet in dry, still air. The Langmuir equation derived on the assumption that the free path of air molecules is small compared with the drop diameter applies:

$$-\frac{dm}{dt} = 4\pi M D \frac{P_s r}{RT} \quad (12)$$

where m = mass of drop; t = time; M = molecular weight of vapour; D = diffusion coefficient of vapour in air; R = gas constant; T = absolute temperature; P_s = vapour pressure of saturation; r = radius of drop.

Thus rate of loss of surface :

$$-\frac{dF}{dt} = 8\pi M D \frac{P_s}{\omega RT} \quad (13) \quad (F = 4\pi r^2)$$

where ω = density of the liquid.

This equation states that at constant temperature the rate of surface contraction $-\frac{dF}{dt}$ is approximately constant. For water droplets at room temperature it amounts to about 10^{-4} cm²/sec. so that a drop with diameter 50 μ evaporates completely in one second. This is roughly the time spent by a drop in the spray chamber of an indirect nebuliser system. Thus droplets with diameters below 50 μ will have lost all solvent before entering the flame.

The approximate constancy of $-\frac{dF}{dt}$ implies that for a finer mist at a given rate the amount of solvent evaporated per unit time increases, an upper limit being set by the saturation of the air.

An idea of the efficiency of an indirect nebuliser is obtained by expressing as a percentage the fraction of the originally aspirated sample which actually reaches the flame. This percentage is called the nebuliser efficiency, and is usually of the order 1 - 10% but can be as high as 20% using organic solvents. While measuring the nebuliser efficiency, evaporation losses should be minimised.

The use of organic solvents for spraying into the flame (27,28) is an important method of increasing the sensitivity of the atomic absorption method, and this can lead to a 5-fold enhancement in sensitivity.

From equation (11) if the carrier gas velocity, V , is kept constant the use of an organic solvent can decrease the surface tension, s , and the density, d , so that a finer mist is produced. This has the effect of enabling more sample to reach the flame, thus increasing sensitivity and detection limits. This is true for solvents miscible with water, e.g. acetone and ethyl alcohol, and also immiscible solvents e.g. ethyl acetate, butanol, etc.

An ultrasonic nebuliser ⁽²⁹⁾ has been developed for use in atomic absorption spectroscopy. This nebuliser provides a reproducibly fine aerosol and enables far more sample to reach the flame. There are two slight disadvantages, (a) a large volume of solution is required, and (b) it is easy for the nebuliser to become coated with different compounds giving rise to a "memory effect".

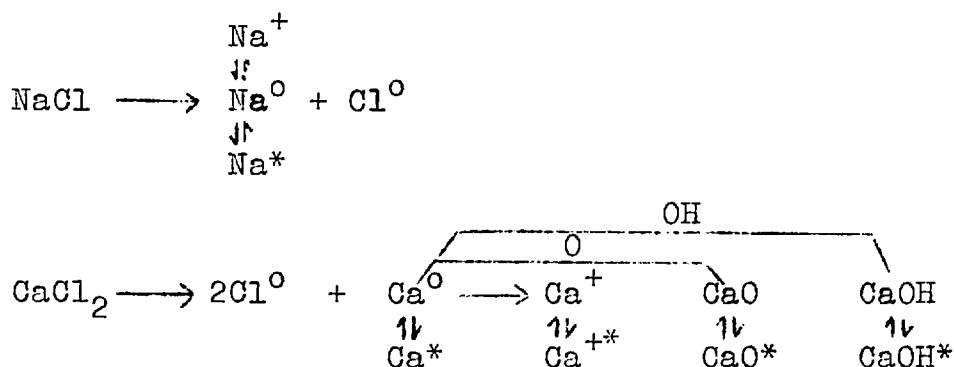
Atomisation.

The flame is used almost exclusively as the atom reservoir for measurements of atomic absorption. Other usable methods of atomisation, however, include L'vov crucible ⁽³⁰⁾, long heated tubes ⁽³¹⁾, low background separated flames ^(32,33), and plasmas ⁽²²⁾.

The aerosol or fine mist of sample produced by the nebuliser is introduced into the base of the flame. It is the function of the flame to convert this sample into atomic vapour containing free ground state atoms suitable

for atomic absorption. The aerosol first loses the solvent by vaporisation. The solid "clotlet" formed melts, then boils and finally vaporises. The liberated molecules dissociate yielding atomic vapour, some of the atoms absorb more energy and become excited atoms. There is also a tendency for some atoms to ionise which leads to the formation of stable compounds in the flame. The heat required for all these processes is a negligible fraction of the total heat content of the flame.

For sodium and calcium chlorides the flame processes have the following effect.



Ca^0 Na^0 Cl^0 ground state atoms - A.A.S.

Na^* Cl^* etc excited atoms - Emission

Na^+ etc. ionised atoms -

The O and OH are provided by the flame gases.

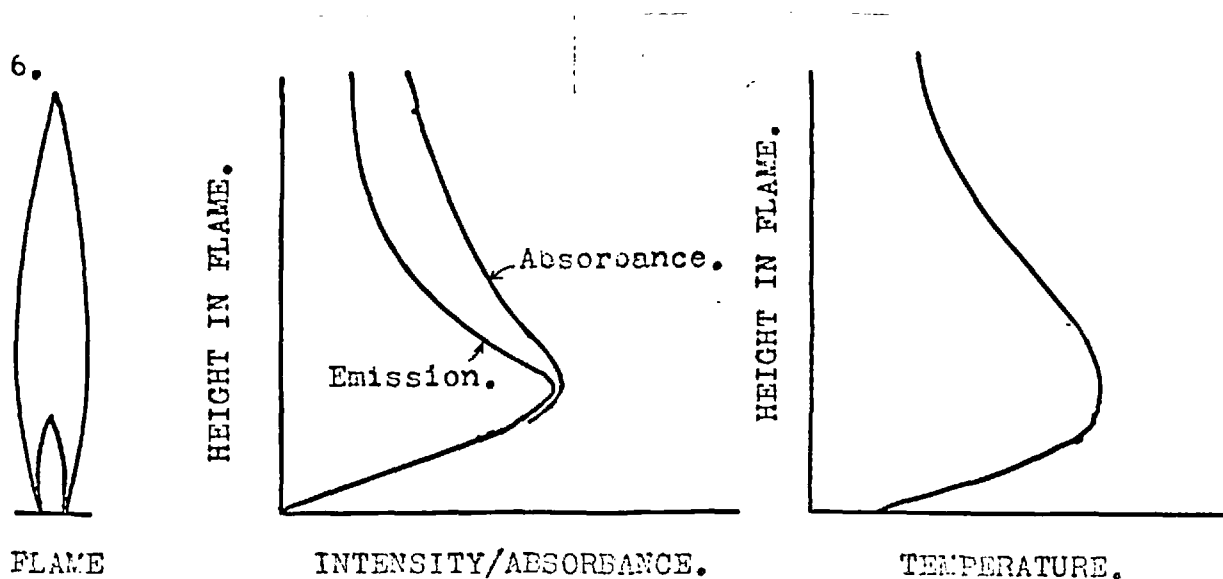
The time, t , for evaporation of a droplet is obtained from the equation

$$d_o^2 = c \times t \quad (14)$$

d_o is the initial diameter of a drop and c is a constant.

Since the life of the drops of solution depends on the speed of ascent of the hot gases in the laminar flame, it is possible to calculate the height in the flame at which a droplet of given size will be completely atomised. For water droplets of initial diameter 1μ in an air/acetylene flame ascending at 10 m./second this height will be 0.05 mm. At a height of 3 mm. drops with initial diameters of 10μ will contribute to the atomic population. Therefore at the customary height of observation in the flame, 1 - 3 cm. above the flame base, practically all the drops will be atomised. This is not necessarily true for the total consumption burner.

FIGURE 6.



If emission intensity is plotted versus height above the burner for most premixed flames, the maximum emission intensity coincides with the hottest region of the flame.

The intensity falls off quickly either side in the cooler parts of the flame, as small changes in temperature cause large variations in emission intensity as would be expected, since $I \propto e^{-E/KT}$. When the corresponding absorption profile is plotted, once again the maximum absorption occurs at a certain point in the flame, usually the hottest, but above this position of maximum absorption the rate of decrease of absorbance with height is not usually as pronounced as for thermal emission. This can be explained by the persistence of a relatively 'cool' ground state atomic population quite high in the flame. If the element forms stable compounds in the flame, however, then the absorption is badly affected, but if the ground state atoms can be protected by the high temperature and the reducing atmosphere, then the absorbance should remain high over a wide region of the flame.

The high temperature of the flame can be a disadvantage for certain elements e.g. calcium, when a high proportion of the element is ionised, thus reducing the atomic population and hence the absorption. This effect of ionisation can be overcome by the addition of other more easily ionised elements e.g. potassium, to the sample. The ionisation $K \rightarrow K^+ + e$ tends to reverse the calcium ionisation equilibrium $Ca \rightarrow Ca^+ + e$.

Generally a compromise must be obtained between

high temperature and reducing atmosphere. The high temperature is required to atomise the element and also to assist in the breakdown of compounds formed in the flame. The reducing atmosphere helps to prevent the formation of stable oxides in the flame.

The dimensions of the burner are important. The author has always used long laminar flow burners and not the total consumption type. The longer burners produce high absorbances in accordance with the Lambert - Beer Law. The absorbance cannot be increased indefinitely, however, by lengthening the burner, due to the dilution of the atomic population by the greater volume of gases required to support the longer flame and the cooling effect of the burner-plate on the flame. If the flame is made narrower an increase in absorption results due to the increase in concentration of the atomic population.

The path of light through the flame affects sensitivity. All of the light from the hollow cathode lamp should pass through the flame, at a height above the burner found experimentally to produce the greatest absorbance signal. In order to increase sensitivity further, multipass systems are in common use (34).

The types of flame used by the author have been air/propane, air/acetylene, nitrous oxide/acetylene and various mixtures of nitrogen, oxygen, air, nitrous oxide,

acetylene and ethylene. The air/propane and air/acetylene flames are very satisfactory for a large number of elements, but difficulties arise when attempts are made to atomise refractory elements. The refractory nature of the oxides prevents the production of sufficient ground state atoms for absorption measurements in these conventional flames. Also when determining other elements in the presence of the refractory metals, the refractory oxides produced bind the required atoms within their lattice and prevent the production of free ground state atoms.

Russell, Shelton and Walsh (14,35) realised that the greatest limitation of the atomic absorption method was the difficulty in atomising various elements. They suggested that the use of the cyanogen/oxygen flame may solve this problem of atomisation. This flame has been used by Robinson (36) but is extremely unpleasant and dangerous to handle, and also the sensitivity obtained was low. It was research of this kind which led to the introduction of the nitrous oxide/acetylene flame (37) for the determination of refractory elements. This flame produces the high temperature and provides the reducing atmosphere required for the production of the ground state atoms of many refractory elements.

Monochromator, Amplification and Detection Systems.

The use of a line spectrum of an element makes it possible to use monochromators of reasonably low resolving power, since line isolation is all that is required. The resolution can be further lowered by the use of modulated light sources and tuned amplifiers. If any background radiation is emitted by the sharp-line source a curved calibration graph will be produced, but the curvature may be minimised by using a narrow band-pass monochromator which reduces the proportion of unabsorbed light. The resolution required depends on the complexity and intensity of the source spectrum. For most transition elements quite a high resolution is necessary, whereas for alkali or alkaline earth elements a monochromator of low resolution is usable. The possibility of using another hollow cathode lamp as monochromator was discussed by Walsh ⁽¹⁴⁾ and a working arrangement has now been produced ⁽³⁸⁾.

The measurement system depends on the ability of the photocell or photomultiplier to measure the reduction in intensity of a resonance line emitted from a high intensity source. This reduction gives a measurement of the concentration of sample solution. Various types of photocell ⁽³⁹⁾ and photomultiplier ⁽⁷⁷⁾ have been used satisfactorily. The amplification system is **tuned** to the modulation frequency of the light source and the output is registered either on a spot galvanometer or a strip chart recorder.

Limitations and interferences.

Atomic absorption spectroscopy has been applied successfully to the determination of a large number of elements⁽⁴⁰⁾. Except for Walsh⁽³⁵⁾ and L'vov⁽³⁰⁾ nearly all these determinations have been performed using solution samples. Although detection limits for refractory elements are quoted⁽⁴¹⁾ very few actual determinations of these elements under real conditions are to be found in the literature.

This thesis describes methods for the determination of trace constituents in refractory elements, and also some studies concerning the determination of refractory elements themselves. The enhancement in sensitivity in the determination of the latter, afforded by the nitrous oxide-acetylene flame has been investigated and the temperature, in various regions of the flame, measured using three different techniques.

The sensitivity of the atomic absorption method compares very favourably with other analytical procedures. The fact that excitation potential has little effect on the sensitivity of the absorption procedure gives an immediate advantage over flame emission methods, where the sensitivity is critically dependent on excitation potential. The higher the excitation potential of the strongest resonance line of an element, the higher the sensitivity of the

absorption method will be, relative to that of the corresponding flame emission procedure.

The main advantage of atomic absorption over other methods is that it is relatively free from interferences. There are three principal types of interference in absorption and emission methods, radiational, physical and chemical. The literature contains much detail concerning the nature of these interferences⁽²⁶⁾ and the following account is only a brief description of these three types of interference with reference to emission and absorption techniques.

(a) Radiational.

Radiation interference in Atomic Absorption Spectroscopy occurs mostly in unmodulated instruments, where radiation from the flame is simply defocussed at the slit of the monochromator. Thus radiation from elements in the flame, other than that for which the sample is being analysed, may pass through the monochromator system and be measured. This type of interference lowers the sensitivity of the absorption method. However, it is much more serious in the flame emission procedure where the optical arrangement employed gathers emitted radiation from the flame as efficiently as possible. By Atomic Absorption Spectroscopy, for example, Allan⁽¹⁵⁾ reports that a solution containing 10 p.p.m. of iron and 10 p.p.m. of manganese, in

the presence of 100-fold excesses of potassium, calcium, sodium, magnesium, and phosphorus, gave exactly the same absorbance signal for iron and manganese as a solution containing only 10 p.p.m. of iron and 10 p.p.m. of manganese. If a similar experiment was conducted utilising the thermal emission of iron and manganese, considerable radiation interference would result, even at moderately high resolution, in the presence of calcium and phosphorus. Flame background emission is also a source of considerable radiational interference in thermal emission spectroscopy, and is difficult to eliminate. Variation in magnitude and stability of this background contributes to high noise levels and lack of precision.

This type of interference is easily overcome in the atomic absorption procedure, by modulation of the light source, so that the signal produced is, in effect, a.c., and tuning the amplifier to this signal. Any radiation from the flame is obviously d.c. in nature and will not therefore be amplified. An exception arises when the incident a.c. radiation stimulates resonance fluorescence from atoms of the element in the flame. The a.c. fluorescence emitted, diminishes the expected absorbance and can cause premature curvature of absorbance growth curves⁽⁴²⁾.

Physical.

Collisions between atoms, molecules and electrons occur within the flame, causing the transference of excitation energy from one species to another. In flame emission methods, where the number of excited atoms is very small, this type of interference can cause a large lowering in sensitivity. Obviously any lowering in the number of excited atoms will decrease the sensitivity. Similarly any excessive supplementation of the number of excited atoms by suprathreshold excitation, e.g. chemiluminescence, will give rise to a positive enhancement.

There is no real counterpart to this in atomic absorption analysis, because the number of absorbing ground-state atoms in the flame is large and virtually constant. Therefore excitation energy transfers, though they may have a large effect on emission from a flame, have a negligible effect on absorption in the flame.

Chemical.

This type of interference is due to the formation of stable compounds in the flame and is the most serious cause of interference. Unfortunately, atomic absorption methods in which flames are used for vaporising the sample, are subject to the same chemical interferences as flame emission methods. The reason for this is that the formation of temperature-stable compounds in the flame causes an equal

and proportionate reduction in the populations of ground-state and excited atoms.

For example Strasheim and Nell⁽⁴³⁾ show how phosphate interferes with the calcium emission method, and David⁽¹⁷⁾ reports that the phosphate interference is similar to that obtained in the determination of calcium by the absorption technique. Also aluminium, which has been shown to interfere with the flame emission determination of alkaline-earth elements by Mitchell and Robertson⁽⁵²⁾ has been shown to interfere similarly with the atomic absorption determination of calcium and magnesium by David⁽¹⁷⁾ and Allan⁽¹⁶⁾ respectively.

The methods for overcoming chemical interference are (a) separation of the required element from interfering ions, or (b) the suppression of the interference by addition of an excess of a substance which will prevent the formation of compounds between the interfering ions and the element being determined. Examples of substances added for this purpose are strontium fluoride^(19, 53, 52) and E.D.T.A.^(19, 54)

However, when the determination of refractory elements is attempted, e.g. aluminium, silicon and molybdenum, which form stable refractory compounds in the flame, additions of the above type are useless, because there is insufficient atomisation in the flame to produce ground state atoms for absorption measurements. It was

this need for a flame which could atomise refractory elements which prevented the application of atomic absorption spectroscopy to a larger number of elements. The introduction of the nitrous oxide - acetylene flame⁽³⁷⁾ enabled the production of a large population of ground state atoms of most of the refractory elements, and hence their determination was possible.

For complete atomisation of the majority of elements, the plasma jet used by Margoshes and Schribner⁽⁵⁵⁾ shows promise. This combines a very high operating temperature with non-oxidising conditions, and should be suitable for the atomisation of refractory elements.

CHAPTER 2.THE DETERMINATION OF TRACES OF COPPER IN NIOBIUM AND
TANTALUM.

Copper has been determined in a variety of materials using atomic absorption spectroscopy. The technique has been applied to the determination of copper in sea-water⁽⁴⁴⁾, brass and bronze^(45,46), ores^(47,48), and agricultural substances⁽⁴⁹⁾. The author's studies were concerned with the application of atomic absorption spectroscopy to the determination of trace amounts of copper in niobium and tantalum, which form refractory oxides in conventional hydrocarbon-air flames. The determination of copper by direct aspiration of sample is therefore difficult, since the refractory oxides formed in the flame bind the copper atoms within their lattice and thus prevent the production of sufficient ground state copper atoms suitable for atomic absorption measurements. This seriously affects the sensitivity of the procedure and the copper must therefore be separated from these refractory elements.

The air-propane flame was used for the determination of copper in niobium in conjunction with an un-modulated atomic absorption spectrophotometer. For reasons described later the determination of copper in tantalum was conducted in an air-acetylene flame and a modulated instrument was used.

In the initial experiments using aqueous copper solutions it was found, contrary to expectations, that the presence of a 100- or 1000-fold excess of niobium or tantalum slightly enhanced the copper absorption signal. This was later shown to be due to copper impurities present in the niobium and tantalum since the refractory elements themselves do not contribute to the absorption signal at the 3247 Å line. However, it is not possible to determine copper at the 1-10 p.p.m. level directly in aqueous solutions of niobium and tantalum because (a) even in pure solution at a workable volume, 100 µg of copper (i.e. 10 g. sample, 10 p.p.m.) does not produce sufficient absorbance in the air-propane flame; and (b) the additional presence of 10^5 - and 10^6 -fold excesses of niobium (or tantalum) and fluoride reduces the nebuliser efficiency and causes the formation of undissociated refractory oxide particles in the flame, thus severely inhibiting absorption due to copper.

An initial separation of the copper into an organic solvent was adopted. This had the advantages of (a) quantitatively removing the copper from a large volume of refractory medium avoiding any interference from oxide formation; (b) giving a volume concentration step; and (c) making available the nebulisation efficiency of an organic solvent.

The extraction system first investigated was capric acid in ethyl acetate (50) at pH 8.0. The extraction of copper was irreproducible and incomplete. It was subject to interference from tartarate, and, in the presence of niobium, the high pH necessary caused precipitation of niobium oxide. Because of these serious limitations this extraction system was abandoned.

The use of 8-hydroxyquinoline in an organic solvent as an extractant for copper from the aqueous niobium solution was next studied. Complete extraction of copper was obtained from both niobium and tantalum at pH 4.5. The organic phase obtained after such an extraction was sprayed directly into the flame for the determination of copper in niobium, but a concentration step was employed in the copper in tantalum procedure.

The large excess of fluoride ions present in the niobium and tantalum solutions after dissolution helped to mask interferences, and only molybdenum and titanium interfered at the 100-fold excess level. The addition of hydrogen peroxide prior to extraction eliminated these interferences. The methods used gave good sensitivity for the determination of 1-10 p.p.m. of copper in niobium and tantalum.

Experimental.

Reagents.

Copper Solution. Dissolve 3.929 g. of analytical grade copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1 litre of distilled water from an all-glass distillation apparatus. This 1,000 p.p.m. stock copper solution may be diluted to 100 and 10 p.p.m. solutions as required.

Tantalum Solution. Dissolve 10 g. of tantalum metal in a mixture of 30 ml. of 40% hydrofluoric acid and 3 ml. of nitric acid (S.G. 1.42). Dilute the solution to 500 ml. with distilled water and add 4M ammonia solution to raise the pH to 4.0. Dilute this solution to 1 litre to produce a 10,000 p.p.m. tantalum solution.

Preparation of Samples.

Dissolve 2 g. of tantalum metal in a mixture of 6 ml. of 40% hydrofluoric acid and 0.5 ml. of nitric acid (S.G. 1.42). Dilute to 100 ml. with distilled water and add 4M ammonia to raise the pH to 4.0. Finally, dilute the solution to 200 ml. with distilled water.

Niobium Solution.

Dissolve 50 g. of niobium metal in a mixture of 150 ml. of 40% hydrofluoric acid and 100 ml. nitric acid (S.G. 1.42). Dilute to 450 ml. with distilled water and add 10% sodium hydroxide solution to raise the pH to 4.0. Dilution to 1 litre produces a 50,000 p.p.m. niobium stock solution.

Preparation of Samples.

Dissolve 10 g. of niobium metal in 30 ml. of 40% hydrofluoric acid and 20 ml. nitric acid (S.G. 1.42). Dilute the solution to 100 ml. with distilled water, add 10% sodium hydroxide solution to raise the pH to 4.0 and dilute the solution to 200 ml. The copper content of this sample solution may now be determined using the recommended procedure described above.

8-hydroxyquinoline reagent.

0.1 and 0.025 per cent solutions of 8-hydroxyquinoline were made up in ethyl acetate
Sodium acetate - acetic acid buffer, pH 4.5.

Dissolve 100 g. sodium acetate in 500 ml. of distilled water and add 150 ml. of acetic acid. Make this solution up to 1 litre to provide a pH 4.5 buffer. All other reagents used were of analytical grade.

A. DETERMINATION OF COPPER IN NIOBIUM.

Apparatus.

The Hilger and Watts Uvispek (H 700) with the unmodulated atomic absorption attachment (H 1100) was used in conjunction with a copper-zinc hollow cathode lamp (FL 165). The flame used was a regulated supply of compressed air and propane. The air pressure used was 25 p.s.i. (1.75 kg/cm^2) and a sufficient flow rate of propane to produce a flame which was just non-luminous. The effective burner head dimensions were 10 cm. long and 1.5 cm. wide.

Initial work performed to optimise the instrument controls and experimental conditions.

The maker's recommended lamp current for the hollow-cathode lamp was 15 mA, but as shown in Fig. 7 due to the higher absorbance reading greater sensitivity will be obtained at a lower lamp current, in this case 4mA was the best current for maximum sensitivity. The lamp gave a steady output at this operating current and the under-running of the lamp over a period of months caused no noticeable ill effects.

Three copper resonance lines were compared for absorption measurements. The 3273 and 2492 Å lines gave very little sensitivity, whereas the 3247 Å line gave good absorbance values for a 10 p.p.m. copper 8-hydroxyquinolate solution. Thus before making any absorbance measurements

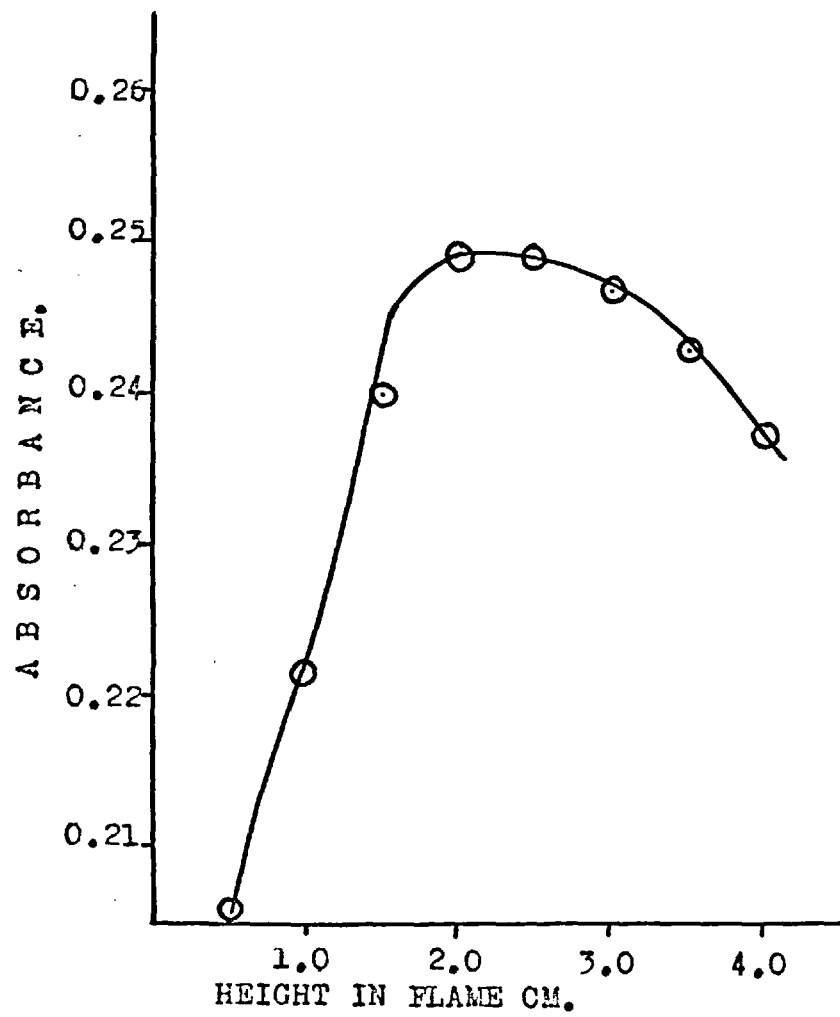


FIG. 8.

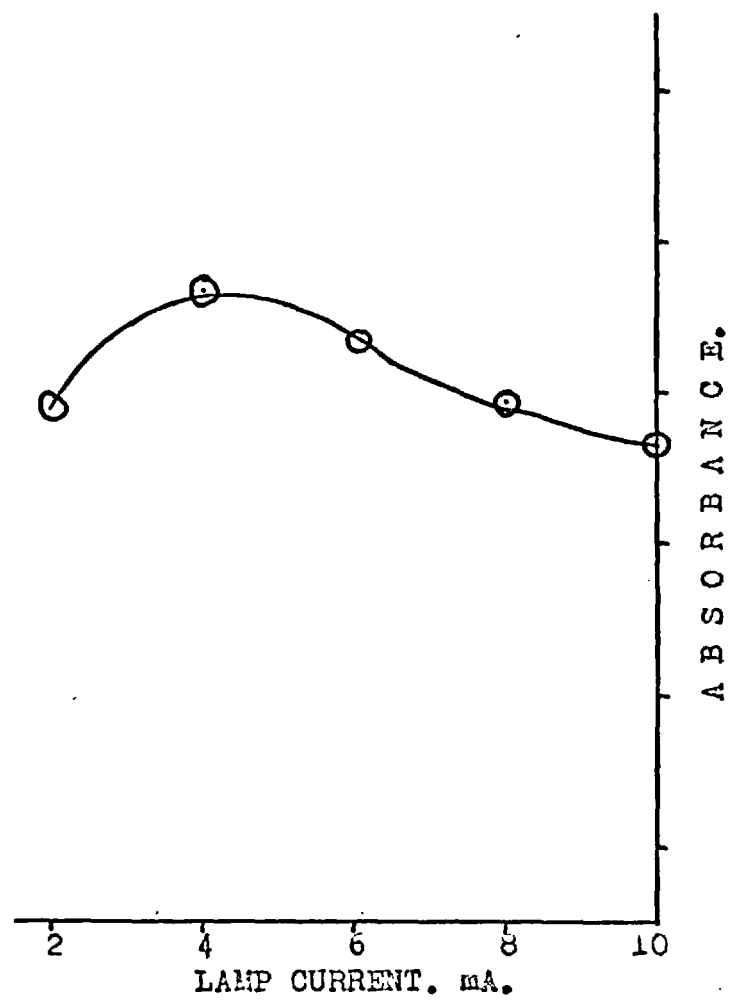


FIG. 7.

the instrument was 'peaked up' to select the 3247 Å line.

The best light path from the hollow cathode lamp through the flame was obtained by varying the height of the burner head. As shown in Fig. 8 the best path of light was just above the primary cones of the air-propane flame, i.e. about 2 cm above the burner palte. This corresponds to position 1 on the burner height control.

To help prevent copper compound formation in the flame, strontium was added to the sample solutions in order that the added ion would remove the radicals, OH, etc. from the flame and allow the copper to exist as atoms. This addition did not effect the desired results since there was no noticeable change in the absorption readings.

The optimum instrument control settings were lamp current 4 mA, wavelength 3247 Å, slit width 0.2 mm. and burner height Uvispek position 1.

Extraction Procedure.

Effect of reagent concentration.

Variation of the concentration of 8-hydroxy-quinoline revealed that at high reagent concentration high absorbance values for the sample were produced but high blanks were also obtained. Thus the absorption due to the sample alone was quite small. The reagent concentration was decreased to a value where there was the greatest

difference between sample and blank absorbances, see Table 4 . This corresponded to a 0.1% 8-hydroxyquinoline in ethyl acetate solution. The concentration was not reduced below the 0.1% level, since in the presence of foreign ions, which consume reagent, there may be insufficient 8-hydroxyquinoline left for quantitative extraction of copper. Under the recommended procedure the 0.1% concentration provides a 300-fold weight excess of 8-hydroxyquinoline over the amount of copper present at the top of the calibration curve.

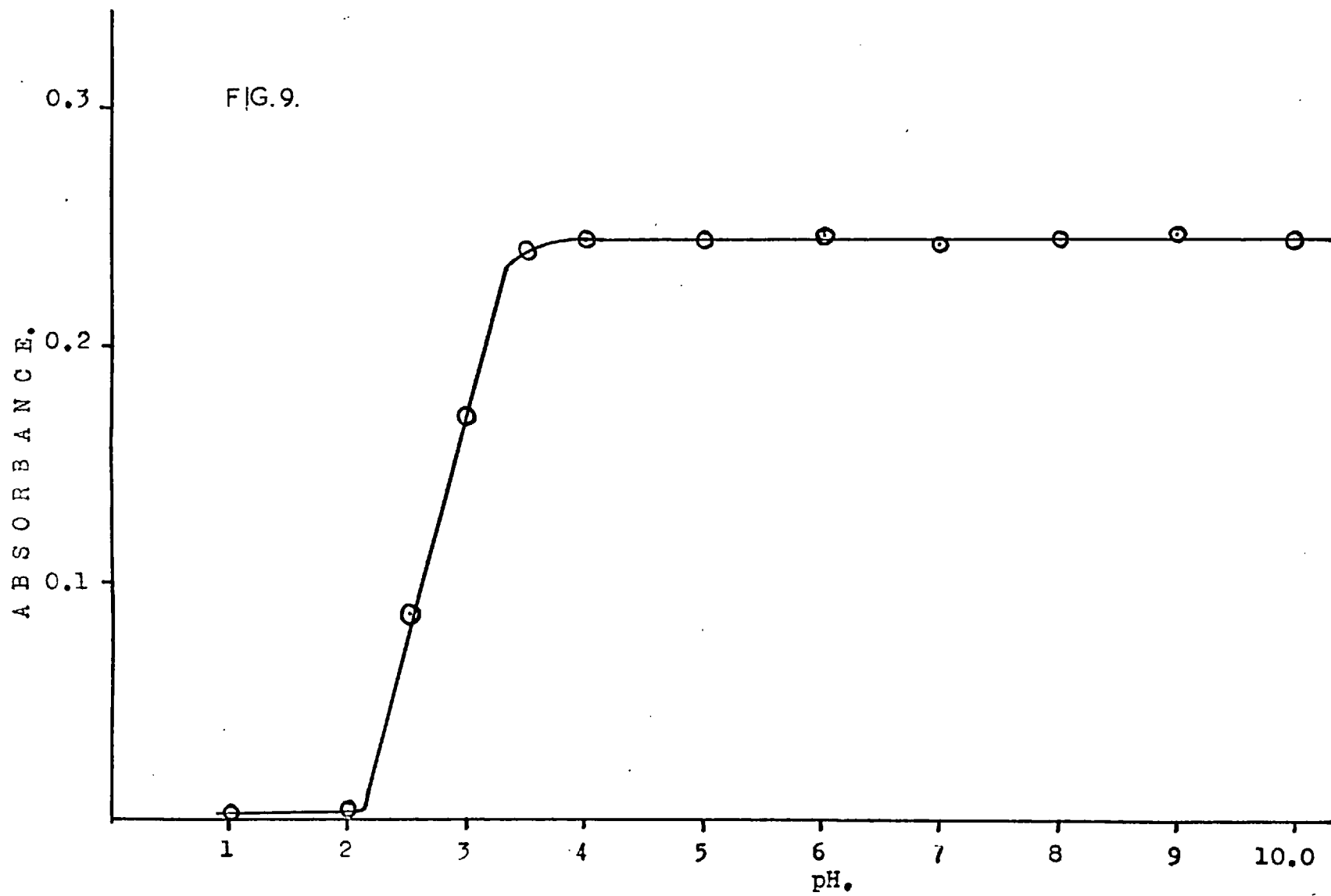
Table 4 .

8-hydroxyquinoline concentration %	Blank absorbance vs. Et Ac	Absorbance due to 10 p.p.m. Cu	Net absorbance due to Copper.
1	1.55	1.70	0.15
0.5	1.04	1.50	0.46
0.25	0.45	1.32	0.87
0.1	0.095	1.02	0.925

Values for 200 μ g. of copper extracted into 20 ml. of ethyl acetate.

Effect of pH.

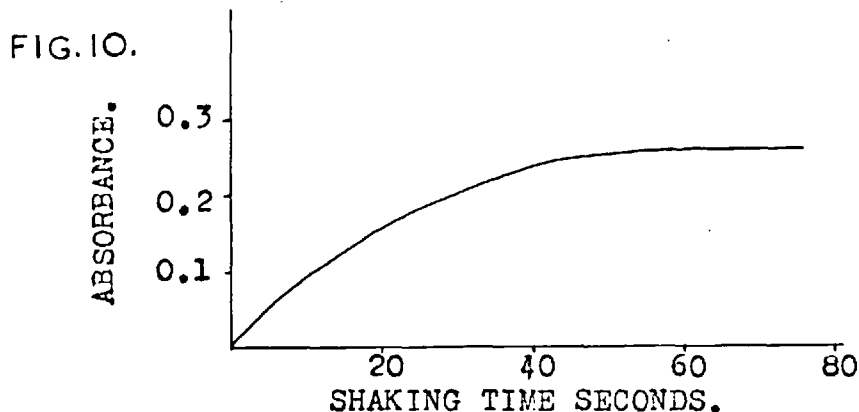
Copper 8-hydroxyquinolinate is reported⁽⁵¹⁾ to extract quantitatively in the pH range 2 - 14.0. Aqueous copper solutions were adjusted to various pH values between 1 and 10. The copper was extracted using 0.1% 8-hydroxyquinoline in ethyl acetate and quantitative extraction was



obtained above pH 3.5, see Fig. 9 . It is not possible to keep high concentrations of niobium in solution as its fluoride above a pH of 5.2, because a large amount of oxide precipitates. Thus a pH of 4.5 was adopted for use, being in the middle of the range 3.5 - 5.2.

Length of shaking time.

Complete extraction is obtained after shaking for 45 seconds and no further increase in absorbance values occurs on shaking for a longer period. A time of shaking of 1 minute was chosen for equilibration.



After shaking the layers separated quite easily and the organic phase was quite stable as there was no difference in the absorbance signal after leaving the solutions standing for several hours.

Organic solvent effect.

The extraction of copper into an organic solvent, before making absorption measurements, should result in an increase in the overall sensitivity due to an increase in

the concentration of copper in the organic phase, and also a further increase in sensitivity due to the increase in spray rate of the organic solvent relative to water. The expected increase in sensitivity from the latter effect may be calculated from a comparison of the nebulisation rates of water and ethyl acetate. The rate of aspiration of ethyl acetate is almost 5 times that of water, and the corresponding increase in absorbance values is in the ratio of 3:1. This ratio is lower than that expected because the ethyl acetate is saturated with water after the extraction, and the presence of the dissolved reagent. The spray rate of the niobium stock solution was included in the table for comparison and it is easily seen how the large concentration of ions affects the spray rate.

Table 5.

Rates of aspiration of distilled water, ethyl acetate and 50,000 p.p.m. niobium solution.

	Distilled water	Ethyl acetate	Niobium solution
Volume taken ml.	10	10	10
Volume recovered ml.	8.2	3.5	8.8
Volume reaching flame ml.	1.8	6.5	2.2
Time taken (seconds)	248	186	316
Rate ml/second $\times 10^2$	0.726	3.49	0.38
Throughput relative to distilled water	1	4.81	0.53

A number of organic solvents were tried before adopting ethyl acetate, see Table 6 . One volume of stock solution containing 10 ug/ml. of copper in ethyl acetate was diluted with 2 volumes of organic solvent and the absorbance produced measured against an identical blank.

Table 6 .

Effect of different organic solvents on the absorbance of standard copper 8-hydroxyquinolate solution in ethyl acetate.

<u>Solvent Added</u>	<u>Absorbance</u>
Ethyl acetate	0.230
Pentyl acetate	0.075
Ethyl methyl ketone	0.183
Iso propyl methyl ketone	0.156
Iso butyl methyl ketone	0.068
Iso pentanol	0.074
Pentanol	0.079
Hexanol	0.068
Butanol	0.104
Diethyl ether	0.110
Di-iso propyl ether	0.214
Light petroleum (b.p. 100°-120°)	0.190
Cyclohexanone	0.105
Acetylacetone	0.084

Calibration Curve and Sensitivity.

The calibration curve obtained is linear in the range 10 - 100 μg of copper, this corresponds to 1-10 p.p.m. of copper in a 10 g. niobium sample. The absorbance values corresponding to these concentrations are 0.155 and 0.540 respectively, and the curve passes above the origin. This is due to the presence of copper in the samples of niobium available to us. Addition of 5 ml. of 10^{-1}M E.D.T.A. to the niobium blank complexes the traces of copper and reduces the blank absorbance to zero. The blank value may therefore be subtracted from all the readings and the calibration curve redrawn to pass through the origin, Fig. 11. The copper content of the niobium samples used in this work was readily established using the above technique.

Precision and Accuracy.

A measure of the precision of the method was obtained by analysing a 5 p.p.m. copper solution 11 times over a period of several weeks using the recommended procedure. The average absorbance was 0.233 and the standard deviation was 0.011 or 4.8%. The accuracy of the method was determined by analysing synthetic niobium solutions containing foreign ions and treating these solutions as unknowns. The results of these analyses are listed in Table 7.

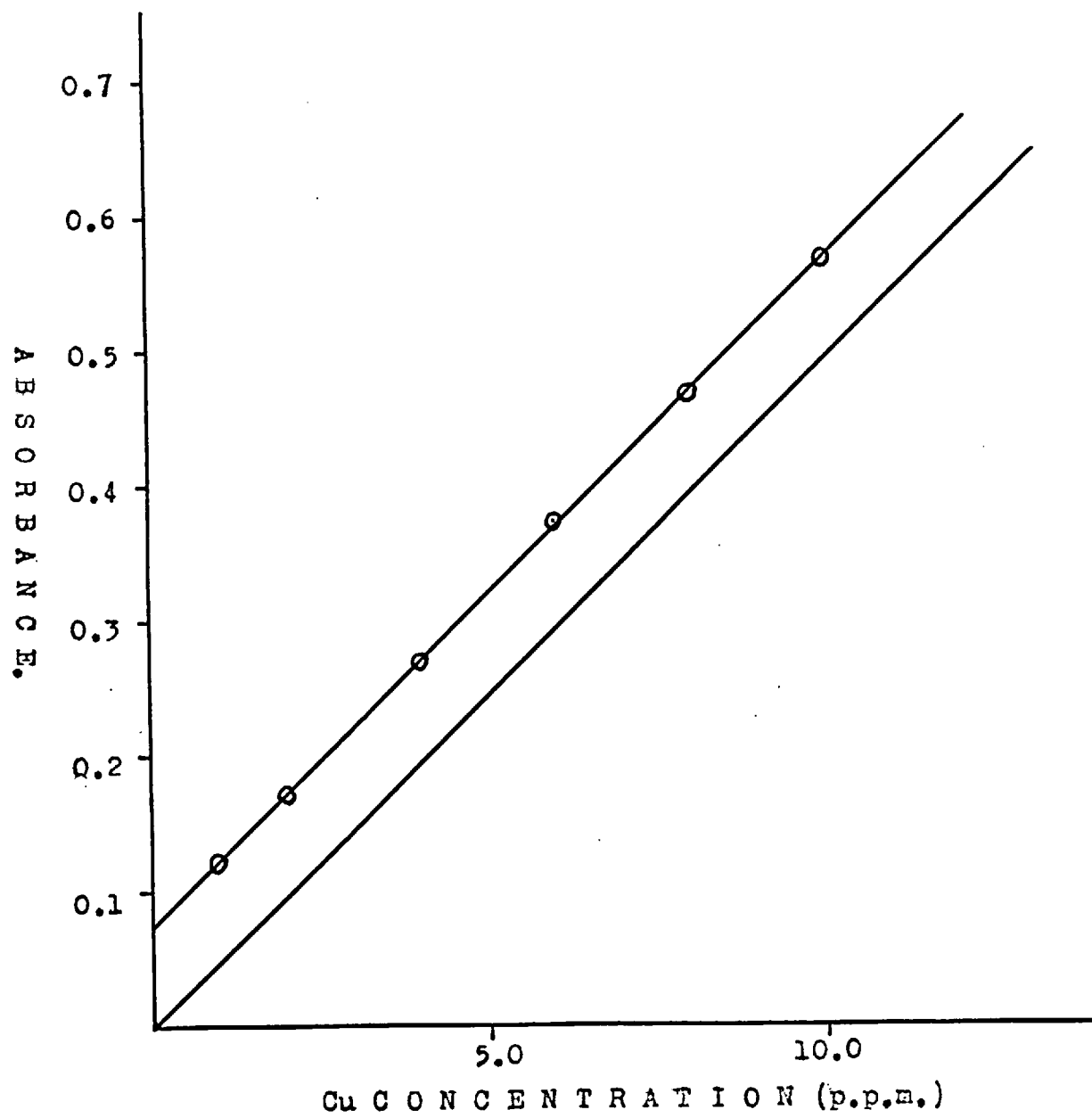


FIG. II

Table 7.

Copper in niobium p.p.m.	Copper found p.p.m.	Error %	Foreign ions added p.p.m.
3.5	3.9	+ 8.5	Zn 250; Mn 100
6.1	6.7	+10.0	Mo 100; Zn 150
7.4	7.25	- 2.0	V 100; Mn 100
5.3	4.6	-13.0	Pb 250; Mn 100; Ti 50
7.8	7.2	- 7.5	Fe 200; Al 100; Ta 100
3.2	3.25	+ 1.6	Co 250; Cr 150; Fe 100
4.9	5.0	+ 2.0	Al 250; W 50; Ni 100
3.8	3.86	+ 1.5	Pb 150.
5.8	6.0	+ 3.5	Zr 100; Fe 150
7.6	8.5	+12.0	Ni 100; Ta 100

Interferences.

The effect was noted of a number of foreign ions on the determination of 5 p.p.m. of copper in niobium (50 μ g of copper in a 10 g. niobium sample) by the recommended procedure. For the purpose of this study an ion was considered not to have interfered if an error in the absorbance value of less than 5% was produced. 100-fold excesses by weight of the following ions caused no interference. Aluminium, ammonium, cobalt(ii), chromium(iii)

iron(iii), lead, magnesium, manganese(ii), nickel(ii), potassium, sodium, tin(iv), tungsten(vi), vanadium(v), zinc, zirconium(iv), acetate, chloride, fluoride, nitrate and sulphate. The presence of 100-fold excesses of molybdenum (vi) and titanium (iv), caused low absorbance results, but these interferences were eliminated by the addition of 5 ml. of 20 volume hydrogen peroxide to the aqueous solution before extraction.

Recommended Procedure.

Transfer 1 - 10 ml. aliquots of a 10 p.p.m. aqueous copper solution to a series of 500 ml. separating funnels. Add 200 ml. of 50,000 p.p.m. niobium solution, 10 ml. of buffer pH 4.5, 5 ml. of 20 volumes hydrogen peroxide and 30 ml. of a 0.1% solution of 8-hydroxyquinoline in ethyl acetate to each vessel. Shake the funnels for 1 minute and allow the phases to separate. Run off the lower aqueous phase to waste and spray the organic phases directly into an air-propane flame for absorption measurements at the 3247 Å copper resonance line, against a 0.1% solution of 8-hydroxyquinoline in ethyl acetate as blank.

B. DETERMINATION OF COPPER IN TANTALUM.

The determination of copper in niobium required a large amount of niobium metal for a single determination, i.e. 10 g. of niobium were used for each absorbance measurement. The process is therefore costly and wasteful, and there is an obvious need to cut down the amount of metal sample used for each determination. It was necessary, however, for the method to be capable of determining accurately 1 - 10 p.p.m. of copper in niobium and tantalum, that is 1 - 10 μ g. of copper in a 1 g. metal sample. For the production of a calibration curve reasonably large concentrations of copper were required to give good absorbance values, and this in turn meant that a large niobium or tantalum sample was needed.

There were two distinct courses open to investigation for an increase in sensitivity. Firstly to increase the amounts of niobium and tantalum used and ... secondly the use of a concentration step. Increasing the niobium and tantalum sample size would effectively increase sensitivity. The absorbance value for 50 μ g of copper would remain the same if extracted from a 10 g. or a 20 g. metal sample. In the former case it would represent an absorbance value for 5 p.p.m. of copper, in the latter case the same signal would correspond to a 2.5 p.p.m. copper level. Thus the sensitivity of the procedure would be effectively

doubled. This is not a sensible course to pursue as it would increase the cost and wastage of the method, and also there is a limit to the amount of niobium and tantalum which can be retained in the aqueous solution even in the presence of complexing agents.

The use of an additional concentration procedure allowed a much smaller tantalum sample to be used i.e. 2 g. per determination. The final volume of solution obtained from the extraction procedure was very small, of the order of 2 ml. The requirements of this method were, therefore, (a) that the final volume produced was reproducible under normal temperature conditions, and (b) that the instrument had a sufficiently rapid response to provide a steady absorbance signal and leave sufficient solution for a check on the absorbance reading. For these reasons the author changed to the Unicam S.P.900A instrument, which was fitted with a recorder. The air-acetylene flame used with the Unicam also enhances sensitivity due to an increase in temperature and an increase in atomic concentration obtained with the shorter and narrower flame.

The concentration step involved extraction of copper as its oxinate as previously. Back extraction of the copper into 0.1M hydrochloric acid was effected, followed by neutralization of this phase with ammonia and re-extraction into a very small volume of ethyl acetate at

pH 4.5. This sample was finally sprayed into the air-acetylene flame for absorption measurements at the 3247 Å line.

Apparatus.

The instrument used was a Unicam S.P.900A, fitted with a Honeywell strip-chart recorder and a copper-zinc hollow cathode lamp (FL 165) (Hilger and Watts Ltd.). The flame used was a regulated supply of compressed air and acetylene. The optimum instrument control settings were determined using a standard copper 8-hydroxyquinolate solution, as in the niobium procedure. These were lamp current 5 mA., wavelength 3247 Å, slit width 0.05 mm, air pressure to atomiser 15 p.s.i. and an acetylene flow rate sufficient to produce a flame which was just non-luminous, the burner head comprised a series of 1 mm holes drilled into the head for a length of 7 cm. The burner height was again arranged so that the light from the hollow cathode lamp passed just above the primary reaction cone.

Extraction Procedure.

Reagent concentration.

The concentration step employed increased the blank readings as well as the overall absorbance signal, and a reagent concentration of 0.1% gave too high a blank reading. The concentration of 8-hydroxyquinoline in ethyl acetate was reduced and the optimum value for this

procedure was 0.025%.

The initial extraction was exactly as for the copper in niobium method, the pH of 4.5 being suitable for this procedure. The copper was thus extracted away from the aqueous tantalum solution into the ethyl acetate layer as its 8-hydroxyquinolate.

Back-Extraction.

0.1M hydrochloric acid was found to extract copper oxinate completely from the ethyl acetate phase, after shaking for 30 seconds. The acid layer was then neutralized with 1M ammonia solution and pH 4.5 buffer added. The copper oxinate was re-extracted into 2 ml of ethyl acetate. The organic phase was finally sprayed into the air-acetylene flame for absorbance measurements.

Initially the organic phase was made up to a known volume, i.e. 5 ml., before aspiration into the flame. However, the reproducibility of the final extract was checked 10 times and the absorbance signals were concordant. Since the final extract had a constant volume, it was sprayed into the flame without making up to a known volume, thus increasing the sensitivity of the method.

Calibration curve and sensitivity.

The calibration curve obtained is linear in the range 2 - 25 μg of copper. Since a 2 g. tantalum sample was taken, this concentration corresponds to 1 - 12 p.p.m.

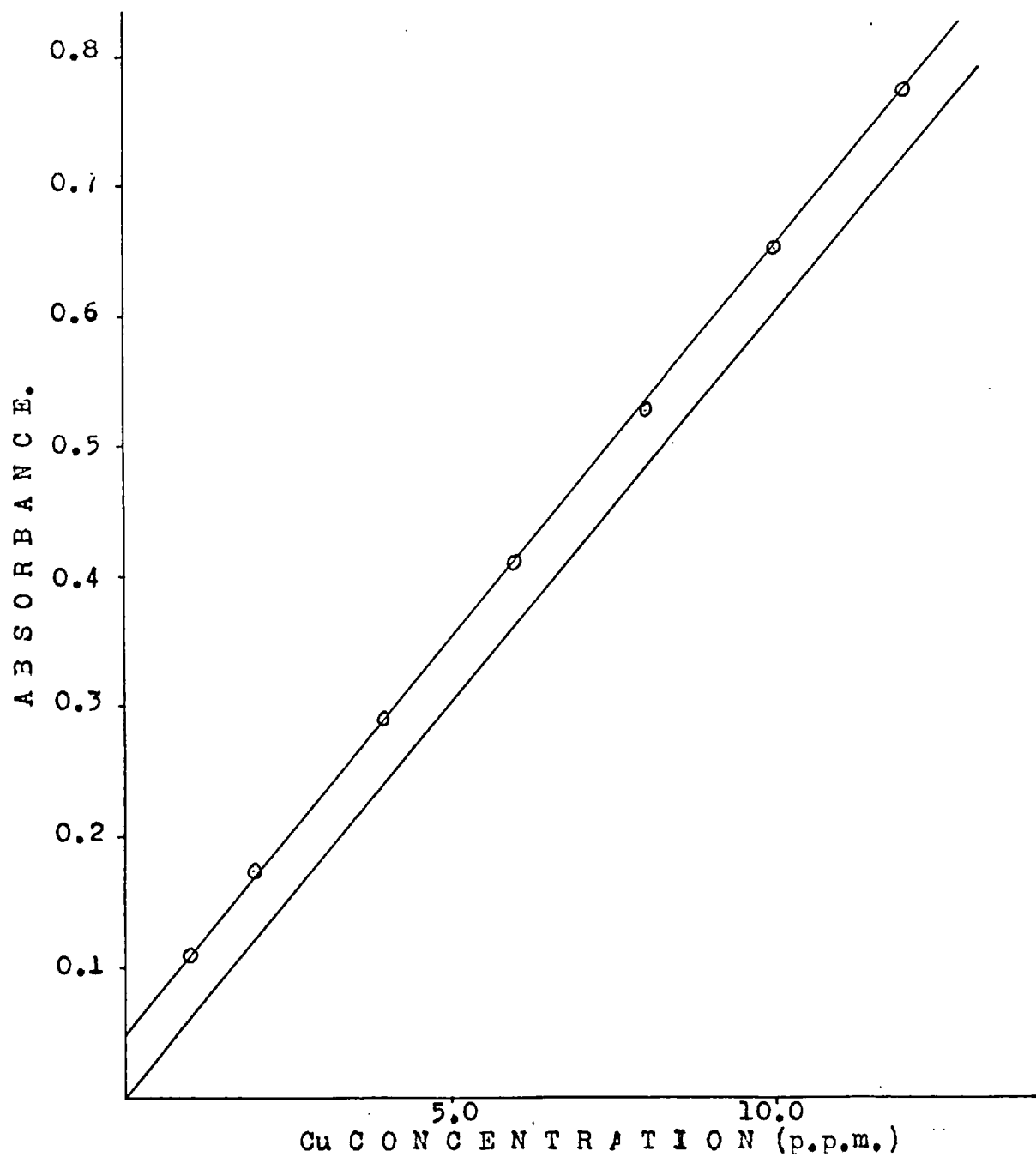


FIG.12.

of copper in tantalum, and the absorbance values relating to these concentrations are 0.110 and 0.772 respectively. Once again the curve passes above the origin due to the presence of copper in the tantalum sample. Addition of E.D.T.A. to the blank complexed the copper and prevented extraction. Thus by subtraction of the blank value from all other absorbance values the curve may be redrawn to pass through the origin. The copper content of the two tantalum samples used was found to be 2.7 and 3 p.p.m..

Precision and Accuracy.

A 5 p.p.m. copper in tantalum solution (10 μ g in 2 g. tantalum) was analysed 6 times by the recommended procedure. The mean absorbance was 0.443 and the standard deviation was 0.023 or 5.2%. A measure of the accuracy was obtained by determining copper in synthetic tantalum solutions and treating these as unknowns. The results of these analyses are shown in Table 8. A sample of tantalum obtained from Murex Ltd. was analysed for its copper content using the recommended procedure. The tantalum was shown to contain 2.7 and 2.85 p.p.m. of copper. These results fall into the range of results obtained for this metal sample in other laboratories using different methods of analysis. This range was 2.5 - 4.0 p.p.m. of copper.

Table 8.

Determination of Copper in Simulated Tantalum Samples
Treated as Unknowns.

Copper in Tantalum p.p.m.	Copper found p.p.m.	Error %	Foreign ions added p.p.m.	
7.3	8.4	+13.0		
16.5	16.3	- 1.2		
16.5	17.7	+ 8.0		
5.0	5.7	+14.0		
13.8	14.7	+ 7.0		
18.5	19.0	+ 2.7		
12.0	11.9	- 0.8	Aluminium 400	Zirconium 200
19.0	17.7	- 7.0	Nickel 300	Zinc 400
11.9	12.8	+ 7.0	Cobalt 400	Tin 300
18.0	17.6	- 2.2	Tungsten 300	Iron 300
20.0	19.1	- 4.5	Magnesium 300	Lead 300
8.0	8.0	0.0	Chromium 300	Manganese 250
23.0	25.0	+ 2.5	Titanium 300	
7.0	7.8	+10.0	Aluminium 500	Nickel 300
14.0	15.5	+10.0	Molybdenum 300	
25.0	27.0	+ 8.0	Vanadium 300	Zinc 200
10.5	11.5	+ 9.0	Aluminium 500	Nickel 300
18.0	16.7	- 7.0	Molybdenum 800	
21.0	20.5	- 2.5	Vanadium 300	zinc 200

Interferences were studied as in the copper in niobium procedure, and again the only two ions found to interfere were molybdenum and titanium. The interference due to these ions was eliminated by the addition of 5 ml. of 20 volume strength hydrogen peroxide prior to extraction.

Recommended procedure.

0.5 - 2.5 ml. aliquots of 10 p.p.m. aqueous copper solution were pipetted into a series of 500 ml. separating funnels. Add 10 ml. of pH 4.5 buffer, 200 ml. of 10,000 p.p.m. tantalum solution and 30 ml. of 0.025% 8-hydroxyquinoline solution to each funnel and shake for a minute. Reject the lower aqueous phase and add 10 ml. of 0.1M hydrochloric acid to the organic phase and shake for 30 seconds. Allow the phases to separate, and run the aqueous layer into a 50 ml. separating funnel. Add 1 ml. of 1M ammonia, 5 ml. of pH 4.5 buffer and 2 ml. of ethyl acetate, and shake for 1 minute. Reject the aqueous phase and spray the organic layer directly into the air-acetylene flame and measure the absorbance at the 3247 Å line against a 0.025% solution of 8-hydroxyquinoline in ethyl acetate as blank.

CHAPTER 3.

DETERMINATION OF MOLYBDENUM IN NIOBIUM AND TANTALUM.

The limitations of atomic absorption spectroscopy are revealed when the determination of refractory elements is attempted. Even greater difficulty is encountered when the element to be determined is present in a matrix which also forms refractory compounds in the flame. In pre-mixed hydrocarbon - air flames, insufficient ground state atoms are produced in the flame to give high absorbance readings, and as a result the sensitivity is low. Increasing the fuel content of the flame, i.e. making the flame more reducing in nature, generally increases the sensitivity obtained. Sternberg⁽⁵⁶⁾ has suggested that the excess of carbon in the flame assists the process $MO + C \longrightarrow CO + M$, so that a greater number of M atoms are produced, but, even so, the detection limits with fuel rich flames are still relatively poor for refractory elements. For a large population of ground state atoms of a refractory element to be produced, the flame should have a high temperature and also be abundant in reducing species.

The high temperature of the flame assists the breakdown of oxide species and the presence of a reducing medium helps to keep this atomic population as free ground state atoms, by excluding oxidants and preventing compound formation.

The introduction of the nitrous oxide - acetylene flame by Willis⁽³⁷⁾ enabled the determination of refractory elements to be performed easily and with increased sensitivity. The author's studies were concerned with the determination of molybdenum in niobium and tantalum. A special slit burner was constructed for use with the Unicam SP 900A in order that the nitrous oxide - acetylene flame, which has a high burning velocity, could be maintained.

Several workers^(57,58) have determined molybdenum by atomic absorption spectroscopy using an air - acetylene flame, the fuel to air ratio being increased so that the flame was luminous and fuel rich. This proved necessary to provide reducing conditions for the production of free ground state molybdenum atoms. The use of incandescent flames, however, tends to be physically unpleasant and the reported sensitivity of these methods is not very high. The background radiation due to the luminosity is received by the photomultiplier and although this is not amplified and measured, it is 'seen' by the photoresponsive surfaces and causes their fatigue.

In the author's laboratory use was made of the non-luminous nitrous oxide - acetylene flame. The flow rate of acetylene was high enough to produce the characteristic 'red feather' secondary zone without any yellow incandescence from particles of carbon. All

absorption measurements were made within this red zone, since above this region of the flame the absorbance due to molybdenum falls off rapidly.

The molybdenum is extracted from aqueous solution into n-butanol as its 8-hydroxyquinolate at pH 4.5. After extraction the butanol layer contains undissolved molybdenum 8-hydroxyquinolate and addition of n-butylamine is necessary to dissolve the solid and provide solutions suitable for spraying into the flame. Absorbance measurements are obtained at the 3132 Å molybdenum resonance line against an n-butanol blank.

The high concentration of fluoride ions helps to mask most interferences, and the addition of E.D.T.A. to the aqueous solutions prior to extraction, eliminates the interference from all ions except V(v) and Cr(vi). The presence of E.D.T.A. also helps to prevent the consumption of reagent by extraneous ions. The interference from V(v) and Cr(vi) may be eliminated by the addition of potassium sulphite and boiling the solution before extraction. The E.D.T.A. complexes of the reduced Cr(iii) and V(iv) ions form quite quickly on heating.

The addition of E.D.T.A. and potassium sulphite makes the method specific for molybdenum. Using the recommended procedure 6 - 64 p.p.m. of molybdenum in niobium and tantalum could be accurately determined with high sensitivity.

Experimental.

Apparatus.

The equipment used was the Unicam S.P.900A flame spectrophotometer, with a Unicam molybdenum hollow cathode lamp. The stainless steel air-acetylene burner was replaced by a brass burner (59) of similar dimensions for the nitrous oxide - acetylene flame (Fig. 13). The burner head plate used had a slit 2 inches long and 0.015 inch wide, and was cooled by an attached water-cooled plate clamped vertically to the side of the burner. This burner requires a larger acetylene jet (0.052 inch in diameter) to be used at the base of the burner, than when an air - acetylene flame and burner are used. Aspiration of samples via the S.P.900A nebuliser was obtained by nitrous oxide at a pressure of 15 p.s.i. and the acetylene flow rate used was sufficient to produce the maximum height of 'red feather' in the flame without any yellow luminosity, this corresponded to a manometer reading of 16 for a full acetylene cylinder. The burner height was adjusted so that as much as possible of the radiation from the hollow cathode lamp passed through the red region of the flame, above the primary reaction zone. The molybdenum absorbance within this region is always much higher than any other region of the flame. The flame was first ignited on an air-acetylene mixture and the air was gradually replaced by nitrous oxide, via two rotameters and

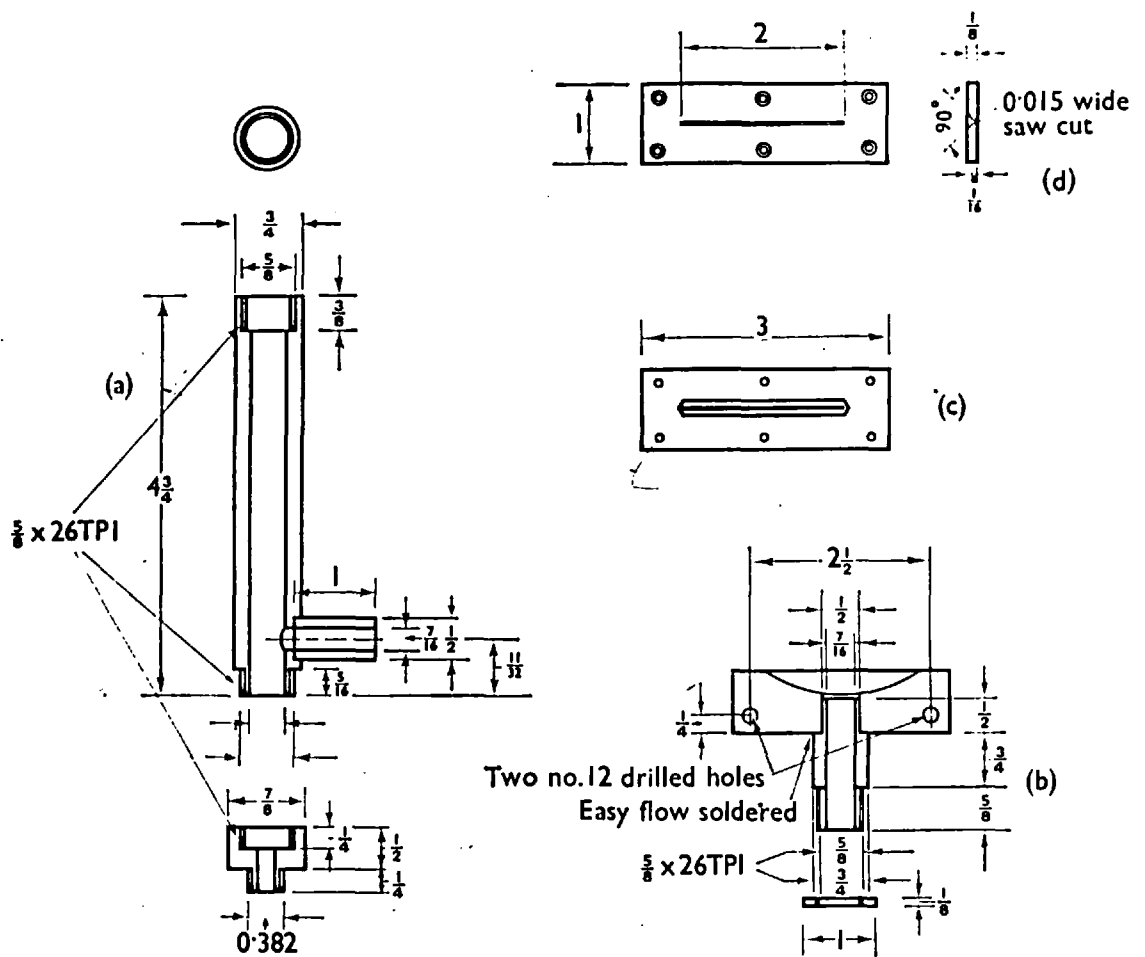


FIG. 13

a T-piece until the air was completely switched off. Throughout this changeover the acetylene flow rate was such that the flame was always fuel rich (such a mixture has then a lower burning velocity and is more safely supported). After the air was switched off, the acetylene flow rate was reduced. When extinguishing the flame the acetylene flow was turned off as quickly as possible. During the changeover from air-acetylene to nitrous oxide - acetylene and when switching the flame off, distilled water only was sprayed into the flame.

The optimum conditions for absorbance measurements were obtained using a 10 p.p.m. molybdenum 8-hydroxyquinolate solution in n-butanol. These were lamp current 15 mA., wavelength 3132 Å, slit width 0.02 mm., height of measurement in the flame about 1 cm. above the burner plate through the red zone of the flame. The use of other molybdenum resonance lines (e.g. 3798.3 Å) for absorbance measurements was investigated but they either gave very little sensitivity, or were so near CN band-heads in the flame that the background noise level was too high.

Reagents.

10^{-2} M Molybdenum solution. Dissolve 1.766 g. of analytical grade ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in one litre of distilled water in a volumetric flask. This provides a 10^{-2} M stock solution (960 µg/ml.) which may be diluted as required.

Tantalum solution. Dissolve 10 g. of tantalum metal in 30 ml. of 40% hydrofluoric acid and 3 ml. of nitric acid (S.G. 1.42). Dilute to 500 ml. with distilled water and adjust to pH 4.0 with 4M ammonia solution. Finally dilute to 1 litre with distilled water to produce a 10,000 p.p.m. tantalum solution.

Niobium solution. Dissolve 10 g. of niobium metal in 30 ml. of 40% hydrofluoric acid and 12 ml. of nitric acid (S.G. 1.42). Dilute to 500 ml. and adjust to pH 4.0 with 4M ammonia solution, dilute to 1 litre to produce a 10,000 p.p.m. stock niobium solution.

Buffered 8-hydroxyquinoline reagent. Prepare a 1% 8-hydroxyquinoline solution in pH 4.5 sodium acetate-acetic acid buffer. (100 g. of hydrated sodium acetate and 150 ml. of glacial acetic acid diluted to 1 litre). All other reagents used were of analytical grade.

Extraction procedure.

Chloroform has been extensively used for the extraction of molybdenum (vi) 8-hydroxyquinolate from aqueous solution, and Stary⁽⁶⁰⁾ has shown that quantitative extraction is obtained in the pH range 1 to 5.5 with 0.01M 8-hydroxyquinoline in chloroform. This solvent, however, is very unsuitable for use in atomic absorption spectroscopy when using the nitrous oxide - acetylene flame. During

aspiration of this solvent the characteristic red feather of the flame is affected and it is impossible to obtain a non-luminous flame in which this red region is well-defined. The flame resembles a fuel-rich air-acetylene flame in its properties and produces a low signal to noise ratio. The formation of carbon on the cooled burner plate occurs very rapidly and causes variation of the flame speed and shape. Thus chloroform was not aspirated into the flame.

Initially the method of Eberle and Lerner⁽⁶¹⁾ was used where extraction of the 8-hydroxyquinolate was carried out from pH 0.85 sulphuric acid into chloroform. Chloroform cannot be sprayed into the flame for absorbance measurements, but it is probably the best solvent for the extraction of molybdenum 8-hydroxyquinolate. Thus an attempt was made to utilise the above extraction procedure followed by a back extraction into aqueous medium which could then be aspirated into the flame. Aqueous solutions of ammonia, hydrochloric acid and nitric acid were tried for the back extraction, also ascorbic acid was added to reduce Mo(vi) to Mo(v) followed by extraction into ammonia and hydrochloric acid. Of the above systems nitric acid gave the best extraction results, but the method was very insensitive and was therefore abandoned.

A solvent was required which could be used for the extraction of molybdenum 8-hydroxyquinolate and also one

Table 9.

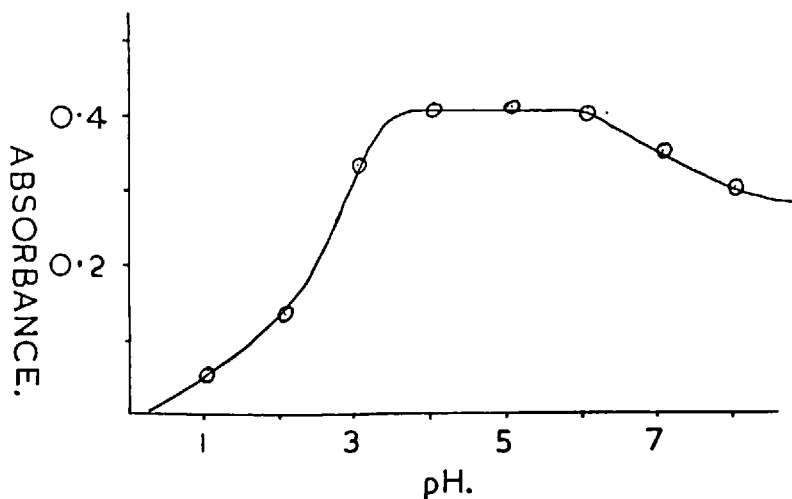
Solvent	Use with Nitrous Oxide -Acetylene Flame.	Observations
acetone	No	Destroys red zone
iso butylmethyl ketone	Yes	Acetylene flow lowered
acetylacetone	Yes	Acetylene flow lowered
methanol	No	Destroys red zone
ethanol	Yes	Acetylene flow lowered
n-propyl alcohol	Yes	Acetylene flow lowered
iso-propyl alcohol	Yes	Acetylene flow lowered
n-butanol	Yes	No effect on red zone
allyl alcohol	Yes	Acetylene flow lowered
hexanol	Yes	Acetylene flow lowered
10% glycerol in water	Yes	Acetylene flow lowered
2-butoxy ethanol	Yes	Acetylene flow lowered
amyl alcohol	Yes	No effect on red zone
ethyl acetate	No	Destroys red zone
iso amyl acetate	Yes	Acetylene flow lowered
diethyl ether	No	Destroys red zone
pet. ether 40/60	No	Destroys red zone
pet. ether 100/120	No	Destroys red zone
n-butylamine	Yes	Acetylene flow lowered
diethylamine	No	Destroys red zone
ethylenediamine	Yes	Acetylene flow lowered
dimethylformamide	Yes	Acetylene flow lowered
dioxan	Yes	Acetylene flow lowered
cyclohexane	No	Destroys red zone
cyclohexanone	Yes	No effect on red zone
benzene	No	Destroys red zone
chloroform	No	Destroys red zone

which could be sprayed into the flame satisfactorily. An investigation into the effect of various solvents on the nitrous oxide - acetylene flame was performed, and the results shown in Table 9.

n-Butanol was chosen for use since no decrease in the acetylene flow was required and a very fine spray was obtained along with an enhancement in nebuliser efficiency.

Effect of pH.

Fig. 14 shows the variation in absorbance readings of the organic phases with change of pH of extraction.



Complete extraction of molybdenum 8-hydroxyquinolate into n-butanol is obtained, within the pH range 2.0 to 5.0.

This was shown by spraying both organic and aqueous phases into the flame. The absorbance values of organic layers produced the curve above. The aqueous layers produced no absorbance signal showing that there was no molybdenum left

in the aqueous solution. This is as expected since molybdenum 8-hydroxyquinolate is very stable. The extraction is not affected at pH 4.5 by the presence of large amounts of fluoride ion, niobium, tantalum and E.D.T.A.

Shaking Time for the extraction.

Complete extraction occurred after shaking for $1\frac{1}{2}$ minutes, thus this shaking time was adopted for the extraction procedure.

Organic solvent effect.

The solubility of n-butanol (S.G. 0.8) in water is appreciable (7.9 g. per 100 ml. at 20°C). Thus an aqueous phase volume of 220 ml. at the room temperature should dissolve about 20 ml. of n-butanol. The high ionic strength of the aqueous phase, containing fluoride, niobium (or tantalum) and E.D.T.A., suppresses the solubility of n-butanol and after equilibration of 20 ml. of n-butanol with 220 ml. of the aqueous solution at room temperature, 4 ml. of organic phase remain after separation. This phase volume is quite reproducible over the normal range of laboratory temperatures encountered. The use, therefore, of 25 ml. or 30 ml. of n-butanol for the extraction drastically decreases the absorbance signals, since the final volume is effectively doubled and trebled by the additional n-butanol giving correspondingly lower signals.

After extraction of the molybdenum (vi) 8-hydroxyquinolate into butanol at pH 4.5 the solution was allowed to stand for 15 minutes for complete phase separation to occur. The aqueous layer was rejected and the n-butanol phase was cloudy and contained solid material. Blank solutions which had contained no molybdenum produced clear n-butanol phases. This indicated that the solid material in these n-butanol phases was molybdenum 8-hydroxyquinolate, and it was identified by filtering off, ashing and testing the dissolved residue, molybdenum trioxide, with 2-amino-4-chlorobenzenethiol hydrochloride (62).

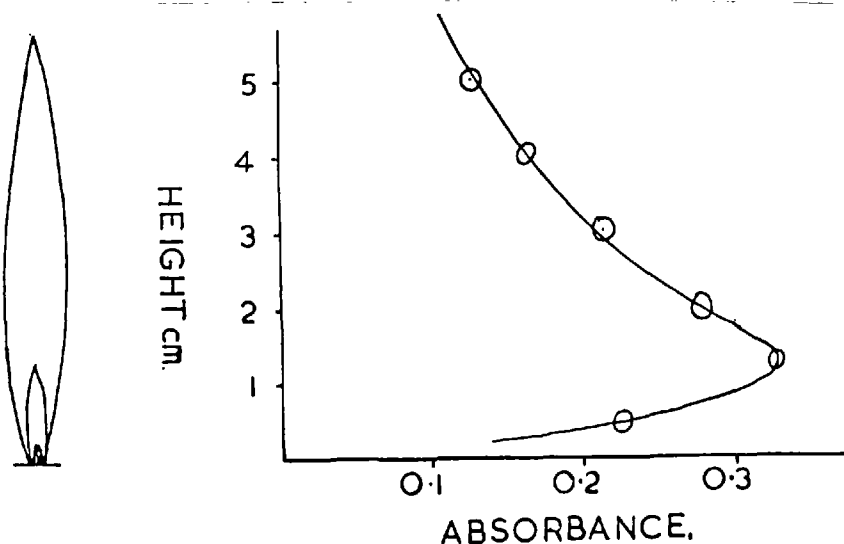
The precipitate of hydrated molybdenum 8-hydroxyquinolate gave rise to poor reproducibility and lack of sensitivity when the n-butanol phases were aspirated for absorbance measurements. 5 ml. of n-butylamine were thus added to each n-butanol phase after separation. The amine displaces the water molecules co-ordinated to the molybdenum in the chelate and thus assists the solubility of the complex in n-butanol. This addition also causes an improvement in the reproducibility of the absorbance measurements as the dissolution renders the system homogeneous. Addition of n-butylamine also results in an enhancement in sensitivity even after allowing for the dilution effect. This is explained by the higher spray rate and increase in nebuliser efficiency which are obtained by using the n-butanol - n-butylamine mixture.

Flame type.

The flame used was obtained by burning acetylene and nitrous oxide in the following ratio: Acetylene flow-rate 4 litres/min. and nitrous oxide 6 litres/min.. The largest red feather region was obtained without any yellow luminosity from the carbon continuum. The height of light path through this flame is critically important, as is the actual gas mixture being burned.

For best absorbance values for molybdenum as much of the radiation as possible from the hollow cathode lamp must pass through the red region of the flame.

Fig. 15 shows an Absorbance v. Height profile of the flame.



The decrease in absorbance signal above the red zone is very pronounced. The blue secondary zone of the nitrous oxide - acetylene flame is oxidising in nature, as are those of the

air/acetylene and air/propane flames, and other flames of hydrocarbons with air. The oxidising region is hotter, however, than the oxidising secondary zones of most other flames. It is obvious from this profile that the red feather region of this flame is all-important. This region must provide the high-temperature and reducing conditions required for the production of ground state molybdenum atoms.

The need for this red zone was further demonstrated by adjusting the fuel to nitrous oxide ratio. Decreasing the acetylene flow-rate reduced the size of the red feather until finally it appeared as a red line above the primary reaction zone. Under these conditions, the atomic absorption of molybdenum is very insensitive although the flame temperature above the primary reaction zone is still high. This, however, slightly increased the absorption signals, due possibly to the additional reducing atmosphere provided by the carbon in the flame, which assists the reaction

$$\text{MO} + \text{C} \longrightarrow \text{CO} + \text{M}.$$

The use of a highly luminous flame is not desirable since the burner soon becomes unusable owing to carbon formation at the slit, and also the background noise level is increased. The sensitivity obtained from the non-luminous flame is sufficiently high for our purposes.

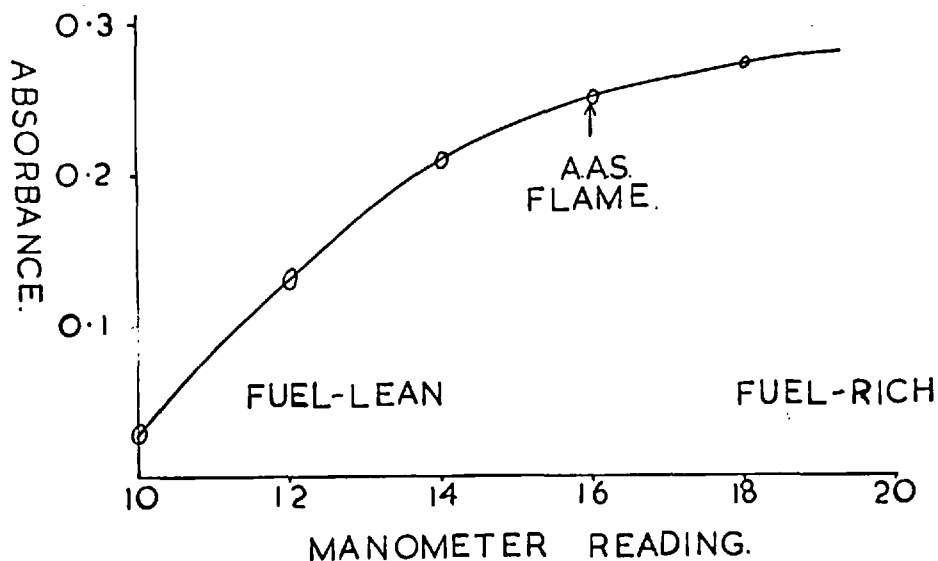


FIG.16

Lamp and Flame emission.

Fig.17 shows the emission from the red feather zone, and considerable flame emission is observed from the 3064 Å OH band system. This occurs in the wavelength region of the molybdenum 3132 Å resonance line and may give rise to background noise in the atomic absorption determination of molybdenum. However, the emission from the molybdenum hollow cathode lamp, fig.18, through the flame is so intense that the noise level from the OH emission is negligible.

Emission from CN in the red zone would probably cause a serious noise problem if the molybdenum resonance line at 3798.3 Å were used, due to overlapping by the strong 3883 Å CN band.

FIG. 17

3064A

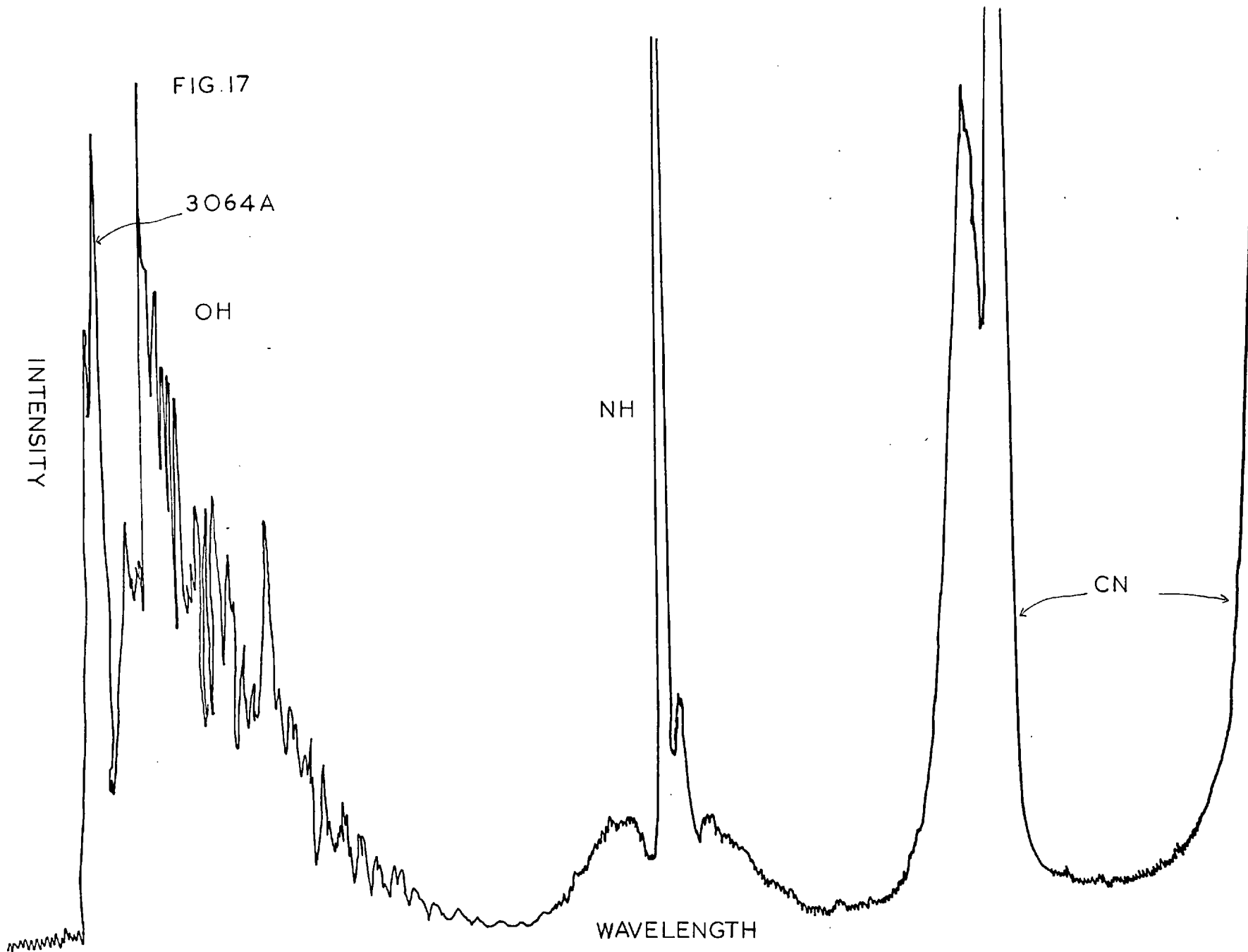
OH

NH

CN

INTENSITY

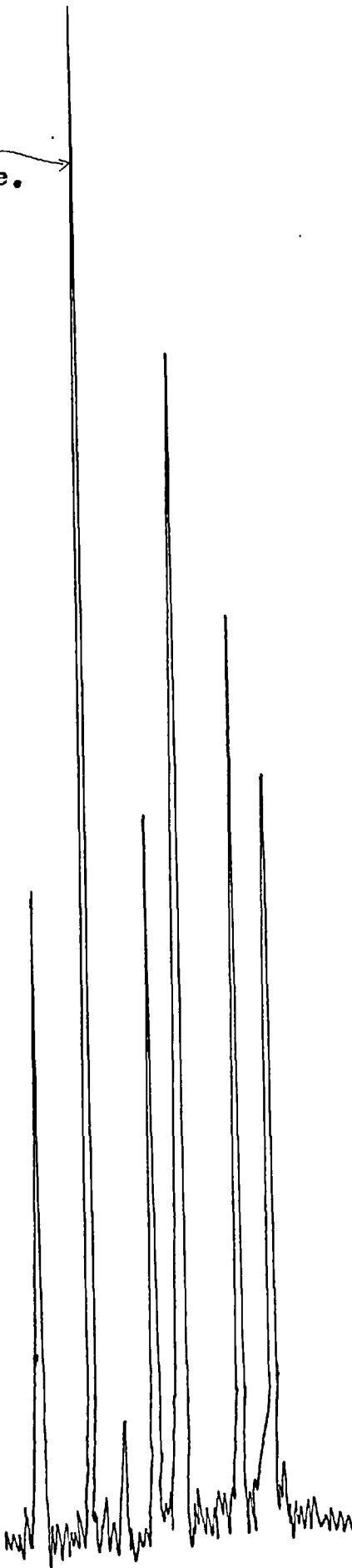
WAVELENGTH



Molybdenum 3132A
resonance line. →

FIG.18

Flame background
noise level.



Calibration curves and sensitivity.

The curves, see Fig.19a,b, obtained using the recommended procedure are linear in the range 96 to 960 μg of molybdenum, corresponding to added 64 to 640 p.p.m. (0.006% - 0.064%) of molybdenum in the 1.5 gm. of niobium or tantalum metal sample taken. The absorbance values corresponding to these concentrations are 0.07 and 0.735 for molybdenum in niobium, and 0.067 and 0.710 for molybdenum in tantalum. Both the calibration curves pass through the origin showing that the niobium and tantalum samples available to us contained no molybdenum.

The lowest amount of molybdenum determined corresponded to 0.0064% i.e. 64 p.p.m. It is unfortunate that molybdenum had to be added to the refractory element in solution to provide 64 p.p.m. solution of molybdenum in niobium and tantalum i.e. 64 μg of molybdenum in 1 g. of tantalum or niobium. Taking a larger sample of niobium or tantalum, say 9 g. in the same volume would effectively increase the sensitivity 6 times, and if scale expansion had been available to us, as reported by David⁽⁵⁷⁾ for the determination of molybdenum in luminous air-acetylene, the determination of 5 - 10 p.p.m. of molybdenum in niobium and tantalum would have been possible using this method.

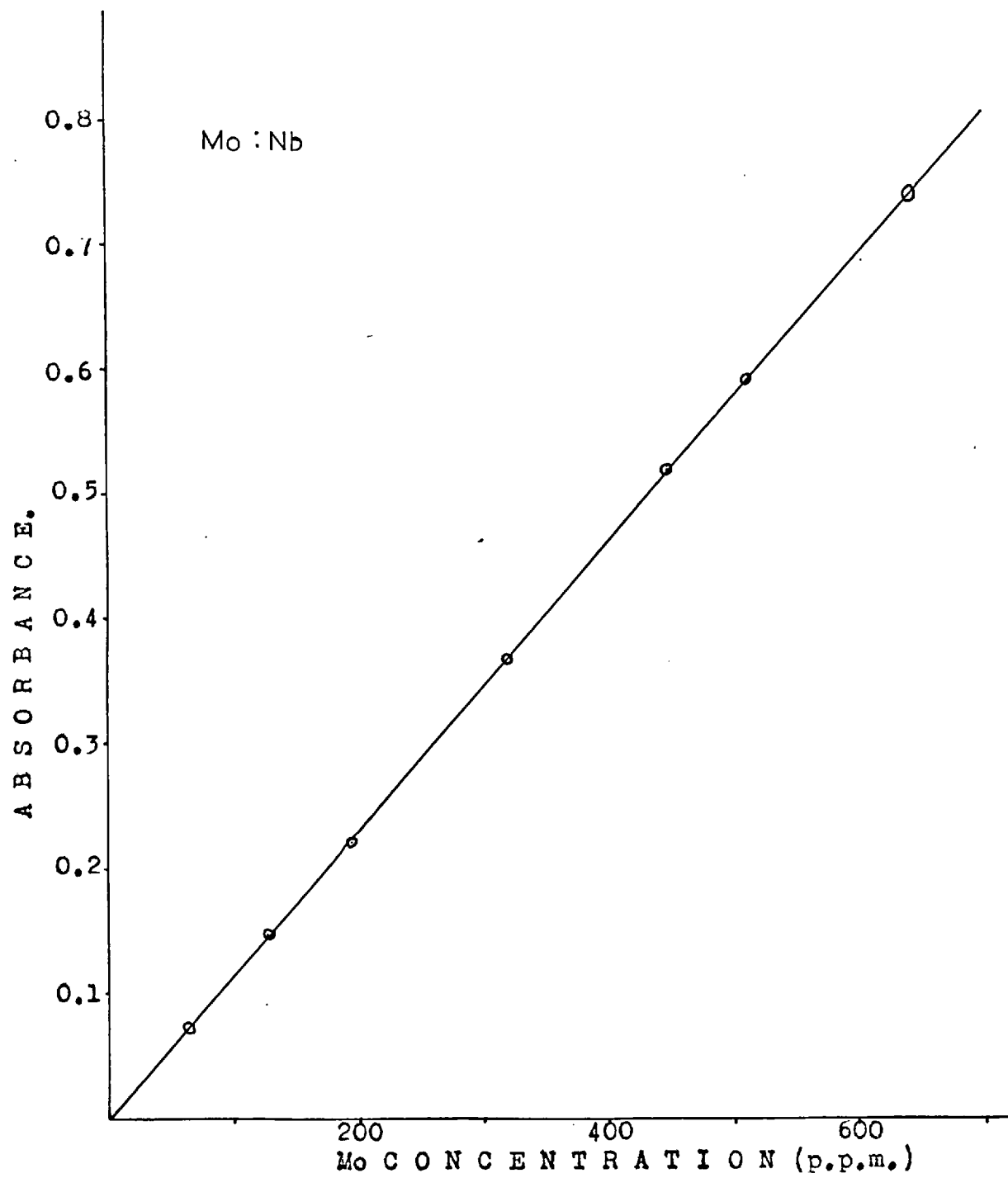


FIG.19a.

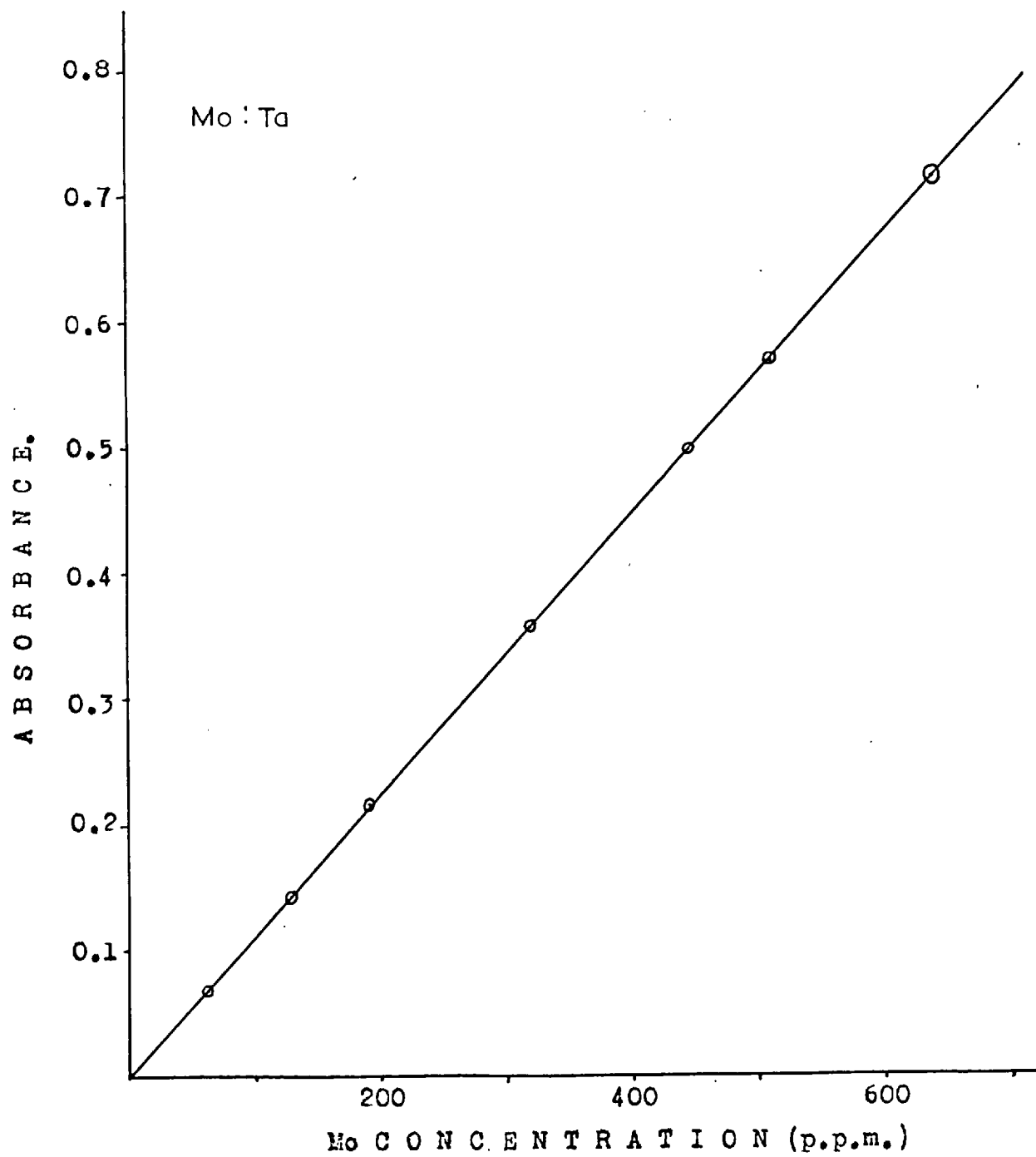


FIG.19b.

Recommended Procedure.

Transfer 1 - 10 ml. aliquots of 10^{-3} M (96 p.p.m.) molybdenum solution to a series of 500 ml. separating funnels. Add to each solution 150 ml. of the 10,000 p.p.m. niobium (or tantalum) solution, 10 ml. of 0.1M E.D.T.A. solution and 50 ml. of the 1 percent 8-hydroxyquinoline reagent-buffer solution. Add 20 ml. of n-butanol to each funnel and shake for $1\frac{1}{2}$ minutes. Allow the solutions to stand for 15 minutes for complete phase separation and discard the lower aqueous layer. Add 5 ml. of n-butylamine to each organic phase and shake for $1\frac{1}{2}$ minutes. Spray the clear organic phase directly into the nitrous oxide - acetylene flame for absorbance measurements at the 3132 Å line, against a butanol solvent blank. The use of a butanol-butylamine mixture is not necessary because it does not affect the absorbance readings.

Sample preparation.

Dissolve 1.5 g. of niobium or tantalum in 4.5 ml. of 40% hydrofluoric acid and nitric acid (S.G. 1.42) 0.5 ml. for tantalum and 1.75 ml. for niobium. Dilute to 75 ml., adjust to pH 4.5 with 4M ammonia solution, and then dilute to 150 ml. with distilled water. These samples may be assumed to contain molybdenum which goes into solution as the sample is prepared. The samples are then used as in the recommended procedure without the addition of more molybdenum.

Precision and Accuracy.

The precision of the method was determined by analysing nine simulated niobium samples and nine tantalum samples containing the equivalent of 320 p.p.m. of molybdenum by the recommended procedure. The mean absorbance of the molybdenum in niobium method being 0.322 and the standard deviation being 2.8%. For the molybdenum in tantalum procedure the mean absorbance was 0.326 and the standard deviation 1.9%.

A measure of the accuracy was obtained by the determination of molybdenum in synthetic niobium and tantalum solutions treated as unknowns. The results of these analyses are shown in Table 10.

Interferences.

The effect of foreign ions on the determination was studied by observing their influence on the absorbance produced in the determination of 480 $\mu\text{g.}$ of molybdenum in niobium and tantalum. For the purpose of this study, an ion was considered not to interfere if an error in absorbance of less than 5% was produced. In the presence of 10 ml. of 0.1M E.D.T.A. and 0.6M fluoride solution, the presence of a 100-fold excess by weight of the following ions produced no interference : aluminium, calcium, cobalt(ii), copper (ii), iron (iii), mercury (ii), potassium, magnesium, manganese (ii), sodium, ammonium, nickel (ii),

Table 10.Determination of Molybdenum in Niobium and Tantalum Solutions.

Molybdenum present per cent x 10^{-2}	Molybdenum found per cent x 10^{-2}	Metal present
3.2	3.0	tantalum
4.5	4.7	tantalum
5.1	5.1	tantalum
1.9	1.9	tantalum
3.2	3.4	niobium
4.5	4.7	niobium
1.9	1.9	niobium
3.5	3.6	niobium
2.3	2.3	niobium

lead, tin (iv), titanium (iv), thorium, tungsten (vi), zinc, zirconium, acetate, chloride, fluoride and sulphate. The presence of a 100-fold excess of V(v) and Cr (vi) caused low results, but this was eliminated by the addition of 2 g. of potassium sulphite to the aqueous solution and boiling to promote the formation of Cr(iii) - E.D.T.A. complex.

Molybdenum (vi) is not reduced under these conditions and this was checked by observing no difference in the molybdenum absorbance for synthetic mixtures of molybdenum with niobium and tantalum in the presence and absence of potassium sulphite. The vanadium (v) is easily reduced to the vanadium (iv) - E.D.T.A. complex. Thus the presence of fluoride ion and the addition of E.D.T.A. and potassium sulphite, make the method specific for the determination of molybdenum at pH 4.5. This is principally due to the production of a very stable molybdenum (vi) 8-hydroxy-quinolate complex and the fact that molybdenum (vi) does not form a stable E.D.T.A. chelate at the pH used.

CHAPTER 4.

SPECTROGRAPHIC INVESTIGATION OF THE NITROUS OXIDE -
ACETYLENE FLAME.

The number of elements which can be determined with good sensitivity by atomic absorption spectroscopy has increased rapidly since the introduction of the nitrous oxide-acetylene flame. Elements such as molybdenum, tungsten, and aluminium, which previously caused great difficulty can be determined easily in this flame. In the more conventional hydrocarbon flames supported by air these elements form refractory compounds which are insufficiently dissociated to yield sufficient ground state atoms for absorption measurements.

In the author's studies on copper and molybdenum, three different premixed flames were used. These were air-propane, air-acetylene, and nitrous oxide-acetylene. It is possible to determine copper in any of these flames, since all produce ground state copper atoms owing to their relatively high temperature and the instability of copper oxide under these conditions. The sensitive determination of molybdenum, however, could only be performed using a nitrous oxide-acetylene flame. The enhancement in sensitivity shown by the nitrous oxide-acetylene flame compared with the luminous air-acetylene flame must arise from the production

of a larger population of free metal atoms in the ground state. There is little evidence in the literature for the cause of the effectiveness of this flame in the production of ground state atoms.

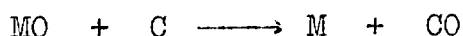
Amos and Willis⁽⁶³⁾ proposed that the combustion reactions involved in the stoichiometric flame were :



i.e. the nitrous oxide decomposes and the fuel gas burns in the liberated oxygen, and the high temperature of the flame is due to the absorption of the energy liberated in the decomposition of the nitrous oxide. The maximum temperature of this flame has been quoted as 2955°C ⁽⁶⁴⁾. This is the sole value in the literature, and it is not clear whether this represents a calculated value of the maximum thermodynamic temperature or one which has been obtained practically. If it is a practical value, no data are available concerning the type of burner at which the flame was supported, nor the mixture conditions nor the region of the flame which produces this value. The effectiveness of the flame for atomising refractory elements has been ascribed to this high temperature of 2955°C (cf. air-acetylene 2300°C). In obtaining this flame, however, more oxygen is supplied for the acetylene combustion by the decomposition of the

nitrous oxide than is used in the air-acetylene flame. The excess oxygen available in the flame might be expected to favour the formation of refractory species and this production of refractory compounds would probably outweigh the ability of the high temperature flame to dissociate the refractory oxides.

The existence of free atomic carbon species in the flame, providing the necessary reducing conditions, is a more important cause of the production of ground state atoms. Such a mechanism has been suggested by Gilbert⁽⁶⁵⁾ and Sternberg⁽⁵⁶⁾ and has also been put forward by Amos and Thomas⁽⁶⁶⁾ to explain the success of the oxy-acetylene flame in the atomic absorption of aluminium. The refractory oxide is reduced by the carbon species to produce ground state atoms of the element :



MO is the refractory oxide form of the metal M. The carbon must be provided immediately above the primary reaction zone, and will produce the yellow luminosity characteristic of fuel-rich hydrocarbon flames.

The nitrous oxide-acetylene flame, however, provides good sensitivity for refractory elements without the need for a luminous yellow flame. The characteristic red feather of the nitrous oxide-acetylene exists in slightly fuel-rich flames. The red zone, between the primary reaction

zone and the outer blue diffusion flame has a definite reaction front of its own, and is clearly a secondary reaction zone. This is the region of the flame which provides the sensitivity increase for refractory elements, and in the majority of instances when this flame is used for atomisation, absorption measurements are made within the red zone.

We have conducted a spectrographic investigation of the emission from various regions of the nitrous oxide - acetylene flame, using different fuel:support gas ratios, and in the presence or absence of elements which form refractory oxides or are difficult to determine in flames of hydrocarbon mixed with air. Particular attention was paid to the red 'feather' region. Gibson, Grossman and Cooke⁽⁶⁷⁾ have shown that the emission intensity is closely related to the ground state concentration of the species concerned, and these investigations are therefore relevant to the interpretation of absorption processes in the flame. The main molecular and atomic species which exist in each region of the flame have been identified. An attempt has been made to account for the analytical utility of the flame and a mechanism proposed for the production of some of the reducing species found in the flame.

Experimental.

Apparatus.

Nitrous oxide - acetylene burner.

The design of this burner has been shown previously, see Fig. (13). It comprises two stainless steel plates separated by spacers 0.015 inches wide, to provide an aperture 0.015 inches by 2 inches. These plates are mounted onto a stainless steel base and premixing chamber, and this burner was not water-cooled. The flame was first lit using an air-acetylene mixture and the change to nitrous oxide - acetylene made by replacing the air gradually with nitrous oxide via two rotameters and a T-piece. The aqueous samples were introduced into the flame using a Hilger and Watts nebuliser and expansion chamber, and aspirating with the nitrous oxide used for combustion.

Spectrographic Equipment.

A Hilger large quartz spectrograph was used and the burner mounted so that it was in the 'end-on' position, i.e. an image of the 0.015 inch side of the flame was presented to the spectrograph slit. This burner position was used so that a greater intensity of radiation from the flame was received at the spectrograph than when the flame was in the 'broadside-on' position. Care was taken to recognize the possibility of self-absorption of the flame

radiation with the burner in this position, but this arrangement has the great practical advantage that it allows much shorter exposure times to be used because of the increased intensity obtained. Exposures were made on Kodak B.10 or Ilford N.30 and R.40 plates depending on the wavelength range to be examined and the speed required. The plates were developed under standardised conditions with Ilford I.D.36 developer and Hypam fixer. The line intensities where necessary were measured using a Hilger photomicrodensitometer.

Metals were generally introduced into the flame as 10^{-1} or 10^{-2} M aqueous solutions of their nitrates, chlorides and sulphates.

Procedure.

Spectra of different types of nitrous oxide - acetylene flames were first obtained. Some of these spectra were of the whole flame, and in other cases various regions of the flame were focussed on the spectrographic slit. The three types of flame investigated were the atomic absorption flame (i.e. slightly fuel-rich with maximum red feather), the fuel-lean flame, and the fuel-rich flame. Spectra were obtained from 6700 Å to 2200 Å and the exposure times varied for the different flames.

Results.

Fuel-lean flame.

These were obtained at a nitrous oxide flow rate of 6 litres/minute, and an acetylene flow rate of 3.6 litres/minute, and appear as fig. 20a. They comprise only two zones, the intense white-blue primary reaction zone and the blue outer diffusion zone, which is characteristic of all hydrocarbon-air flames. The characteristic blue colour of this outer zone arises from the banded continuum chemiluminescence of the process $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$.

The emission spectra of the fuel lean flame are shown in fig. 21.3a. The species which have been indentified in emission in the primary zone are OH, NH, CH, CN, C_2 and NO. The only species which emits in the outer zone is OH, which shows heads at 2811 Å from the ${}^2\Sigma^- - {}^2\Sigma (1,0)$ transition, and 3064 Å [${}^2\Sigma^- - {}^2\Pi (0,0)$ transition] along with the CO continuum described previously, which produces the emission between 3000 and 5000 Å.

The emitting species found in the primary zone will be described in more detail later. Comparison of the fuel lean nitrous oxide-acetylene flame with a lean acetylene-air flame shows that the species present in the two zones are the same in each, with the exception that NO could not be identified in the air-acetylene flame. The only difference between the two spectra is that the intensity from these species is

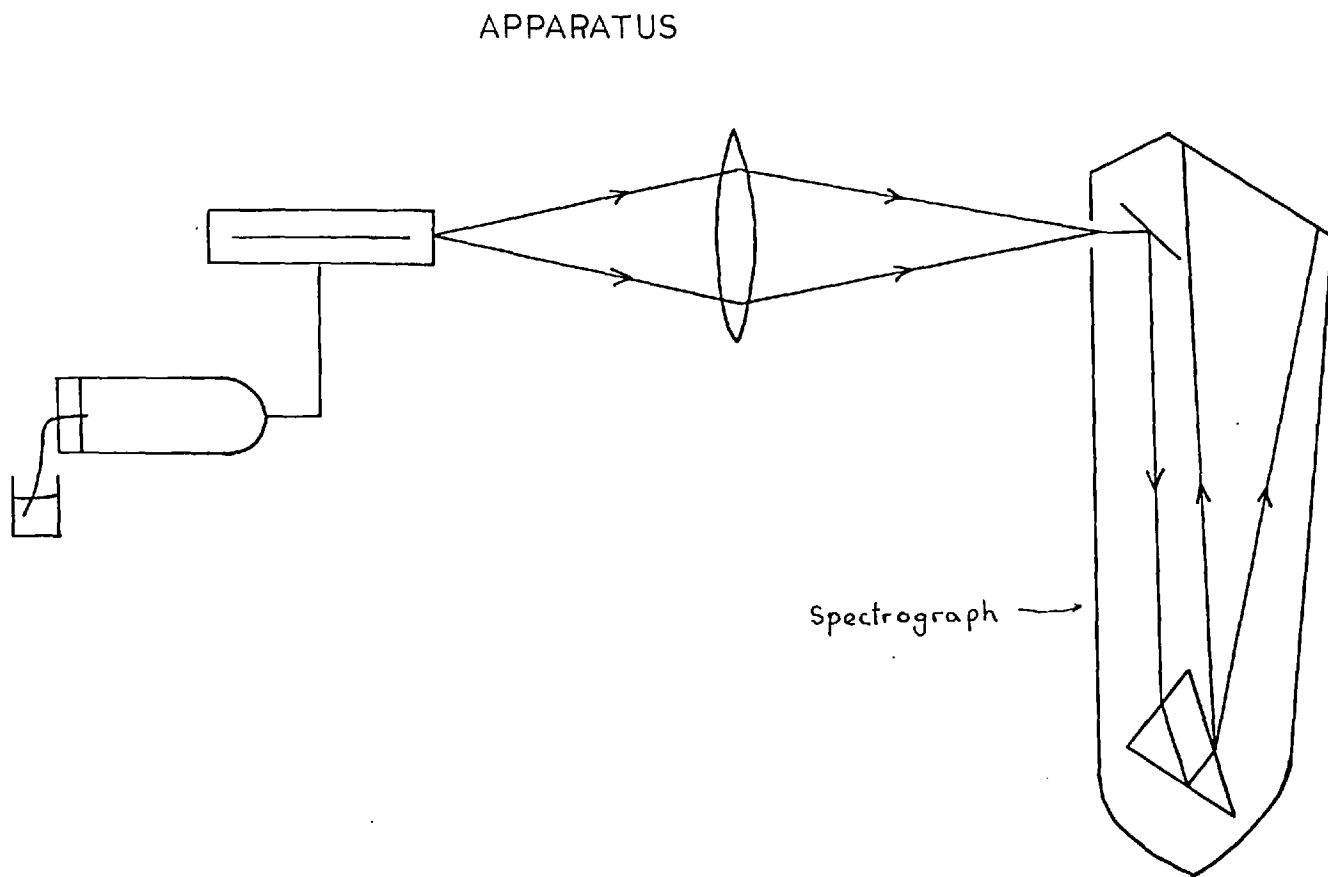
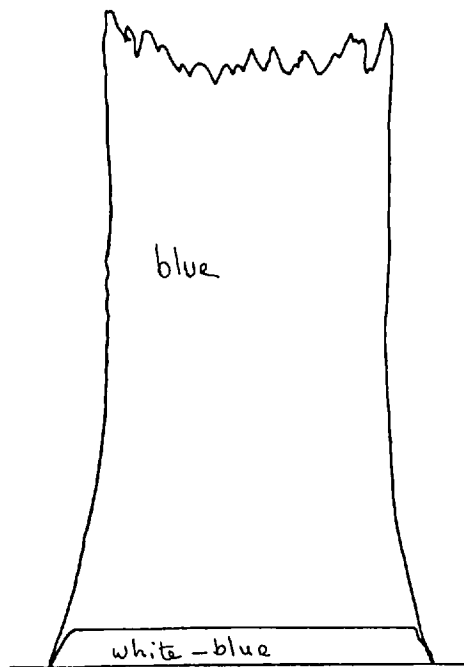


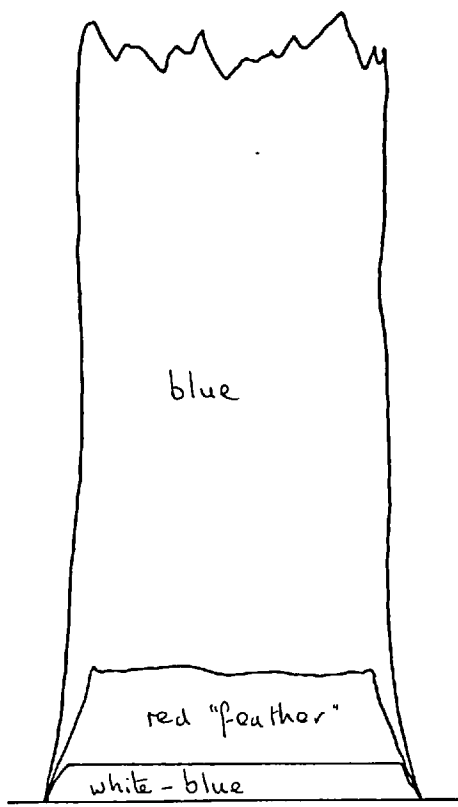
FIG. 23

fuel-lean



a.

atomic-absorption



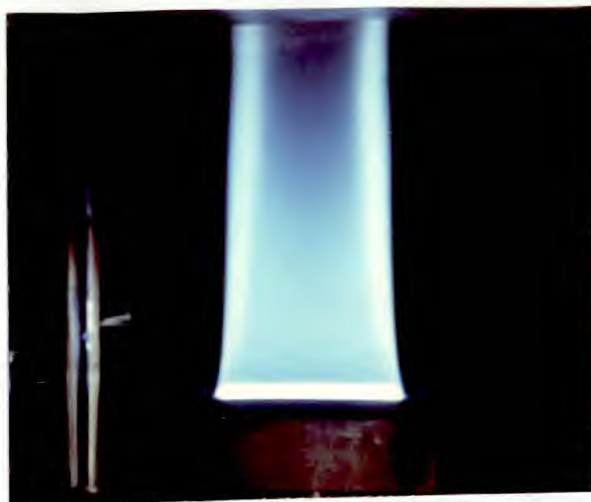
b.

fuel-rich

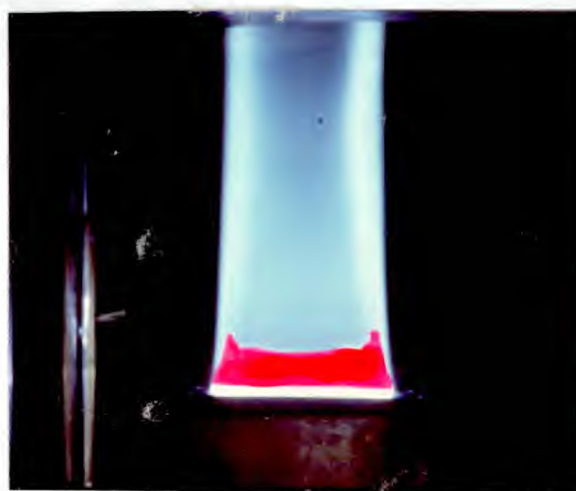


c.

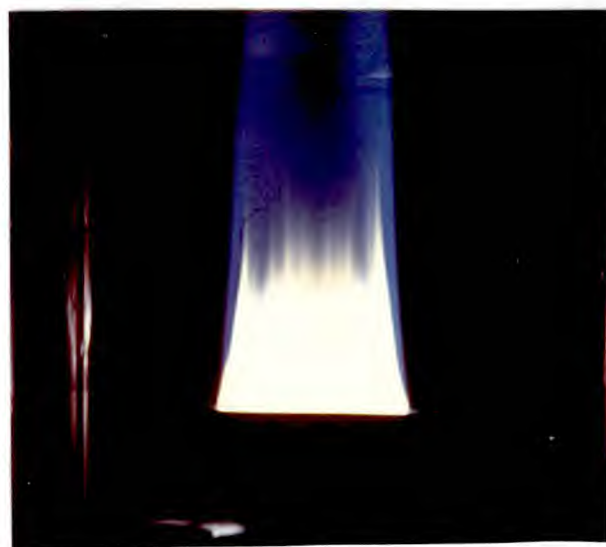
FIG.20



a



b

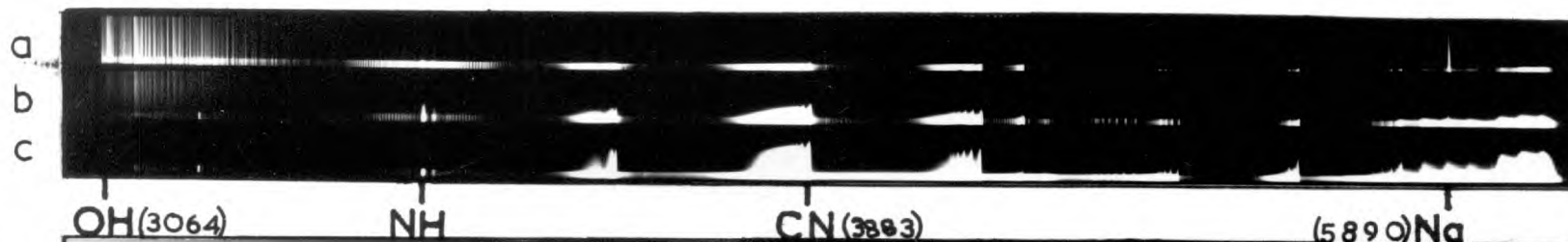


c

FIG. 20.

3.

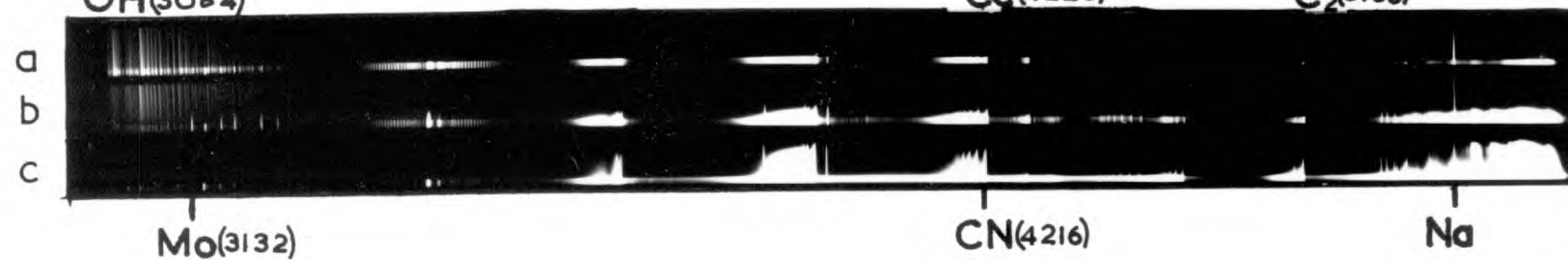
FIG. 21

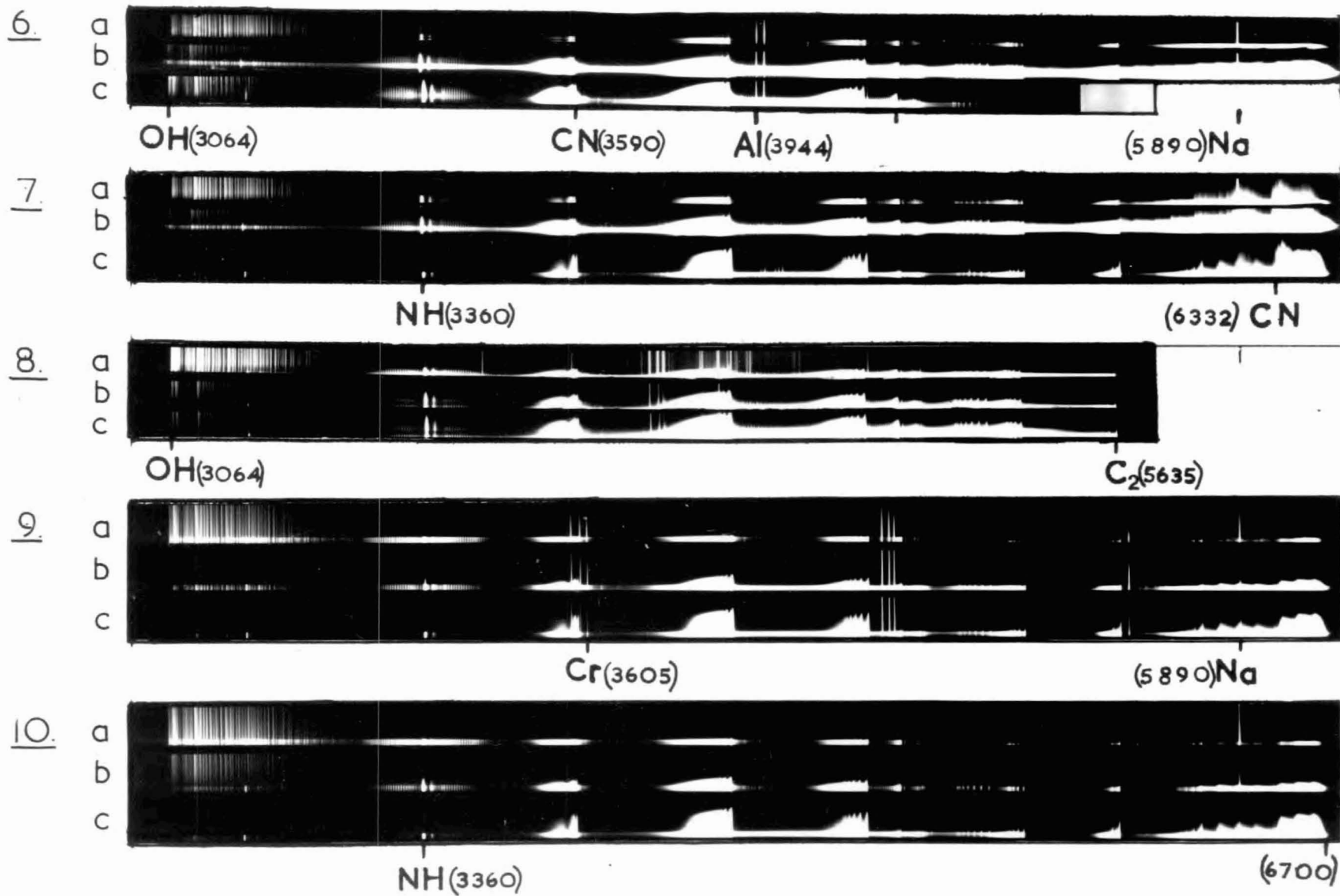


4.

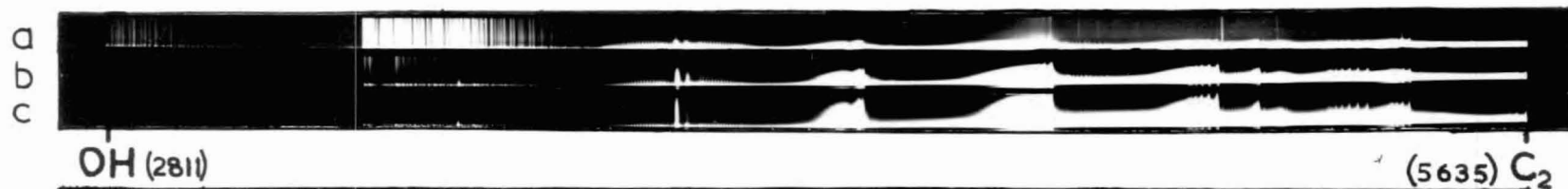


5.

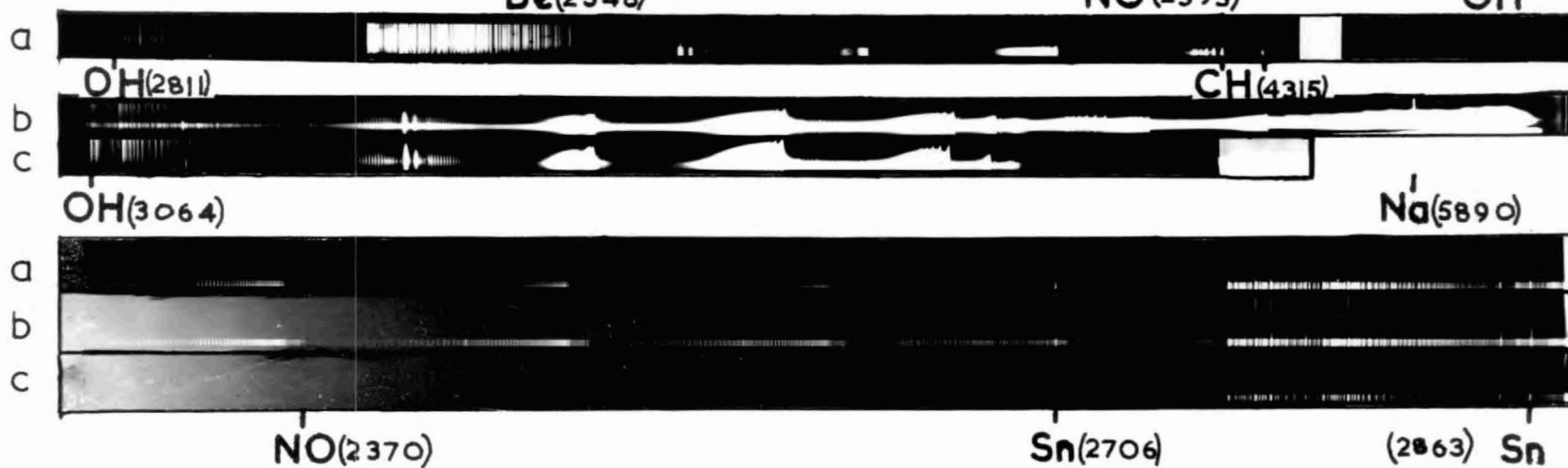




11.



12.



greater in the nitrous oxide-acetylene flame owing to the higher excitation energy available in the hotter flame plasma.

Atomic Absorption Flame.

This flame, which has been used for the determination of molybdenum, was obtained using flow rates of 6 litres/minute of nitrous oxide and 4 litres/minute of acetylene. As previously described, the flame consists of three distinct zones, (a) the white-blue primary reaction zone, (b) the 'red feather' zone, which is the secondary reaction zone, and (c) the outer blue diffusion zone, see fig. 20b.

The emission spectra of this flame over the wavelength range 2800 - 6700 Å are shown in fig. 21.3b. This flame, which is slightly fuel-rich, gives emission from the same species as the fuel-lean flame in the primary and outer zones, and therefore resembles most premixed flames of hydrocarbons and air. The OH emission in the outer zone is weaker than in the lean flame as is the CO continuum. This is to be expected since there is less oxygen available for the combustion of CO since the flame is slightly fuel-rich.

More attention was paid to the 'red feather' zone, which exists between the primary and outer zones, as a definite secondary reaction zone with its own reaction 'front'. The height of this zone could be as much as 2 cm., and was proportional to the amount of acetylene supplied to the flame. The predominating species which emit in this red zone are NH

and CN, the latter giving the stronger emission. The CN red and violet systems are clearly visible. The violet system has heads at 3590 Å, 3883 Å, and 4216 Å degraded to the violet, the 3883 Å(0,0) sequence being the strongest. The 3590 Å(1,0) sequence, often shown in hot flames containing nitrogen is clearly observed and is free from major overlapping features. The 4216 Å(0,1) head is not generally seen since it is frequently obscured in many flames by the 4315 Å(0,0) CH system, but as can be seen in the emission spectrum this sequence is well defined. The CN red system is visible but owing to the loss of dispersion of the quartz prism in the red region of the spectrum, the heads are not as well defined as those of the violet system. However, heads at 5730 Å(6,1), 5858 Å(7,2), 6191 Å(4,0), 6332 Å(5,1) and 6468 Å(6,2) are easily identified, and these heads are similar to those obtained in the oxy-cyanogen flame⁽⁶⁸⁾. Only the strongest NH sequence, the (0,0) ($^3\Pi - ^3\Sigma^-$) 3360 Å head is visible, but the emission from this head is intense and persists throughout the red zone.

Emission from CH molecules is restricted to the base of the red zone, immediately above the primary reaction zone. The 4315 Å(0,0) head is the strongest and arises from the transition $^2\Delta - ^2\Pi$, and is weakly degraded to the violet. The 3900 Å system $^2\Sigma^- - ^2\Pi$ of CH is shown degraded to the red and its rotational structure is quite open. The 3143 Å $^2\Sigma - ^2\Pi$

system, the weakest CH head, cannot be observed easily in the red zone, but it can be observed in the primary zone. This head is usually obscured by the rotational structure of the 3064 Å OH system, as is the case in the red zone.

C_2 emission manifests itself only at the base of the red zone. The heads are quite strong and are degraded to the violet. Heads at 4737 Å, 5165 Å, and 5635 Å are observed from the (1,0), (0,0) and (0,1) transitions respectively.

The NO bands observed in the primary reaction zone persist into the base of the red zone, and bands of the γ system of NO are observed at 2370 Å (0,1), 2478 Å(0.2) and 2595 Å(0,3). The (0,2) head prevents the detection of the 2478 Å atomic carbon line reported to exist in very hot carbon rich flames.

Emission from OH is weaker in the red zone than in the primary and diffusion zones. The OH intensity also appears weaker at the base of the red zone and strengthens further up the zone. Heads are observed from OH at 3064 Å and 2811 Å.

The species responsible for the red emission of the 'feather' of the flame is undoubtedly CN, and this species, together with NH, is present in great abundance throughout the red zone **as it has** been observed in absorption against CN emission from a carbon arc background. C_2 , CH, and NO all exist at the base of the zone and their disappearance coincides with the position in the red zone where OH emission is weakest.

Fuel-rich flame.

This flame was obtained with flow rates of 6 litres/minute of nitrous oxide and 4.6 litres/minute of acetylene, and appears as fig. 20c, comprising two visible zones, the primary zone and the yellow luminous zone. Although emission similar to that from the red zone is observed, the yellow luminosity from the incandescent carbon particles prevents any red zone being seen. The emission spectrum of the fuel-rich flame is shown in fig.21.3c, and there is little difference between the emission from this flame and that of the atomic absorption flame. The whole of the visible region, as expected, is overlaid by a continuum emission from the yellow luminosity. The δ NO and OH systems are further weakened in this very fuel-rich flame, presumably due once again to the smaller proportion of oxygen available. It is possible to identify the CN and NH sequences which emit strongly in this flame. These sequences persist higher up the flame than in the atomic absorption flame.

C_2 and CH emission is present, but found to be relatively weak, and the red CN emission is obscured to a large extent by the luminous carbon continuum.

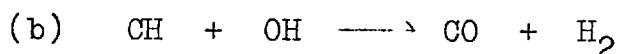
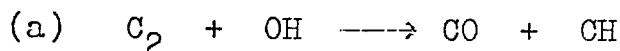
Discussion.

The same species are found in the primary zone for the three types of flame, though the emission intensity varies slightly. NO and OH emission is stronger in fuel-lean flames

than in the fuel-rich flames for the outer blue diffusion zone, there is only emission from OH and CO. The OH is produced from atomic hydrogen which must be present in the red zone, and which burns in the atmospheric oxygen forming OH. In the atomic absorption and fuel-rich flames, very strong emission is observed from CN and NH in the secondary zone.

In the primary zone of the atomic absorption flame, emission from NO, CN, NH, OH, C₂, and CH is observed. As these species proceed into the red zone only CN and NH emit strongly: NO, C₂, and CH emission is confined to the base of the red zone, and at this point in the flame OH emission is weakened. In the blue secondary zone, only emission from OH and CO is observed, see fig. 22.

From the above observations it is possible to suggest an explanation of the analytically useful properties of the red zone in slightly fuel-rich flames. The CN, NH, C₂, and CH species only occur when there is insufficient oxidant to convert all the carbon to carbon monoxide. Under these reducing conditions, the CN and NH molecules have a longer lifetime than usual and so persist throughout the red zone. The weakening of the OH emission in the red zone corresponds to the disappearance of the C₂ and CH species due to the reactions :



PERSISTENCE IN FLAME.

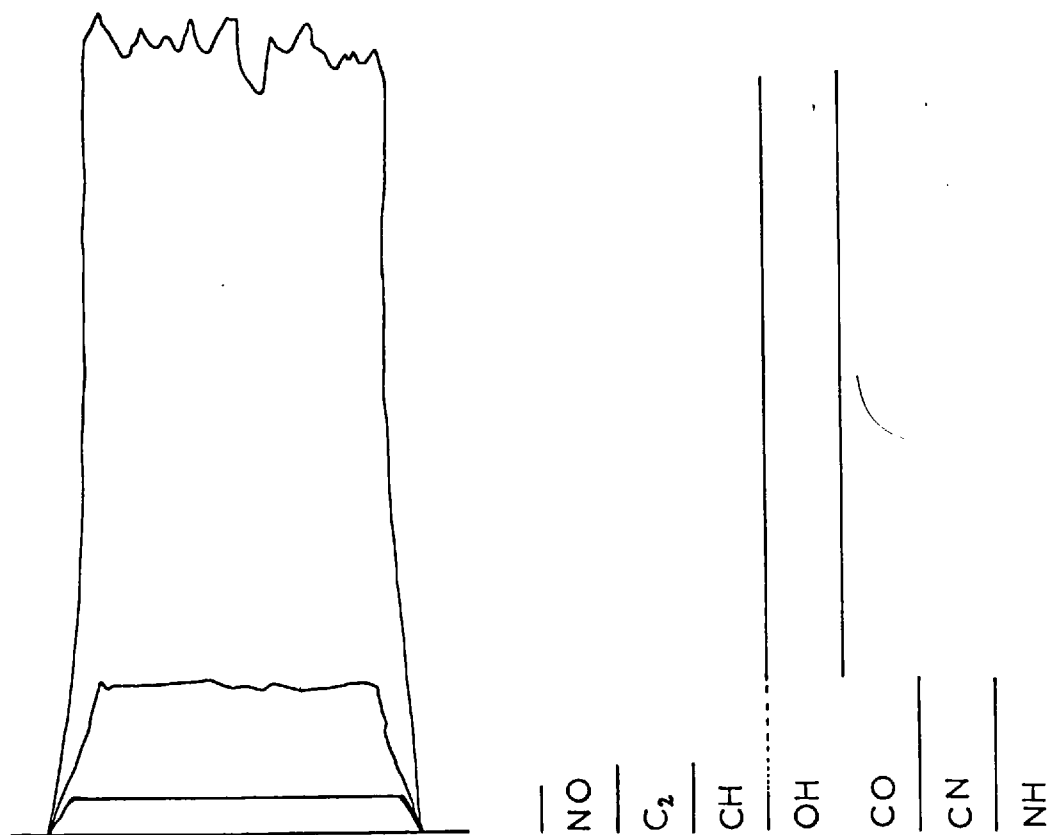


FIG. 22

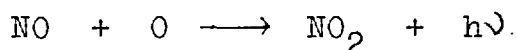
There is strong evidence to suggest that most of the CH produced in hydrocarbon flames is from C_2 as in (a) (69).

The red zone shows a clearly defined reaction front, similar to those observed by Parker and Wolfhard⁽⁷⁰⁾ in other flames supported by oxides of nitrogen. The formation of more than one reaction zone is often linked with the fact that different reactions occur at different temperatures in the combustion wave. For example, Parker and Wolfhard suggested the above mechanism to account for the production of the double reaction zones shown by flames of hydrogen burning with a mixture of nitrous oxide and nitric oxide. The second upper reaction zone is due to the burning of hydrogen with nitric oxide which requires a higher temperature than the hydrogen-nitrous oxide reaction. In the nitrous oxide-acetylene flame, the situation might be complicated by this type of effect where the nitric oxide produced in the primary reaction zone does not burn with degraded fuel molecules until well above this zone.

The red zone is not a diffusion flame since it does not depend on oxygen from the atmosphere diffusing into the zone. This may be demonstrated by sheathing the flame in argon when there is no change in the appearance or emission of the red zone. The reaction front of this zone thus appears similar to that of a premixed flame where the reactants are both present behind the reaction front.

The evidence obtained suggests that the nitrous oxide is not completely decomposed to nitrogen and oxygen in the primary reaction zone, since from the emission spectra obtained there is an appreciable quantity of NO present in this zone. This must be formed either directly from nitrous oxide at the reaction front or as a product from the initial reaction of a fuel molecule with nitrous oxide. The latter mechanism is suggested by Gaydon⁽⁶⁹⁾ since the band systems of species containing nitrogen are so strong that it cannot be explained if decomposition of the nitrous oxide to nitrogen and oxygen occurs. The formation of NO from oxygen and nitrogen is known to be a slow process in most flames.

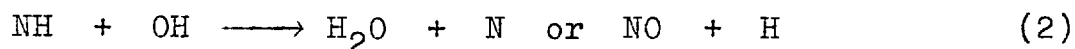
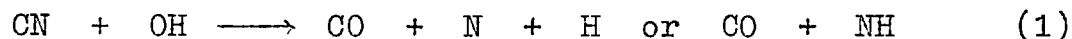
The λ NO system in the primary zone and slightly above is seen quite strongly, and there is little evidence that appreciable atomic oxygen is present. The test for atomic oxygen is to add small amounts of nitric oxide to the flame gases. A continuum from 4000 Å to the near infra-red is observed due to the reaction



if any oxygen is present. Even though the emission from NO low in the flame is quite strong there was no trace of a continuum due to atomic oxygen.

The way in which the nitrous oxide and acetylene fuel molecules react initially in fuel rich flames results in the high concentration of CN and NH species. The long

lifetimes of these species is due to there being insufficient oxidant present in the form of OH, NO or atomic oxygen to consume these species. As there is no CN or NH emission from the blue zone, all the CN and NH species must be consumed before leaving the red zone, and reactions of the following type account for their slow consumption,



Reactions (1) and (2) explain the weakening of the OH emission in the red zone. Reactions (3) and (4) account for the slow consumption of CN and NH and the disappearance of NO from the red zone and also the weakening of NO emission in the primary zone of fuel-rich flames. The production of atomic oxygen and its consumption by CN and NH (5) and (6) is described later. All the reactions account for the similar lifetimes of the CN and NH species as they both react with the same oxidant molecules, and in (3) and (4) the reactions are dependent upon the production of NO in the primary zone by the combustion of acetylene and nitrous oxide.

It seems probable that in slightly fuel-rich nitrous oxide-acetylene flames, even though the carbon atomic line has not been observed, the production of metal atoms may be assisted by the reaction postulated by Sternberg⁽⁵⁶⁾

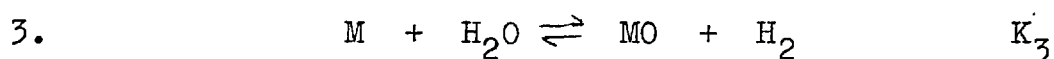
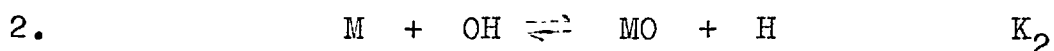
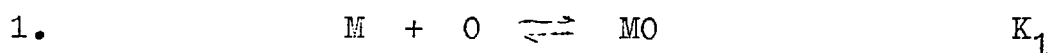


and that this occurs with elements with relatively stable monoxides in flames. Sugden⁽⁷¹⁾ has pointed out that little is known about the concentration of atomic carbon in flames, and there is no spectroscopic or mass spectrographic evidence for its presence in air-acetylene flames. Atomic carbon has been detected in the oxy-acetylene flame, but this emission does not ascertain that its concentration is high, and it may be chemiluminescent. This is suggested by the observation of Dean and Carnes⁽⁷²⁾ that its maximum emission in oxy-acetylene occurs nearly at the same point in the flame as the chemiluminescence of other species. At most the process may be effective for oxy-acetylene but even in this case it is difficult to account for the emission of several added elements in this flame by application of the above reaction⁽⁵⁶⁾. Sugden quotes the case of tin, some lines of which require excitation of 148 K cal/mole (6.42 eV), whereas only 124 K.cal/mole (5.36 eV) are available. [256 K.cal/mole (dissociation energy of CO) - 132 K.cal/mole (dissociation energy of SnO)].

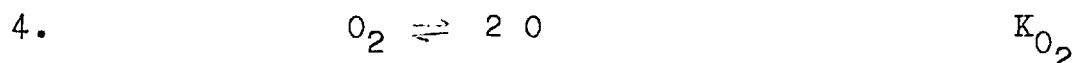
We have been unable to detect atomic carbon, at 2478 Å, spectroscopically above the primary zone of the

nitrous oxide-acetylene flame, even on prolonged exposures. Its observation in the primary zone is obscured by the NO band emission in the region around 2478 Å.

The presence of gaseous oxides in flames may be accounted for by the equilibria,



Atomic oxygen arises from the thermal dissociation of molecular oxygen,



and is linked to H and OH by



The partial pressure of atomic oxygen, P_O , may be calculated from P_{O_2} , the partial pressure of molecular oxygen, and the equilibrium constant K_{O_2}

$$P_O = (K_{O_2} \cdot P_{O_2})^{\frac{1}{2}}$$

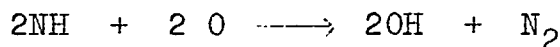
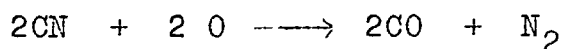
$K_{O_2} = 5.5 \times 10^{-5}$ atm. at 2360°K (air-acetylene flame temperature).

All these processes are effective, and the partial pressure of free atoms, P_M , is related to the other partial pressures by the law of mass action

$$P_M = K_1 \times \frac{P_{MO}}{P_O} = K_2 \times \frac{P_{MO} \times P_H}{P_{OH}} = K_3 \times \frac{P_{MO} \times P_{H_2}}{P_{H_2O}}$$

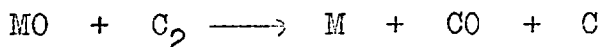
It is evident that under reducing flame conditions, i.e. when the fuel-rich flames are used, even at relatively high temperatures when dissociation of molecular oxygen is favoured, the reducing species in the flame seriously deplete the concentration of atomic oxygen, and this results in more complete dissociation of the gaseous monoxide (equ.1), by forcing the equilibrium to the right.

Therefore, in fuel-rich nitrous oxide-acetylene flames atomic oxygen may be consumed by the reactions,

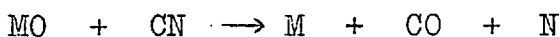
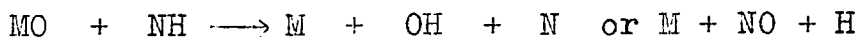


and these species may assist the free atom production by this mechanism.

Other reactions which may assist in the production of a larger ground state population in the red zone are given below.



The contribution of this reaction is small, since the C_2 emission is probably chemiluminescent and hence its actual concentration in the flame is uncertain and lower than expected. The NH and CN may also attack the metal oxides directly,



but this mechanism is not as probable as that described previously.

The effectiveness of the fuel-rich nitrous oxide - acetylene flame for the production of ground state atoms for atomic absorption spectroscopy of refractory elements, cannot be explained solely by (a) the high flame temperature available for oxide dissociation or (b) to the presence of free carbon species for the reaction $MO + C \longrightarrow CO + M$ to occur. These two conditions assist in the metal atom production, but the reactions involving CN and NH predominate in the production of free ground state atoms.

From the results for elements such as molybdenum, emission from the principal resonance lines only occurs in fuel-rich flames, and predominantly in the red feather region. Emission from fuel-lean flames is generally absent or weak.

Emission spectra of metals in the flame.

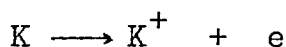
Spectra of the fuel-lean, atomic absorption and fuel-rich flames were recorded with a series of metals present in the flame, as aqueous solutions of their simple salts. The metals were chosen for examination because they are elements which are difficult or impossible to determine by atomic absorption in flames supported by air, due to the formation of refractory species which prevents their complete atomisation. The emission spectra yield information concerning the existence and position in the flame of free

excited atoms, as well as molecules, such as CaOH . Another important feature is that by looking at the spectra obtained it is possible to see if the resonance line of an element is too near to a strong emission band from the flame species. If this is so excessive background noise will be observed when attempting the atomic absorption procedure. The intensity of the emission, provided that it is thermal, rather than chemiluminescent, is closely related to the ground state concentration of the species concerned⁽⁶⁷⁾ at any given temperature, and thus information on position and intensity of emission is useful in the study of the absorption procedure.

Calcium.

The calcium emission spectra in the three types of nitrous oxide-acetylene flame are shown in figure (4a, b and c). The emission in a fuel-lean flame (4a) resembles that in hydrocarbon-air flames. Greater sensitivity for calcium determination in the nitrous oxide-acetylene flame has been reported⁽⁶³⁾, and this is attributed to a higher degree of atomisation. However, even in this flame there is a large proportion of calcium present as its hydroxide, shown by the CaOH band emission at 5498 Å and 6097 Å. The 4226 Å line most commonly used for the calcium determination is very intense throughout the whole length of the flame. The lines at 3933.7 Å and 3968.5 Å arise from the emission

of singly ionised calcium atoms, Ca^+ , and the strength of these lines bears out the observation of Amos and Willis⁽⁶³⁾ concerning the high degree of ionisation in the nitrous oxide-acetylene flame. They estimate that 43% of the calcium atoms are ionised in the nitrous oxide-acetylene flame, compared with only 3% in the air-acetylene flame. Fig.4(d) shows the calcium emission in an air-acetylene flame and the two ion lines are barely visible. The ionisation is suppressed by the addition of excess potassium chloride to the solutions, shown in Figs. (4e and f) for nitrous oxide-acetylene and air-acetylene. Potassium (Ionisation potential 4.3volts) is more easily ionised than calcium (Ionisation potential 6.1volts) and the high concentration of electrons formed by the reaction



reverses the ionisation $\text{Ca} \longrightarrow \text{Ca}^+ + \text{e}$, and thus the Ca^+ ion lines are not visible in the presence of potassium.

This technique enables straight line calibration curves to be produced.

In the atomic absorption flame and the very fuel-rich flame (Figs. 4b and 4c) calcium emission is similar to the fuel-lean flame, except that the CaOH band at 5498 Å is narrower in the fuel-rich flame, suggesting that the reducing nature of these flames results in more complete atomisation. Broadening of the CaOH bands on the plates is also evident

higher in the flame, due to the production of more CaOH in this region by a three-body recombination reaction.

Molybdenum.

The emission spectra of flames containing molybdenum are shown in Figs. 5a, b and c. No line emission is observed in the fuel-lean flame, 5a, and, except for a diffuse continuum around 5600 Å and 6500 Å attributable to MoO species⁽⁷³⁾, the spectrum is identical to the fuel-lean spectrum of nitrous oxide-acetylene alone. However, in slightly fuel-rich and very fuel-rich flames (5b and 5c) molybdenum lines at 3132.6 Å, 3158.2 Å, 3170.3 Å, and 3194.0 Å are emitted strongly and persist throughout the red zone, as do the ion lines at 3798.3 Å, 3864.1 Å, and 3903.0 Å. Other lines are observed weakly in the red zone but there is no line emission above this zone. In the very fuel-rich flame when molybdenum is sprayed in, a larger red zone can be seen due to the masking of the yellow carbon continuum by the green colour produced by the molybdenum in the outer zone. The red cone also appears more red due to band emission above 6000 Å from MoO species. Hence the molybdenum species exist further up the very fuel-rich flame. The band emission occurs at 5990 Å, 6010 Å, 6250 Å and 6300 Å. and cannot be seen clearly due to the presence of the CN red emission in this wavelength region.

Aluminium.

Emission spectra of aluminium introduced into the nitrous oxide-acetylene flame are shown in Figs. 6a, b and c. In all three types of flame the two strong resonance lines at 3944.0 Å and 3961.5 Å are seen, and they are present over the total length of the flame. The aluminium doublet at 3092.7 Å used for the determination of aluminium by atomic absorption⁽⁶⁶⁾ can just be distinguished in the fuel-rich flames but is not present in the fuel-lean flame. The OH band at 3064 Å partly obscures the aluminium doublet at the 3092.7 Å and 3082.2 Å resonance lines. The outer zone of the flame exhibits a series of reasonably strong bands with heads at 4470.5 Å, 4648.2 Å, and 5079.3 Å, and one weak band at 5336.9 Å. These bands have been attributed to the vibrational structure within the $^2\Sigma^- - ^2\Sigma$ ground state electronic transition for AlO⁽⁷⁴⁾. In the fuel-rich flame, emission from these bands is weakened considerably and only the strongest are observed. The AlO bands are barely visible in the very fuel-rich flame. This supports the argument for the production of a larger population of ground state atoms by the slightly fuel-rich and very fuel-rich nitrous oxide - acetylene flames.

Titanium.

Figs. 7a, 7b, 7c, show the emission spectra of titanium in the various flames, and its behaviour is similar to that of aluminium. Only bands due to the TiO systems

are present in the fuel-lean flame (Fig.7a). The χ -red system of TiO shows some bands above 6125 Å but most of the sequences of this strong system lie outside the upper limit of the plates used in this investigation, i.e. above 6800 Å. The α blue-green system with heads between 4462.1 Å and 6214.9 Å is observed. This is due to ${}^3\Pi - {}^3\Pi$ ground state electronic transition (75). Superimposed on these bands are those of the β TiO orange system with heads between 5597.8 Å and 5694 Å. No titanium resonance lines are observed in this flame. In the slightly fuel-rich flame (Fig.7b) these TiO band systems are weakened in the outer zone and are obscured to some extent by C_2 and CN emission. Many titanium resonance lines appear in the red zone but not above, the strongest being 3635.5 Å, 3642.7 Å, and 3653.5 Å. Thus titanium could be determined by atomic absorption spectroscopy if the path of light from the source is passed through the red zone. The spectrum of the very fuel-rich flame (Fig.7c) is very similar, with the exception that the titanium resonance lines persist higher in the flame and emission from the TiO bands is weakened further.

Iron.

The iron spectra are shown in Figs. 8a, b, c, and there is little difference between the fuel-lean, fuel-rich, and very fuel-rich spectra. More of the principal resonance lines exist over most of the flame length than in the

corresponding air-acetylene flame, presumably due to the higher temperature of the nitrous oxide-acetylene flame. It is possible that the fuel-lean flame may be better for the determination of iron due to the lack of background radiation from CN etc.

Chromium.

Figs. 9a, b, c, show the emission spectra from this element. Two intense groups of three resonance lines appear at 3578 Å, 3593.5 Å, and 3605.3 Å, and at 4254.3 Å, 4274 Å, and 4289.7 Å. The lines generally used for atomic absorption spectroscopy of chromium in the air-acetylene flame, 3578.7 Å and 3593.5 Å, lie on the 3590 Å CN sequence in the nitrous oxide-acetylene fuel-rich flames. Therefore, for greater precision, it is better to use another resonance line or a fuel-lean flame. Greater sensitivity for chromium is obtained in the red feather region than above it or in fuel-lean flames, but the noise levels at the recommended resonance lines are too great to allow good precision. The 3605.3 Å line should provide good sensitivity for absorption measurements with less background noise. The 4254.3 Å line should give even less noise, but probably much less sensitivity.

Vanadium.

Vanadium emission spectra are shown in Figs. 10 a, b, c. No strong lines are observed in the fuel-lean flame above the primary reaction zone. The vanadium lines at 3066.4 Å, 3183.4 Å, 3184.0 Å, and 3185.4 Å are not strong enough to show up against the strong OH emission observed in this region. In fuel-rich flames the persistent lines at 3183.4 Å, 3184.0 Å, and 3185.4 Å are observed at the base of the red zone, and higher in the very fuel-rich flame, against the weakened OH emission. The 3703 Å line and the three lines 4379.2 Å, 4384.7 Å, and 4390.0 Å are clearly visible and persist in the reducing atmosphere. The lines at 3840 Å and 3855.8 Å examined by Amos and Willis are obscured by the intense 3883 Å CN band. Bands due to the VO system were not observed. From these results, the determination of vanadium by atomic absorption spectroscopy would best be carried out at the 3184 Å line in fuel-rich flames, where OH background emission is minimal.

Beryllium.

Figs. 11 a, b, c, show the emission spectra of beryllium introduced into the various nitrous oxide-acetylene flames. The BeO blue-green system⁽⁷⁶⁾ is shown well in the fuel-lean flame. Heads occur at 4708 Å and, a weak one, at 4427 Å attributable to the (0,0) and (1,0) vibrational bands within the $c'\text{ }^1\text{P} - x'\text{ }^1\text{P}$ electronic transition. No

beryllium resonance lines are observed in the fuel-lean flame, but in the slightly fuel-rich flame, the beryllium resonance line at 2348.6 A is visible at the base of the red zone but does not persist throughout the zone. The 4708 A BeO band is not detectably weakened in this flame. In the very fuel-rich flame, the beryllium resonance line is not detectable, even against the weakened NO system, so the atomic absorption of beryllium would best be carried out in slightly fuel-rich flames, at the base of the red zone, using the 2348.6 A resonance line.

Tin.

The emission spectra of tin in the three flames are shown in Figs. 12 a, b, c. The most prominent features of the spectrum of the fuel-lean flame are from the impurities of iron and chromium. The persistent tin lines in the U.V. below 3300 A are not shown above the primary zone. In the atomic absorption flames, the emission of the atomic tin lines at 2354.8 A, 2429.5 A, 2546 A, 2706.5 A, 2840.0 A, 2863.3 A, 3175.1 A, and 3262.3 A are visible in the red zone. The lines at 3009.1 A and 3034.1 A are quite strong and persist above the red zone. Lines above 3262 A are obscured by flame bands. There is no band emission assignable to SnO, SnH, or SnCl in these flames. The very fuel-rich flame is similar to the atomic absorption flame but the emission

from the above lines is stronger and persists higher in the flame. The emission spectra from niobium and tantalum were obtained, but on identifying the lines and species present they were found to be due to impurity emission, and no line or band emission assignable to niobium or tantalum was found.

Conclusions.

From the results obtained above, by far the most useful type of flame for the atomic absorption of many refractory or difficult elements is the fuel-rich nitrous oxide-acetylene flame. If the resonance line is chosen away from the wavelength regions where flame noise is excessive and the radiation from the light source is directed through the red zone, sensitive determinations should result.

The reactions which occur in the nitrous oxide - acetylene flame to provide and maintain an atomic population for refractory elements are too complex to be explained by the reducing action of incandescent carbon particles postulated for the oxy-acetylene flame. It appears that in the primary reaction zone, the nitrous oxide decomposes partially with the provision of oxygen to raise the temperature and burning velocity of the flame. Some of the nitrous oxide decomposes to form nitric oxide and this, or the nitrous oxide molecule itself, reacts directly with a fuel molecule in the primary zone to produce more CN and NH than are produced in

conventional air-hydrocarbon flames. The lifetimes of these species are prolonged since there is insufficient oxidant for their rapid consumption. Due to this slow rate of consumption, a reducing atmosphere is provided in the red zone which protects, and therefore maintains, the atomic population produced by the high temperature in the primary reaction zone. It is also possible that any metal oxide molecules produced above the primary zone may be reduced by the action of NH and CN. As the flame is made fuel-rich, the reducing action of CN and NH is supplemented by that of free incandescent carbon particles. Therefore as long as fuel-rich flames are used, and absorption measurements are confined to the red 'feather' region of the flame, good sensitivity for the determination of refractory elements should be obtained.

CHAPTER 5.

A STUDY OF THE TEMPERATURE PROFILES WITHIN NITROUS
OXIDE SUPPORTED ACETYLENE FLAMES AT ATMOSPHERIC PRESSURE.

The study of the emission spectra of premixed flames of nitrous oxide with acetylene in the presence of a range of refractory elements was recorded in the previous chapter. The effectiveness of this flame for the determination by atomic absorption spectroscopy of refractory elements arises from the production of a larger population of free metal atoms in the ground state in this flame, compared with the conventional air-acetylene flame. However, there is little evidence to explain how appreciable populations of atoms of refractory elements result in this flame. Amos and Willis⁽⁶³⁾ have compared the properties of the nitrous oxide-acetylene flame for atomic absorption spectroscopy, with flames of oxygen-nitrogen- and acetylene. They conclude that as both types of flame yield similar results the high temperature of the flames is responsible for their utility for the determination of the refractory elements. However, good sensitivity for most refractory elements is only obtained in fuel-rich (i.e. reducing) flames. Thus the high population of the CN radical found in these flames appears to create a reducing atmosphere in which free atoms of the elements are produced and maintained. The

variation in temperature in different zones of the flame burning at different mixture strengths has an important bearing on any mechanism postulated to account for the high populations of ground state atoms produced. The maximum temperature of the nitrous oxide-acetylene flame burning at atmospheric pressure has been quoted as $2955^{\circ}\text{C}.$ ⁽⁶⁴⁾. This is the only value available in the literature and it is not clear whether this represents a calculated value of the maximum thermodynamic temperature or one which has been obtained practically. If it is a practical value, no data are available concerning the type of burner at which the flame was maintained, or the mixture conditions or the region of the flame where the measurement was made. A study has therefore been made of the temperatures in a premixed nitrous oxide-acetylene flame burning under different mixture conditions at a 5 cm. burner of the type commonly used for atomic absorption measurements.

The thermal energy of the flame, which is reflected in its temperature, is distributed between activated particles to the various translational, rotational, vibrational, electronic and ionisation states. Each of these states has its own temperature, and the flame is said to be in thermal equilibrium when the values for all these temperatures are similar within the limits of experimental error. In the absence of equilibrium in the flame gases it

is difficult to define the 'temperature' of the system. Gaydon and Wolfhard ⁽⁷⁸⁾, however, note that deviations from equilibrium are small for the interconal or burnt gases of most small, steadily burning, premixed flames, and hence a temperature may be assigned to these systems.

A flame temperature investigation in the various zones of the nitrous oxide-acetylene flame would therefore give relevant information concerning the equilibria existing in these regions of the flame. For example, temperature measurements in the outer zone of stoichiometric premixed combustion flames using various procedures and excitation states (rotational, vibrational, etc.) produce results which are in agreement with each other and also with the calculated value. Whereas similar measurements made in the primary reaction zones of these flames differ widely. This evidence suggests that the outer zones of these flames are in thermal equilibrium and the intensity of the radiation is thermally controlled. On the other hand, thermal equilibrium is not achieved in the primary zone, and the radiation from excited species in this zone is predominantly chemiluminescent.

The methods of measurement of flame temperature may be divided into two types (a) thermometric and (b) optical. Thermometric measurements are usually made by introducing a metallic wire or thermocouple into the various regions of the flame, and the temperature of the wire

determined. Thus the advantage of these methods is that the metal probes may be made very small, and the temperature at a given point in the flame measured, enabling good temperature profiles to be obtained. However, the results obtained using these methods are generally low, due to their heat loss from the flame by conduction and radiation on introduction of a wire. Also interference is frequently caused by catalytic action at the wire surface. Probably the most serious disadvantage of thermometric methods is that the materials used as probes have a relatively low melting point, e.g. platinum M.pt. 1775°C , and are therefore of little use for the measurement of high temperature premixed flames.

Optical methods of measurement are based on the radiation properties of hot gases. These procedures produce an average value for the temperature of a given region of the flame. They are therefore not as precise as thermometric methods for plotting temperature profiles of flames. However, the temperature values obtained are probably more reliable, since measurements are made without disturbing the conditions of flow or the geometry of the flame. There is also no limit to the temperature of flames which may be determined using optical methods of measurement. Excellent reviews of the extensive range of methods available for the measurement of flame temperature have been written by Gaydon⁽⁶⁹⁾ Gaydon and Wolfhard⁽⁷⁸⁾ and Mavrodineanu and Boiteux⁽⁷⁹⁾.

This chapter reports the results obtained by the line-reversal method and the 'two-line' method for the effective electronic excitation temperatures for sodium and iron respectively. The 'two-line' method was conducted by one of the author's colleagues in this laboratory, and the results of his investigations are recorded here for comparison purposes only.

Measurements have also been made by emission spectrography of the effective rotational temperature for NH and the effective vibrational temperature for CN in the flame gases above the primary zone.

Experimental.

Burner Arrangement: The burner arrangement used was similar to that described previously ⁽⁸⁰⁾. The burner head was constructed of stainless steel and comprised two steel plates bolted to a massive steel head to form a slit 0.015 inches (0.375 mm) wide and 2 inches (5 cm) long. The burner head was mounted on a stainless steel base and premixing chamber similar to that employed in the air-acetylene burner used on the Unicam S.P.900A flame spectrophotometer. The flame was lit on air-acetylene, and the change to nitrous oxide-acetylene effected by the gradual replacement of the air with nitrous oxide, via a T-piece and two rotameters. The sample solutions were introduced as aqueous 10^{-2} M sodium chloride (line-reversal) or ferric chloride (two-line

method) via a Hilger and Watts nebuliser and glass expansion chamber. Aspiration was by the nitrous oxide supply to the flame.

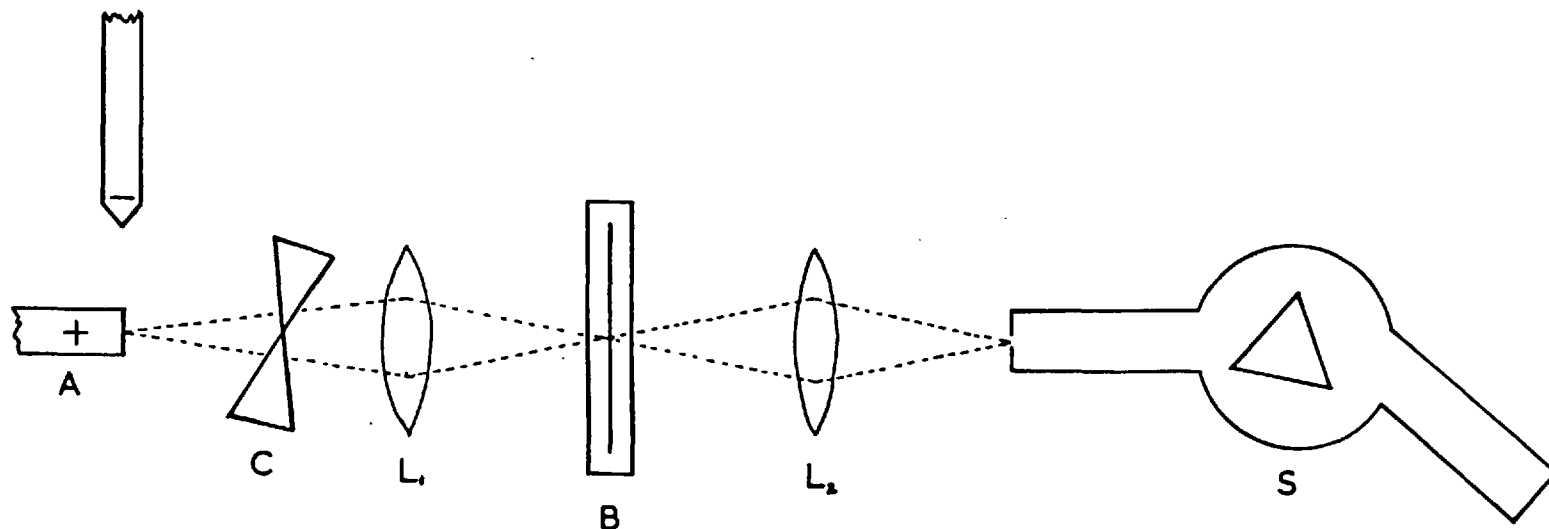
The sodium-line reversal method.

This is one of the most convenient methods for the measurement of flame temperatures and the actual value obtained is the effective electronic excitation temperature for sodium. This method was first introduced by Kurlbaum⁽⁸¹⁾ and Fery⁽⁸²⁾ and has since been used extensively. Workers in the field have confidence in the results obtained, largely through the efforts of Kohn⁽⁸³⁾ who exhaustively tested the validity of the method.

The method depends on Kirchhoff's Law. When sodium is introduced into a flame it emits the yellow doublet at 5890 Å and 5896 Å. It can be shown from Kirchhoff's Law that when light from a bright background continuum is passed through a flame containing sodium vapour, the sodium D-lines will appear either in absorption or emission, according to whether the brightness temperature of the background source is higher or lower than the flame temperature. Thus if the brightness of the background can be varied until the sodium lines are not seen either in absorption or emission (the reversal point) and the brightness temperature of the background under these conditions determined with a calibrated pyrometer or thermopile, the temperature of the flame may be measured.

The apparatus used is shown diagrammatically in Fig.24. The background continuum source used was provided by the anode of a d.c. arc burning at pure carbon electrodes (Johnson Matthey Ltd.). The diameter of the anode electrode was 6.5 mm and the cathode diameter was 5.5 mm. The arc was supported at 10 amps. from a 220 volt d.c. spectrographic power pack. With the electrode assembly used the voltage drop was 60 volts when the arc gap was maintained at 1 cm. The effective temperature of the background radiation from the anode was obtained by direct measurement of the radiation from the anode spot received at the face of a calibrated standardised thermopile. The average value obtained in this way for the anode spot brightness temperature was $3772^{\circ} \pm 60^{\circ}\text{K}$.

The spot of radiation from the anode is focussed into the flame through a quartz convex lens, diameter 2.5 cm focal length 5 cm, to give an image of the anode in the flame. As shown in Fig.24 the flame was used in the broadside-on position, i.e. the 5 cm side of the flame was perpendicular to the radiation from the arc. A second quartz convex lens, diameter 2.5 cm and focal length 7.5 cm, forms an image of both flame and anode spot on the slit of the spectroscope (Beck, London). The loss by reflection at the air-glass interfaces of radiation from the background was estimated by measuring the apparent temperature of the anode using the thermopile, with and without the lens in position, to be



A = ANODE.

B = BURNER.

C = CHOPPER.

L_1 & L_2 = LENSES.

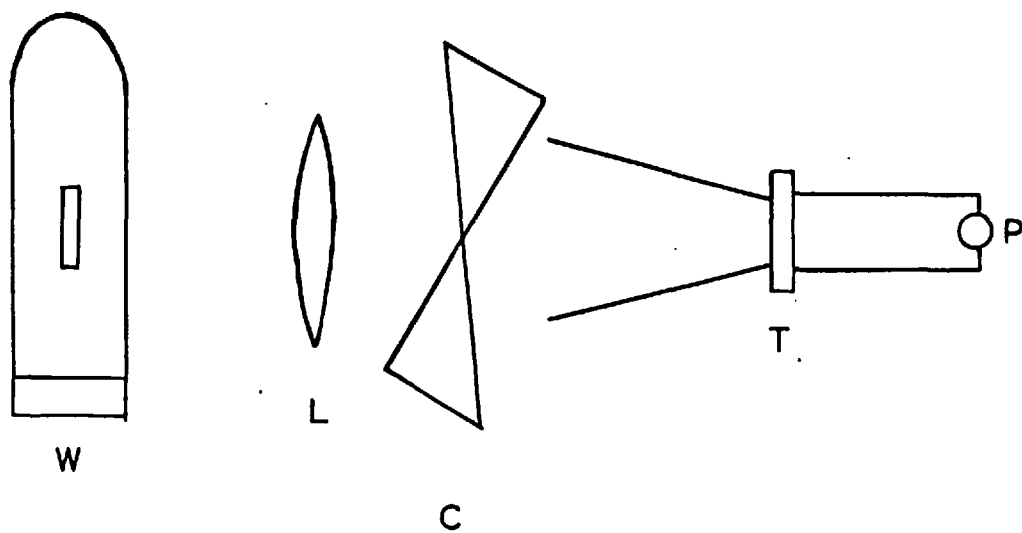
S = SPECTROSCOPE.

FIG.24

8.75%. The intensity of the radiation from the anode was reduced with a rotating sector of variable aperture. This was driven at constant speed by a synchronous motor (B.S.R. IH 1978, Hilger No. F.1083).

Measurement of temperature.

A 10^{-2} M sodium chloride solution was aspirated into the flame and the sodium doublet at 5890 Å arranged to be in the middle of the cross wires when viewed through the spectroscope, thus making identification easy. The arc discharge was then initiated and the background brightness between 5800 and 6000 Å, together with the flame emission, viewed through the spectroscope, which was used with as narrow a slit as possible. Under these conditions the background is much hotter than the flame and the sodium doublet is seen in absorption. The rotating chopper blades were set to produce a narrow aperture, and rotated in front of the convex lens (F 958). The sodium doublet is now seen in emission against the attenuated background. The blade angle of the sector was then decreased gradually until the sodium doublet was invisible i.e. the reversal point. The brightness temperature of the background was then equal to that of the flame. The sector was removed from the optical bench and the blade angle at the reversal point measured by placing the chopper between a standard tungsten ribbon filament lamp (Mazda 6 v, 108 w. R/1 projector lamp) operated at stabilised



W=LAMP. L=LENS. C=CHOPPER. T=THERMOPILE.

P=POTENTIOMETER.

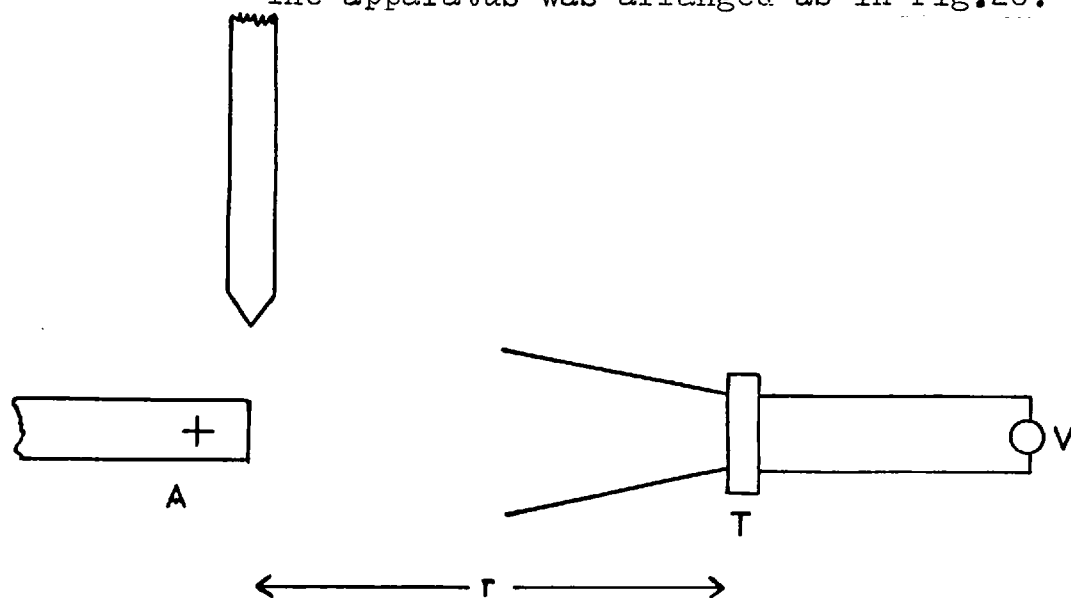
FIG.25

controlled current and the thermopile and potentiometer. This arrangement is shown in Fig.25. The attenuated radiation from the tungsten filament lamp is received at the thermopile and the blade angle of the chopper determined from a calibration graph of energy received at the detector vs. blade angle of the chopper. Thus the temperature of the background source, and hence the flame, was obtained.

Results.

Determination of arc temperature.

The apparatus was arranged as in Fig.26.



V = VOLTMETER.

FIG.26

Krygsman ⁽⁸⁴⁾ and Henning and Tingwaldt ⁽⁸⁵⁾ have reported temperatures for the anode of a carbon arc of 3800°K and 3818°K respectively. Since the arc radiation was unstable,

it was decided to determine the arc temperature directly and not accept the quoted literature values. The radiation intensity was measured on a direct-reading millivoltmeter as the arc instability prevented the use of the potentiometer which required laborious balancing to the "null point" against a standard cell. The millivolt reading obtained when the thermopile was at a distance r cm from the arc, arises from the radiation striking the active area of the thermopile. Thus the total radiation from the arc is calculated from the surface area of the sphere of radius r cm. The millivolts reading must be multiplied by $\frac{4\pi r^2}{a}$ where a is the active area of the thermopile.

The Stefan-Boltzmann Law may be applied, since the radiation from the arc anode approximates to that of a black body at the same temperature.

$$R = \sigma T^4$$

where, R = Radiancy, T = Temperature, σ = Stefan-Boltzmann constant = 5.67×10^{-12} .

Thermopile output, 380 mV/watt/cm²

Active area, a , of thermopile, 4.155 cm².

$$\therefore R = \frac{mV}{380} \times 4.155 \text{ watts}$$

where mV is the millivolt reading.

Thus the total output from the anode

$$= \frac{mV}{380} \times 4.155 \times \frac{4\pi r^2}{4.155}$$

$$= \frac{\text{mV} \times 4\pi r^2}{380} \text{ watts}$$

$$R = \sigma T^4$$

$$T = 4 \sqrt{\frac{R}{\sigma}}$$

$$T = 4 \sqrt{\frac{\text{mV} \times 4\pi r^2 \times 10^{12}}{5.67 \times 380}} \text{ } ^\circ\text{K}$$

$$= 4 \sqrt{5.834 \times 10^9 \text{ mV } r^2} \text{ } ^\circ\text{K}$$

Table 11.

<u>r cm</u>	<u>mV</u>	<u>°K</u>
20	85	3752
20	81	3708
20	78	3673
20	79	3684
20	83	3731
24.5	61	3823
24.5	60	3807
24.5	58	3775
24.5	57	3758
42.0	21.2	3832
42	21.0	3843
42	20.8	3824
42	21.0	3832

Mean temperature = 3772°K, Standard deviation 60°K or 1.6%.

Even though the millivoltmeter reading varies appreciably, this does not cause a large error in the anode temperature since the fourth root of the millivolt reading is taken.

Lens correction.

Radiation from the arc is lost at the two air-glass interfaces of the first lens (F 958) by reflection and absorption. Gaydon (69) estimated that 5% of the radiation is lost at each air-glass interface. The correction factor to be applied was determined using the apparatus shown in Fig.27.

The current through the lamp was maintained constant and the thermopile was placed at a known distance from the lamp. The millivolt reading at the thermopile was obtained in this position, and also when the lens was used at the same distance to collect and focus light on to the thermopile. The value of the correction was obtained allowing for the difference in area of the lens and the thermopile faces. It was assumed that the percentage of radiation lost at the lens would be approximately the same for the arc (3800°K) as for the tungsten filament lamp (2500°K) within experimental error.

Area of thermopile face 4.155 cm²

Area of lens 5.31 cm²

$$\text{Correction factor} = \frac{x - \left(y \times \frac{4.155}{5.31} \right)}{x} \times 100$$

x is the mV reading for the thermopile alone

y is the mV reading for the lens.

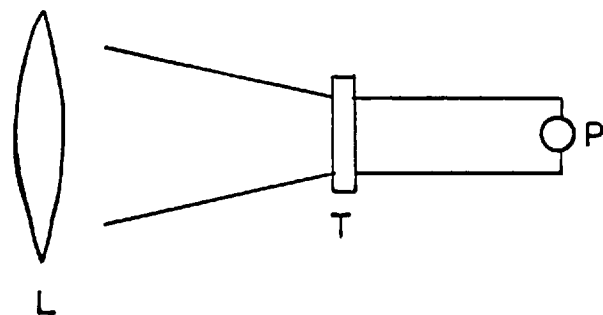
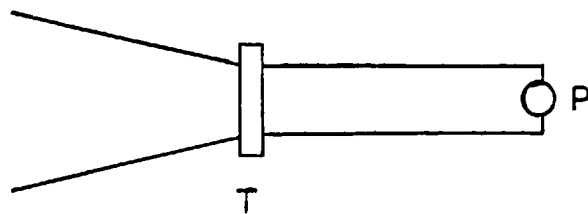
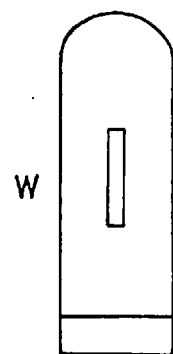
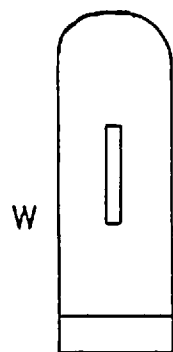


FIG.27

Table 12.

mV reading x	mV reading y	y corrected for area mV	Correction factor %
23.2	27.0	21.13	8.9
24.0	27.8	21.80	9.2
35.0	40.7	31.84	9.0
35.0	40.4	31.81	8.9
36.0	41.3	33.05	8.2
35.8	41.0	32.83	8.3

Mean correction factor 8.75%

Flame Temperature Results.

The temperatures of the flame, T_f , in the various zones of the flames were measured using

$$T_f = T_a \cdot \frac{(360 - L)}{360} \cdot \frac{100}{C}$$

T_a = arc temperature, L = blade angle,

C = lens correction factor.

The height of measurement above the burner head is noted.

Slightly fuel rich, atomic absorption flame, obtained with flow rates of 5.6 litre/minute nitrous oxide and 3 litre/minute acetylene.

Total flame height 13 cm.

Table 13.

142.

0.5 - 1.2 cm above the burner head, (red zone temperatures).

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
84	3177	2904
85.5	3154	2881
88	3130	2857
85	3159	2886
88.5	3125	2852
96	3038	2765
99	3003	2730
94.5	3055	2782
99	3003	2730
94.5	3055	2782
91.5	3089	2816
84	3177	2904

Mean temperature $2824 \pm 65^{\circ}\text{C}$.

2 cm above the burner plate (Just above the red zone)

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
118.5	2779	2506
118.5	2779	2506
123	2727	2454
127.5	2675	2402
115.5	2814	2541
119.0	2773	2500
121.5	2745	2472

Mean Temperature = $2483 \pm 45^{\circ}\text{C}$.

4.0 cm above the burner plate.

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
128.5	2641	2368
135	2589	2316
138	2566	2293
142	2520	2247
135.5	2583	2310
136	2572	2299
138.5	2555	2282

Mean Temperature = $2302 \pm 37^{\circ}\text{C}$.

5.0 cm above the burner plate.

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
166	2232	1959
166	2232	1959
172	2175	1903
173	2158	1885
166.5	2227	1954
168	2210	1937

Mean Temperature = $1933 \pm 32^{\circ}\text{C}$.

Fuel rich flame, obtained with flow rates of 5.6 litre/min. nitrous oxide and 3.7 litre/min. acetylene. Total flame height 13 cms.

0.5 - 1.2 cm. above the burner plate.

<u>Blade height</u> °	<u>Temperature</u> °K	<u>Temperature</u> °C
118	2785	2512
121.5	2745	2472
120	2762	2489
120	2762	2489
120	2762	2489
118.5	2779	2506

Mean Temperature = $2493 \pm 14^{\circ}\text{C}$

2 cm above the burner plate

<u>Blade angle</u> °	<u>Temperature</u> °K	<u>Temperature</u> °C
135	2589	2316
134	2601	2328
138	2555	2282
136.5	2572	2299
136.5	2572	2299

Mean Temperature = $2305 \pm 18^{\circ}\text{C}$

4.0 cm above the burner plate

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
168	2210	1937
166	2232	1959
167	2221	1948
165	2244	1971
171	2175	1902
169.5	2193	1916

Mean Temperature = $1939 \pm 26^{\circ}\text{C}$.

Fuel lean flame, obtained using flow rates of 5.6 litre/min. nitrous oxide and 2.6 litre/min. acetylene.

Total flame height 10 cm.

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
0.5 - 1.2 cm above the burner plate.		
137	2566	2293
135	2589	2316
135	2589	2316
133.5	2607	2334
139.5	2537	2264
140	2531	2255
134	2601	2328
138	2555	2282
136	2577	2304

Mean Temperature = $2299 \pm 28^{\circ}\text{C}$.

2 cm above the burner plate.

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
156	2347	2074
154.5	2365	2092
159	2313	2040
155	2359	2086
160	2301	2028
157.5	2331	2058
158	2325	2052
162	2279	2006

Mean Temperature = $2055 \pm 30^{\circ}\text{C}$

4 cm. above the burner plate.

<u>Blade angle °</u>	<u>Temperature °K</u>	<u>Temperature °C</u>
167.5	2215	1942
171	2175	1902
169.5	2193	1920
168	2210	1937
165	2244	1971
172	2164	1891

Mean Temperature = $1927 \pm 30^{\circ}\text{C}$

The two-line method.

This method of temperature measurement was introduced by Ornstein and Brinkman⁽⁸⁶⁾ in 1934, and is based on the comparison of the intensities of two lines emitted by an element. The transition probabilities of the two lines must be known and also the energies of the initial (i.e. excited) states.

$$\frac{I'}{I} = \frac{A' g' \nu'}{A g \nu} \frac{e^{-E'/kT}}{e^{-E/kT}}$$

I = line intensity. A = transition probability.

g = statistical weight. ν = frequency.

T = temperature. E = energy of initial level

K = Boltzmann constant.

This may be written

$$\frac{I'}{I} = \frac{A' g' \nu'}{A g \nu} e^{-(E' - E)/kT}$$

and Bohr's relation may be used if the two lines which are compared fall back to the same level.

$$E = \frac{h c}{\lambda} = h c \nu$$

$$\therefore \frac{I'}{I} = \frac{A' g' \nu'}{A g \nu} e^{-hc/kT (\nu' - \nu)}$$

Thus if the two intensities are measured, A , g and ν values may be obtained from tables and the temperature of the exciting source measured.

Apparatus.

A Hilger large quartz spectrograph was used and the burner mounted on the optical bench in the end-on position, an image of the 0.015 inch side being focussed onto the spectrograph by a convex lens. The distances between the burner and convex lens, and between the spectrograph slit and lens were equal to twice the focal length of the lens, thus there was no magnification of the image formed. The arrangement is shown in Fig.28.

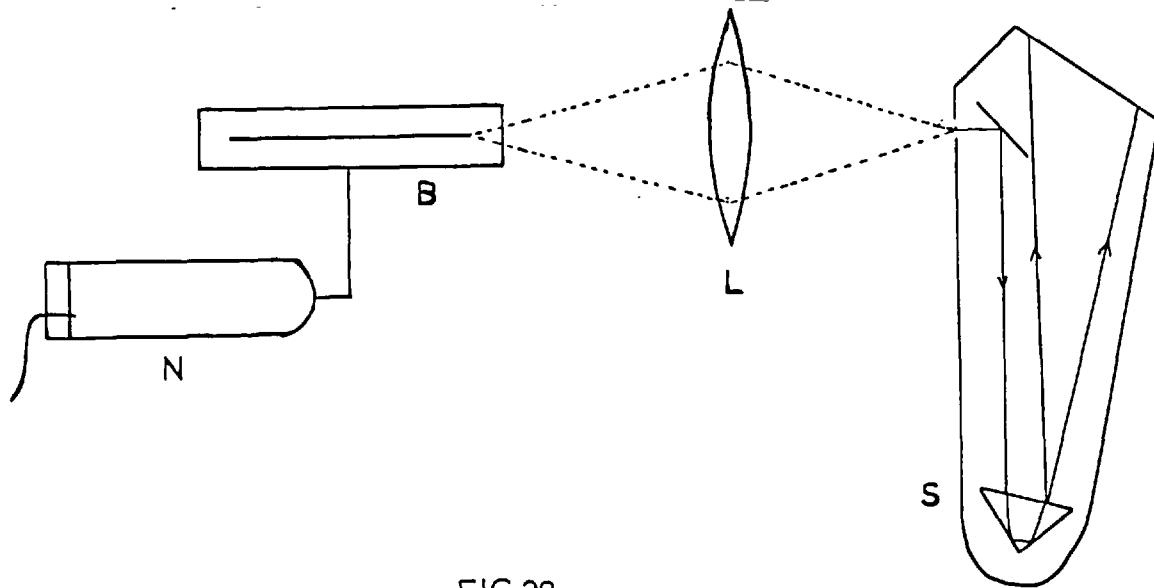


FIG.28

10^{-2} M ferric chloride solution was aspirated into the flame. Spectrograms obtained in this way show the variation of emission intensity with height, resolved with respect to wavelength for species in the flame. The spectra were recorded on B.10 and R.40 plates, depending on the

wavelength region being examined. The plate emulsion was calibrated at the wavelengths used with a Hilger stepped sector. Plate standardisation for variation in emulsion sensitivity at the wavelength of the iron spectral lines to be compared was also undertaken using a black body continuum source. The spectral line intensities were measured using a photomicrodensitometer. The lines were all within 100 Å of each other and the correction for change in plate sensitivity over the range was negligible.

Results.

Table 14 shows the temperatures obtained in the various regions of the nitrous oxide-acetylene flame.

Table 14

Temperature of the slightly fuel-rich nitrous oxide - acetylene flame.

Height above burner mm.	Pair of lines used Å.	Temperature °K
4.5	3647 - 3679	3040
	3749 - 3705	3100
	3749 - 3772	3020
	3749 - 3705	2990
	3749 - 3722	2930
	3758 - 3705	3100
	3758 - 3722	3045
	3758 - 3733	2955

Table 14 (continued)

Height above burner mm.	Pair of lines used A.	Temperature °K
6.0	3749 - 3705	2880
	3749 - 3722	2890
	3734 - 3733	2940
	3749 - 3705	2920
	3749 - 3722	2880
	2749 - 3722	2890
	3749 - 3722	2890
7.5	3749 - 3705	2840
	3749 - 3722	2820
	3749 - 3705	2820
	3749 - 3722	2810
	3749 - 3705	2810
	3749 - 3722	2875
	3749 - 3705	2875
	3749 - 3722	2825
	3749 - 3705	2820
	3749 - 3722	2830
	3734 - 3748	2825
12.0	3734 - 3748	2785
	3749 - 3733	2815
	3749 - 3705	2830
	3749 - 3722	2810

Table 14 (continued)

Height above burner mm.	Pair of lines used A.	Temperature °K
17.0	3749 - 3705	2800
	3749 - 3722	2770
	3734 - 3748	2760
	3749 - 3705	2780
	3749 - 3722	2760
	3734 - 3748	2765
	3734 - 3748	2750
	3820 - 3824	2760
	3734 - 3748	2770
	3749 - 3722	2775
	3820 - 3824	2760
	3749 - 3705	2785
	3734 - 3748	2785
	3749 - 3722	2775
	3820 - 3824	2780
35 - 40	3734 - 3748	2740
	3734 - 3748	2725
	3749 - 3705	2745
	3749 - 3722	2735
	3734 - 3748	2735
	3820 - 3824	2730
	3825 - 3878	2720

Table 14 (continued)

Height above burner mm.	Pair of lines used A	Temperature °K
55	3734 - 3748	2700
	3820 - 3824	2705
	3825 - 3878	2710
70	3734 - 3749	2690

Mean Temperatures obtained from above Table 14

Height above burner mm.	Mean Temperature °K
4.5	3024 $\pm$ 85
6.0	2900 $\pm$ 25
7.5	2830 $\pm$ 30
12.0	2810 $\pm$ 20
17.0	2770 $\pm$ 30
35-40	2730 $\pm$ 10
55	2705 $\pm$ 5
70	2690

Table 15.

Temperature of the fuel-lean nitrous oxide-acetylene flame.

Height above burner mm.	Pair of lines used A.	Temperature °K
3.5	3749 - 3705	2930
	3749 - 3722	2950
	3758 - 3722	2940
7.5	3749 - 3705	2850
	3749 - 3722	2855
	3758 - 3722	2845
15	3749 - 3722	2775
	3734 - 3748	2830
	3758 - 3733	2800
	3820 - 3824	2785

Precision of the two-line method.

From,

$$\frac{I'}{I} = \frac{A' g' \nu'}{A g \nu} e^{-\frac{h' c}{kT} (\nu' - \nu)}$$

Any errors in I'/I or A'/A will produce considerable error in the temperature value obtained. Broide⁽⁸⁷⁾ has expressed the relative error $\Delta T/T$, mathematically

$$\frac{\Delta T}{T} = \frac{k T}{E' - E} \times \frac{\Delta r}{r}$$

where Δr is the error in the measurement of the ratio, r of the intensities or transition probabilities. A typical value of $E' - E$ is 0.75 eV, and ratios may be measured to an accuracy of 0.05. Thus for a gas at 3000°K, $\Delta T = 52^\circ$. This is the error for a single determination and obviously the more values which are averaged to find the final temperature, the more the error will be reduced.

Rotational and Vibrational Temperatures (69).

It is possible to determine the temperature of a gas from the distribution of intensities among the lines of the rotational fine structure of a band spectrum. The NH band at 3360 Å was chosen for measurement because of its open rotational structure and it was well separated from other band systems. The principle of the method is the same as the two-line method. The intensity I of a line in the rotational fine structure of a band is given by ,

$$I = C.A.\nu^4 e^{-E_r/KT}$$

where C = a constant; A = rotational transition probability; ν = frequency; E_r = rotational energy of initial state. Knowing A , and E_r it is possible to determine the temperature, T , from measurement of the intensity of two lines.

There are three main methods of measurement of the rotational temperatures, (1) from the position of maximum intensity in a single branch of the band; (2) the iso-intensity method, in which lines of equal intensity are found one near the beginning and the other in the tail of the branch, thus avoiding actual quantitative intensity measurement, and (3) the plotting method, i.e. the above equation may be written

$$\log_e I = \log_e C + \log_e (A.\nu^4) - E_r/KT$$

thus plotting $\log_e I - \log_e (A \cdot \nu)^4$ against E_r gives a straight line, the slope of which produces T , the temperature.

The simplest method using the NH (0,0) sequence at 3360 Å (${}^3\Pi - {}^3\Sigma$) is the maximum intensity method⁽⁸⁸⁾ for the R-branch of this band. The position of maximum intensity is easily obtained and the corresponding J value is substituted into,

$$J_{\max} = \sqrt{\frac{KT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2}$$

B = rotational constant = 16.67 cm^{-1} for NH.

The measurement of the effective vibrational temperature from the vibrational intensity distribution of bands within a system, is very similar to the measurement of effective rotational temperatures. The intensity ratio measured is either that of the maximum intensities of two heads of each band or the ratio of the integrated intensity for the whole of the two bands, including associated rotational structure. The CN vibrational system (${}^2\Sigma - {}^2\Sigma$) with heads at 3590 Å (1,0), 3883 Å (0,0) and 4216 Å (0,1) was selected for the measurement of the effective vibrational temperature. This is the only system which persists throughout the red zone and also has clear and easily identifiable vibrational structure. CN also appears to be one of the flame species which plays an important role in the production and maintenance of free atoms of elements

introduced into flames, its 'internal' vibrational temperature is therefore important.

The basic equation again is

$$\frac{I'}{I} = \frac{A'g'\check{v}' e^{-E'/KT}}{A g \check{v} e^{-E/KT}}$$

$$\text{or } \log_e \left[\frac{I'}{A'g'\check{v}'} \right] - \log_e \left[\frac{I}{Ag\check{v}} \right] = - \frac{E' - E}{KT}$$

When A, g, $\check{v}$ and E values are known from tables, the intensity values are measured and T, the temperature in $^{\circ}\text{K}$ can be calculated.

Apparatus.

The Hilger large quartz spectrograph was used, with the flame in the broadside-on position. The flame was focussed on to the slit of the spectrograph using an equi-convex quartz lens of focal length 5 cm. The spectrum obtained after 1 hour exposure was recorded on a B.10 plate. The intensities of the lines were measured using the Hilger photomicrodensitometer.

The Techtron A.A.3 atomic absorption spectrophotometer was also used. The intensity measurements for the rotational lines and vibrational bands were recorded using a Sargent strip-chart recorder.

Rotational Temperatures.

Figs. (29) and (30) show the curves of intensity versus J number obtained from the B.10 plates.



NH 3360

For the R-branch of the NH (0,0) band, the position of maximum intensity corresponds to a J-value between 8 and 9.

The P-branch curve shown in Fig.(31) is not as useful since the curve produced is rather flat and exhibits no clear maximum so that it is difficult to assign the J-values to the various lines of the band, or obtain a good value for the rotational temperature from this branch.

Fig.(32) shows the chart tracing obtained from the Sargent recorder for the red zone emission around 3360 Å and this gives a value of 9 for $J_{\max}$.

When	$J_{\max} = 8$	$T = 3294^{\circ}\text{K}$
	$J_{\max} = 9$	$T = 4141^{\circ}\text{K}$

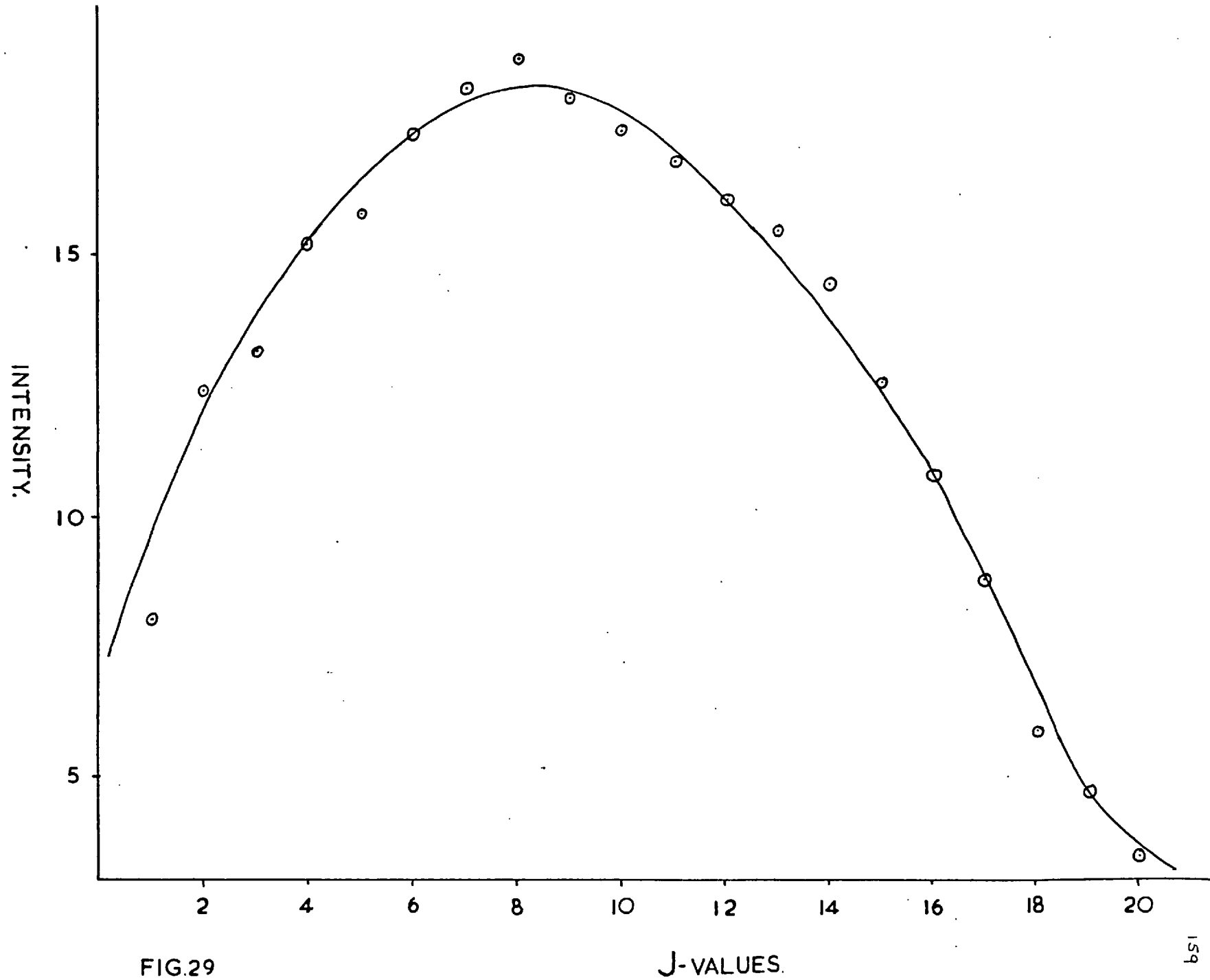


FIG.29

J-VALUES.

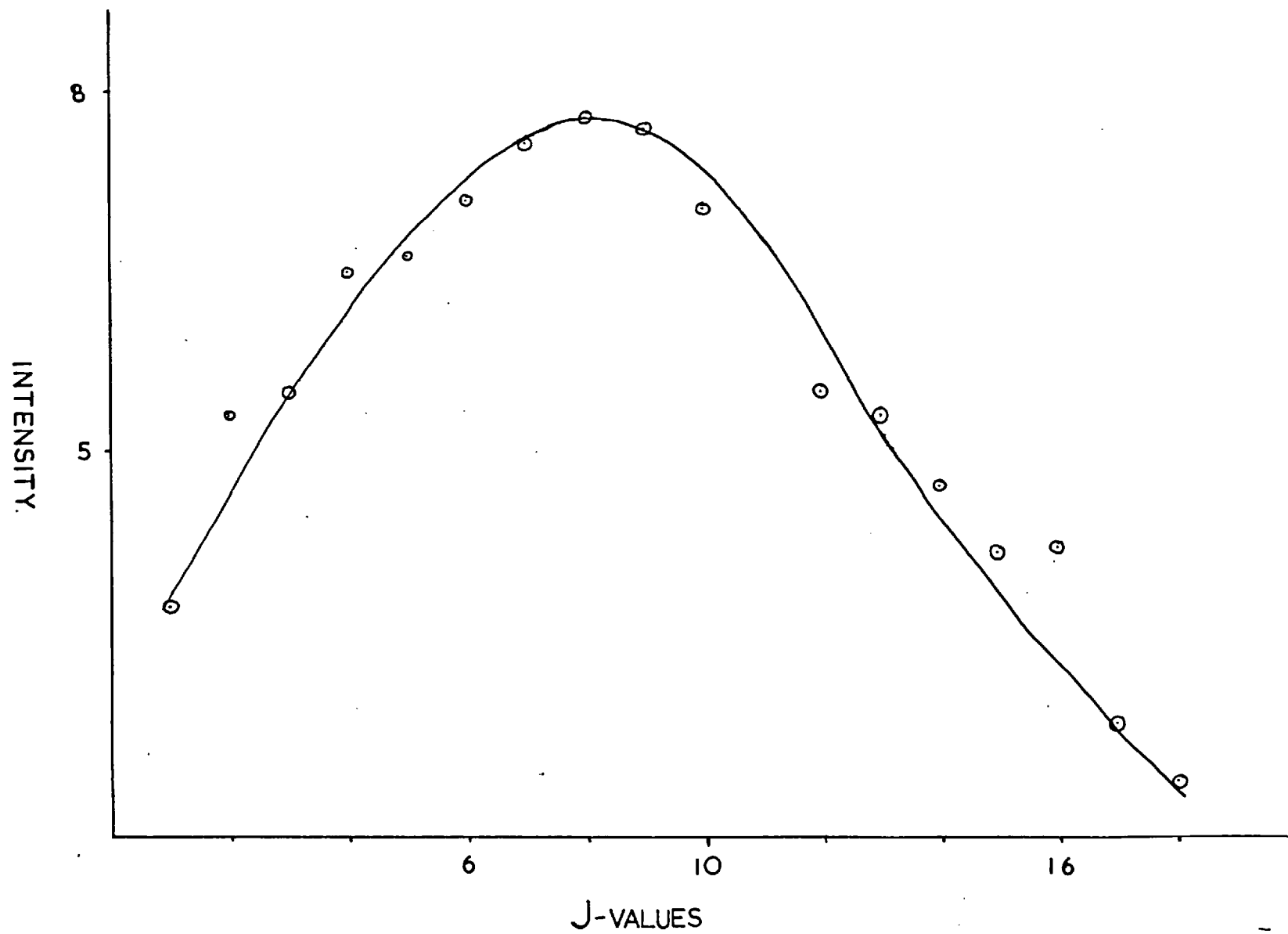


FIG.30

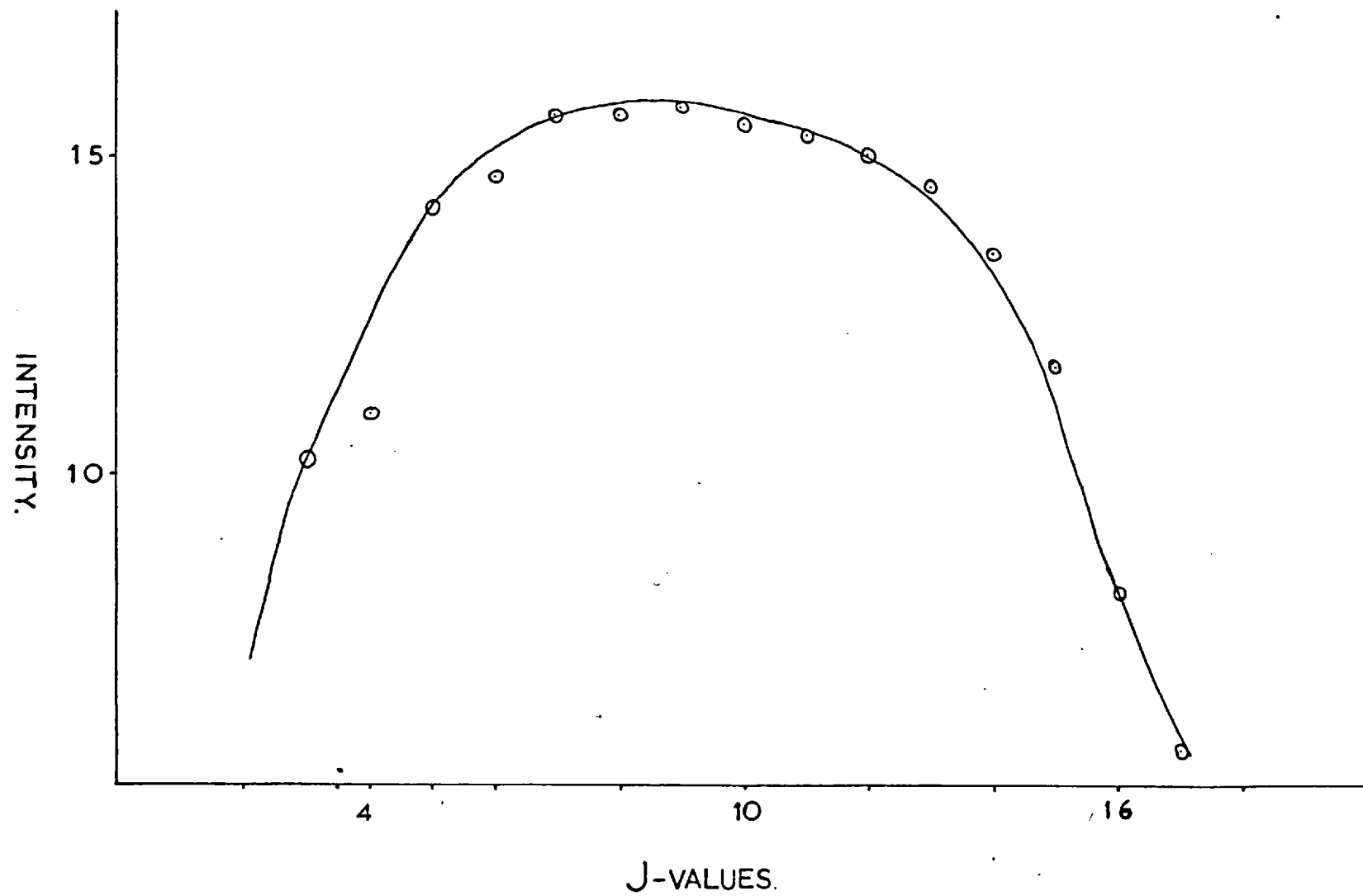


FIG.31

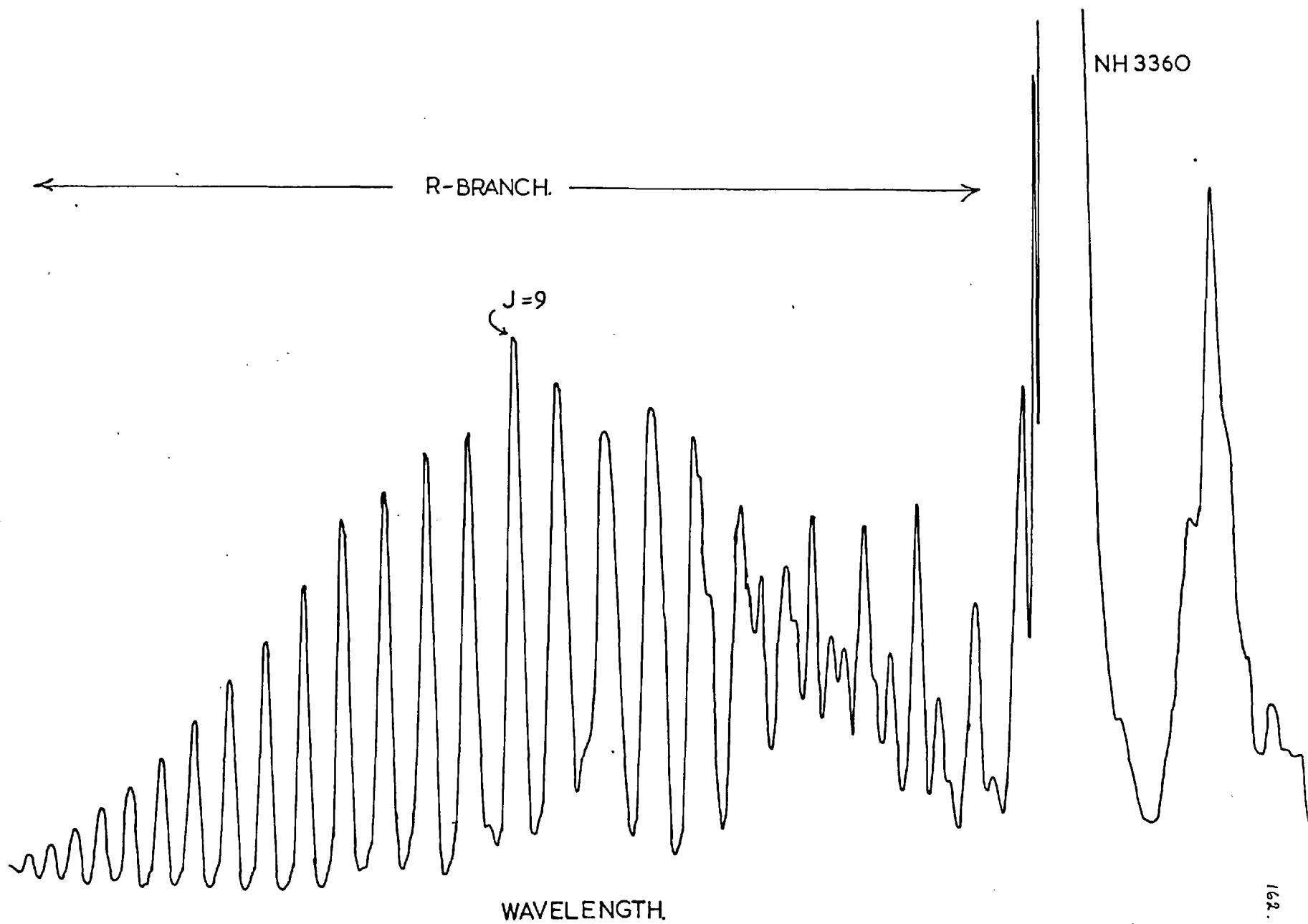


FIG.32

Effective vibrational temperatures.

The CN bands at 3590 Å (1,0), 3883 Å (0,0) and 4216 Å (0,1) were used for this determination. The intensity of heads within each band were compared as well as heads from different bands. The transition probabilities were taken from values obtained by Fraser, Jarman and Nicholls (89). Other values in the equation

$$\ln \left[\frac{I'}{A'g'\nu'} \right] - \ln \left[\frac{I}{Ag\nu} \right] = - \frac{(E' - E)}{KT}$$

were obtained from Mavrodineanu and Boiteux (79)

Using the spectrographic plate.

Table 16 .

(V',V'')	Line	Intensity	Transition Probability (89)
1,0	3590.4	37.9	0.077
2,1	3585.9	34.9	0.134
3,2	3583.9	27.5	0.174
0,1	4216.0	37.1	0.073
1,2	4197.2	27.2	0.121
2,3	4181.0	11.8	0.150

Table 17 .

Pair of lines compared A.	Temperature °K
3590.4 - 3585.9	5277
3585.9 - 3583.9	5866
3590.4 - 3583.9	5556
4216.0 - 4197.2	3721
4197.2 - 4181.0	2844
4216.0 - 4181.0	3228

From the chart recording

Table 18 .

Line	Intensity	(V'-V'')	Transition Probability (89)
4216.0	89	0,1	0.073
4197.2	66	1,2	0.121
4181.0	45	2,3	0.150
3590.4	60	1,0	0.073
3585.9	41	2,1	0.134
3583.9	37	3,2	0.174
3883.4	96	0,0	0.917
3871.4	34	1,1	0.785
4197.2	59		
4181.0	33		

Table 19.

Pair of lines compared A.	Temperature °K
4216.0 - 4197.2	3770
4216.0 - 4197.2	3309
4216.0 - 4181.0	4287
4216.0 - 4181.0	3516
4197.2 - 4181.0	4971
4197.2 - 4181.0	3751
3590.4 - 3585.9	3897
3590.4 - 3583.9	3371
3585.9 - 3583.9	3774
3883.4 - 3871.4	3444

Discussion.

The simplest method of temperature measurement, is that using the line-reversal method. Once the reversal point has been obtained visually the effective temperature of the background source and hence the flame is obtained without great difficulty (79). For temperatures below 2500°K the temperatures may be measured with an accuracy of $\pm 10^\circ\text{K}$. The high sensitivity of the method is due to the rapid variation of radiation intensity with temperature. At 2500°K and 5890 Å the intensity varies as the tenth power of the temperature.

For high temperatures e.g. at 3000°K the

temperature of nitrous oxide-acetylene, the reversal point may be set within $\pm 10^{\circ}\text{K}$ but the variation in the background source may be of the order of $\pm 50^{\circ}\text{K}$, thus affecting the accuracy appreciably.

This method is entirely dependent on Kirchhoff's law, which states that for a flame in thermal equilibrium, the emissivity for any wavelength is equal to the absorption coefficient. The main difficulties arise when the flame gases are not in thermal equilibrium. There must also be no loss of light from the flame by reflection, and in non-luminous flames reflection is negligible. Thus results for the fuel-lean and slightly fuel-rich flames are not affected by reflection losses. The very fuel-rich flame, however, containing an abundance of carbon particles will lose an appreciable amount of radiation by reflection, and these results are probably not as reliable as those for the fuel-lean and slightly fuel-rich flames.

The two-line method, although producing results in good agreement with each other, is subject to large errors if the flame gases are not in equilibrium. As stated previously ⁽⁸⁷⁾ the error in measurement of a ratio of intensities or transition probabilities can lead to an error of $\pm 50^{\circ}$. However, the transition probabilities themselves are not known to better than 15% ⁽⁹⁰⁾. The results obtained using this method, however, are concordant and this

suggests that the method itself is reliable. These same errors affect the rotational and vibrational temperatures obtained.

To establish confidence in the methods used the temperatures of air-acetylene and air-propane flames were measured using the line-reversal method, and the temperatures of air-acetylene and oxy-hydrogen flames determined by the two-line method. The temperatures obtained were

	<u>Literature values</u>
Air-acetylene 2054°C	2125°C (91)
Air-propane 1870°C	1935°C (91)

by the line-reversal method and

Air-acetylene	2125°C
Oxy-hydrogen 2427°C	2660°C (91)

using the two-line method.

Thus the values obtained agree very well with reported values.

The value obtained for the NH rotational temperature is in good agreement with the value given by Gaydon (69) of $3760 \pm 300^\circ\text{K}$.

The temperatures obtained using the four methods of measurement, are in good agreement. This suggests that the red zone of the nitrous oxide-acetylene flame is either in thermal equilibrium, or that deviations from equilibrium are slight. Fig. 33 shows the temperature profiles of the slightly fuel-rich (atomic absorption) flame using the results from the line-reversal and two-line methods.

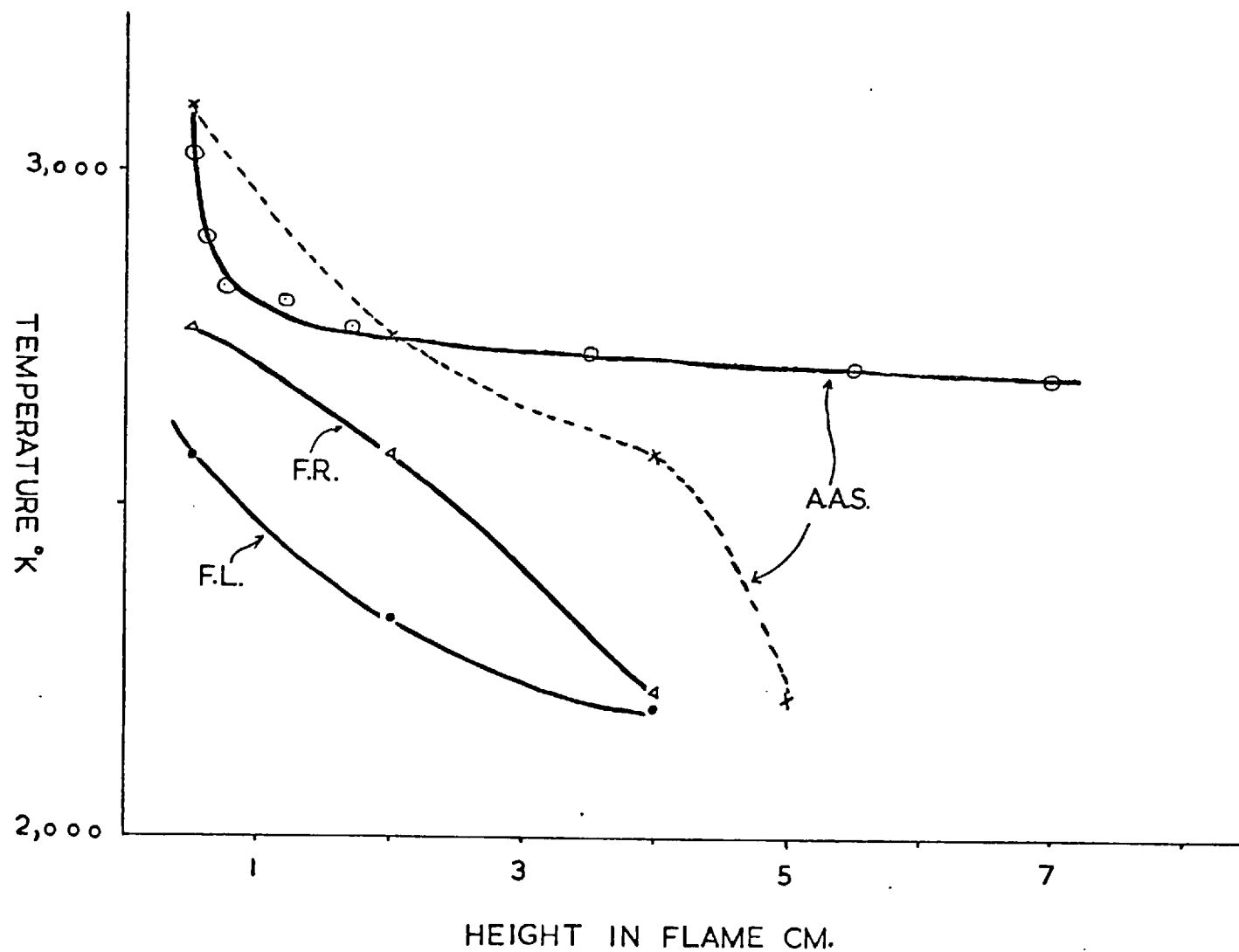


FIG. 33

CHAPTER 6.SPECTROGRAPHIC INVESTIGATION OF OTHER PREMIXED FLAMES
AT ATMOSPHERIC PRESSURE.

There is a dearth of information in the literature concerning the properties of hydrocarbon flames supported by gases other than air or oxygen. The reason for this no doubt lies in the wider technical application of air-supported flames. However, some of the problems associated with the use of conventional air-hydrocarbon flames in inorganic spectroscopic analysis may be eliminated by using other gases to support the hydrocarbon combustion. These mixtures may also provide relevant information concerning the excitation processes which occur during combustion. The difficulty of completely atomising samples in atomic absorption spectroscopy has been the main limitation of the technique. The introduction of the nitrous oxide-acetylene flame greatly increased the number of elements which could be determined with sensitivity using this procedure. The flame provides the required conditions for the production and maintenance of a large ground state atomic population of most refractory elements. For a flame to be of wide application in atomic absorption spectroscopy it must (a) have a high temperature, (b) provide a reducing atmosphere so that the atomic population is maintained and (c) have a burning velocity low enough for the flame to be supported safely at a

laminar flow, slit burner.

In an attempt to find better flames for use in atomic absorption work, various gas mixtures were studied spectrographically. Some of the flames were oxygen (or air) supported and others were supported by nitrous oxide. The emission spectra of these flames are recorded in this chapter and the principal emitting species have been identified. The properties in A.A.S. of some of the more useful flames have been compared with air-acetylene and nitrous oxide - acetylene mixtures.

Apparatus.

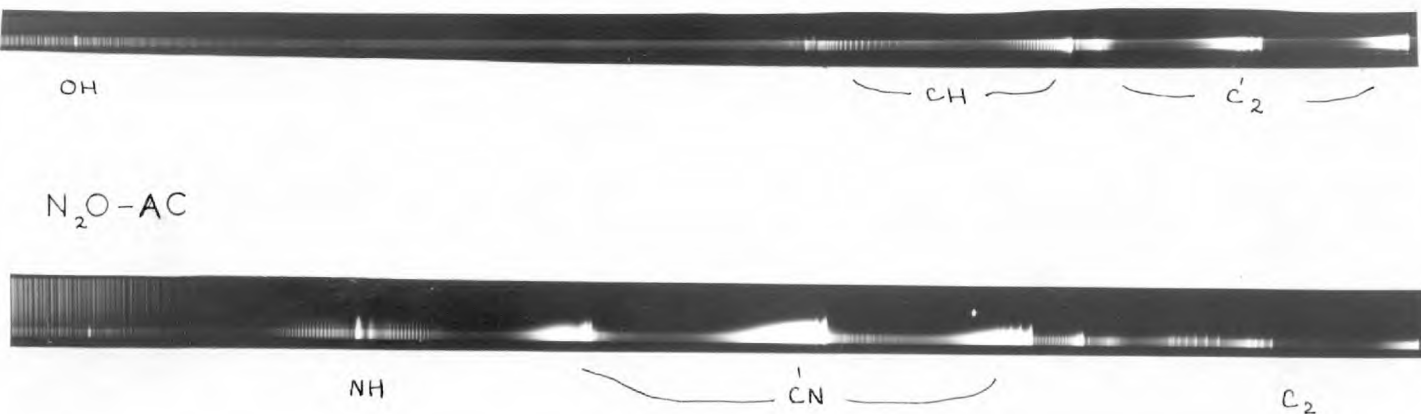
A Hilger large quartz spectrograph was used for the emission study and the spectra of the various flames were recorded on R.40 plates.

Comparison of the properties of the mixtures for A.A.S. of different elements was performed using the Unicam S.P.900A flame spectrophotometer.

Results.

Air-acetylene and nitrous oxide-acetylene flames.

These spectra are recorded initially for comparison purposes.



The species which emit strongly in the air-acetylene flames are CH, C₂, CO and OH. Weak emission from CN and NH occurs in the primary zone. This flame is very useful for the atomisation of non-refractory elements and good sensitivity may be obtained. Its use in the determination of refractory elements is severely limited and absorption signals can only be obtained using very fuel rich flames^(57,58).

The emitting species in the nitrous oxide - acetylene flame have been described in detail in Chapter 4. The slightly fuel-rich flame has been used for refractory element determination⁽⁹²⁾ and the enhancement in sensitivity obtained is appreciable.

Ethylene - air.

The emission flame spectrum from the region around the primary zone of this flame is shown on the next page.

OH

CH

 C_2

Again the main emitting species are C_2 , CH, OH and CO. The flame emission is similar to that of the air-acetylene flame. The burning velocity of ethylene-air mixtures is lower, and when used at an air-acetylene burner the flame tends to lift off the burner. The absorbance of copper and zinc in the air-ethylene flame is not as good as in the air-acetylene flame.

Nitrous oxide - ethylene.

OH

CN

 C_2

This flame, like the corresponding nitrous oxide-acetylene flame has three zones. The secondary reaction zone in this case is a yellow 'feather' region. The main emitting species present are C_2 , CH, OH, CN and CO. The emission from CN is much weaker in this flame than in nitrous oxide - acetylene. In the nitrous oxide-acetylene flame the strong

CN emission at 3590 Å prevents the use of the most sensitive chromium resonance lines at 3578.7 and 3593.5 Å, and other lines have to be used or the flame made fuel-lean, giving a corresponding loss in sensitivity. In the nitrous oxide - ethylene flame, the background noise level from the CN band would not prevent the use of these resonance lines and this flame may provide an increase in sensitivity over the nitrous oxide-acetylene flame. However, for M/50 molybdenum solutions the absorbance signal using the nitrous oxide - acetylene flame was 0.5, and in the nitrous oxide-ethylene flame the signal was 0.047. This decrease in sensitivity is probably due to the lower concentration of CN and NH species in the flame and to its lower temperature.

Nitrogen-oxygen-acetylene.

The emission spectrum of this flame is shown below.



The flame was produced using flow rates of 4 litres/minute of nitrogen, 2 litres/minute of oxygen and 3 litres/minute of acetylene. These flow rates were used since the actual mixture being burned corresponds in oxygen and nitrogen content to the slightly fuel-rich nitrous oxide-acetylene flame.

The species present in the flame are the same as those in the nitrous oxide-acetylene flame but the intensity of emission is much weaker.

Amos and Willis (63) have compared the absorption properties of the nitrous oxide-acetylene and the nitrogen-oxygen-acetylene flames and report similar sensitivities using these mixtures. In the author's laboratory using molybdenum as the test element, an absorbance signal of 0.5 was obtained for a M/50 aqueous molybdenum solution in the nitrous oxide-acetylene flame, compared with an absorbance value of 0.12 using the nitrogen-oxygen-acetylene flame. The greater absorbance signal using the nitrous oxide-acetylene flame is due (1) to the higher temperature of nitrous oxide-acetylene, which results from the energy liberated by decomposition of nitrous oxide,



and (2) to the abundance of CN and NH species present above the primary reaction zone to provide the reducing conditions required for the removal of atomic oxygen via ,



Thus shifting the monoxide dissociation to the right



and hence producing more ground state atoms capable of absorption.

Also if the nitrous oxide decomposed to give a mixture of 33% oxygen and 67% nitrogen, one might expect the properties of the two flames to be very similar, but this marked difference in the absorbance properties of the two flames suggests that the actual combustion process in the nitrous oxide-acetylene flame involves a direct reaction between the fuel and nitrous oxide molecules, whereas the oxygen-nitrogen-acetylene flame simply involves the burning of the acetylene in oxygen, with the nitrogen taking no part in the combustion process (66).

Oxy-acetylene.

The very high burning velocity of this mixture necessitated the use of a Beckman total consumption nebuliser burner. The flame produced is a turbulent flame and the emission spectrum is shown below.

CN

CH

C₂

Again the main emitting species are C_2 , CH, OH and CO with weak emission from CN and NH. The absorption properties of this flame were not obtained since the use of the different burner made any comparison meaningless.

Nitric oxide - acetylene.

Perhaps the most interesting flame for investigation is the nitric oxide - acetylene flame. Manning ⁽⁹³⁾ has found that the sensitivity for aluminium in the nitric oxide-acetylene flame is 60% greater than in the nitrous oxide-acetylene flame. The nitric oxide-acetylene flame is ideal for use since it combines a very high flame temperature $(3080^{\circ}C)^{(70)}$ with a relatively low burning velocity (0.87 metres/sec.). (cf. N_2O/Ac $2830^{\circ}C$. burning velocity 1.6 metres/sec.).

The flame was first lit on a nitrous oxide - acetylene mixture and the nitrous oxide was gradually **replaced** by nitric oxide. About 2 cm above the burner head the flame exhibited an intense yellow reaction zone. Unfortunately no emission spectra were obtained for this flame, since the only nitric oxide cylinder available was exhausted after five minutes of use. However, the analytical properties of this flame should be very **interesting** and require much more attention. The use of this flame as an atomiser for atomic absorption purposes should provide sensitivity as good as the nitrous oxide-acetylene flame but

the cost of nitric oxide compared to nitrous oxide may be a prohibitive factor. Gaydon and Wolfhard (78) report that hydrocarbon-nitric oxide flames lack the excess excitation energy in the primary zone which is prominent in oxygen and nitrous oxide supported flames, and gives rise to abnormal excitation of atoms and molecules. This is due to the small reaction rates in these flames, as evidenced by the low burning velocity, coupled with the high adiabatic flame temperature. Thus the rotational temperature of OH in nitric oxide flames is normal.

Conclusion.

By far the most useful gas mixtures for atomic absorption purposes are air-acetylene and nitrous oxide - acetylene. The nitrous oxide-ethylene and the nitrogen-oxygen-acetylene flames may be of use when the strong resonance lines of an element fall on the CN systems. In the nitrous oxide-acetylene flame the emission from CN would give rise to considerable background noise, and thus prevent the use of lines which are in close proximity. The nitrous oxide-ethylene and nitrogen-oxygen-acetylene flames which show far weaker CN emission would allow these strong resonance lines to be used and hence greater sensitivity may be obtained. This is an exception and in general the nitrous oxide-acetylene flame would be used to give the corresponding enhancement in sensitivity associated with this flame.

Flames supported by other nitrogen oxides should give good sensitivity in atomic absorption spectroscopy. Premixed nitric oxide - acetylene flames combine a high temperature with a low burning velocity, which enables the flame to be used safely. CN and NH species are produced in this flame and these should provide the reducing atmosphere in rich mixtures, which appears to be required to maintain the atomic population of refractory elements.

CHAPTER 7.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

During the last fifteen years atomic absorption spectroscopy has become established as one of the most important techniques for inorganic trace analysis. The versatility, speed and freedom from interference of this method makes it ideal for the analysis of many elements. The sensitivity provided is generally high but in cases where there is severe chemical compound formation in the flame, the complete atomisation of samples creates many problems.

There are many ways in which the sensitivity of the atomic absorption technique may be improved by instrumental development. The hollow cathode lamps available at present give intense and stable radiation for long periods of time, but for some elements e.g. the rare earths, it is difficult to prepare a hollow cathode lamp, and in this sphere the use of continuum sources or electrodeless discharge tubes needs investigation. More sensitive detectors and amplification systems together with recorders fitted with scale expansion facilities would help to increase the sensitivity of the procedure and detection limits would be lowered.

These improvements in instrumentation could be easily made, but the main limitations regarding the sensitivity and applicability of the absorption method, arises

from the processes of nebulisation and atomisation. Although advances have been made over the last ten years, the conclusion reached by Walsh in 1951 that "... at the present state of its development, by far the most serious difficulty in the absorption method is due to the difficulty in atomising various elements" still applies. The difficulties begin at the nebulisation stage since even the most efficient indirect nebulisers deliver only 20% of the aspirated sample to the flame. Use of an ultrasonic nebuliser, which produces a very fine aerosol does not alter the fact that 80% of the sample is lost, and the small amount which does reach the flame is diluted many times by the flame gases before absorption measurements are made. Thus, there is a need for a better nebulisation system. A possible method of overcoming the loss of sample in the spray chamber is by using charged colloids or actually producing sample droplets which are charged. These droplets may then be beamed into the flame using external electric fields. To avoid the need for nebulisation, methods involving the introduction of solid sample (in dust form) into flames should be investigated.

Flames are used almost exclusively for the atomisation of samples. The cooler air-coal gas, air-propane and air-acetylene flames are used for the determination of non-refractory elements, and of elements, such as the alkali metals where a hot flame would cause

excessive ionisation. For atomisation of refractory elements, however, the higher temperature and reducing atmosphere provided by the nitrous oxide-acetylene flame are usually required. Even using this flame there are a number of elements which are incompletely atomised and low sensitivity is obtained. A study of the chemistry of the stable compounds formed, and of the reactions involved in their dissociation into atoms may lead to the more effective use of flames. Little is known concerning the reactions which occur during the combustion of premixed gases and the effect of these reactions on the atomic population. Obviously the type of solvent used will affect the flame processes, aqueous and organic solvents would cause different reactions to occur, and the enhancement in sensitivity due to the organic solvent effect may not arise solely from the increase in spray rate, but there may be some intermediate chemical reaction involved which enables a larger ground state atomic population to be produced. Hence the need for more efficient atomisers is apparent. The atomic absorption properties of other premixed flames should be investigated and the sensitivity obtained compared with the flames in use at present, and nitric oxide supported acetylene flames should be studied thoroughly. It is likely, however, that alternatives to flames will be necessary. The general introduction of plasma jets may enable more elements to be atomised completely. Development of sputtering procedures,

arcs and furnaces may all increase the scope and sensitivity of atomic absorption methods.

Any background radiation problems which arise using the high temperature flames may be overcome by using separated flames. Air-acetylene and nitrous oxide-acetylene flames have both been separated and the OH emission from the interconal zones is negligible. This decrease in background radiation will be of greater importance in emission flame photometry. For example the emission from molybdenum at 3132 Å is seriously affected by emission from the 3064 Å OH band in the unseparated nitrous oxide-acetylene flame. Separation of this flame, however, enables molybdenum to be determined sensitively due to the removal of the background radiation.

The future of atomic absorption spectroscopy is very promising and the problems associated with this technique as well as providing a challenge hold much interest for the researcher.

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