APPLICATIONS OF MICROWAVE-EXCITED PLASMAS TO THE ANALYSIS OF VOLATILE AND GASEOUS COMPOUNDS

by

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

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October 1972.

ABSTRACT.

This thesis is concerned with the application of microwave-excited plasmas as detectors in gas chromatography. An emissive detector system was first investigated. Eluates from a gas-chromatographic column were passed into the plasma of a 2450 MHz electrodeless discharge in argon at atmospheric pressure. The compounds were fragmented, excited and caused to emit characteristic emission spectra which were monitored photoelectrically to provide selective detection of the eluates. A variety of optical and electronic read-out systems were used.

Secondly, the emissions from a range of simple organic eluates containing chlorine, iodine, bromine, phosphorus or sulphur hetero-atoms were monitored simultaneously at two characteristic emission wavelengths. It was found that the ratio of the emissions for each compound could be used to determine the quantitative relationship between the number of hetero-atoms and the number of carbon atoms in the compound.

A non-selective detector using a novel mode of operation based on the measurement of reflected microwave power was developed. This detector provided sensitive detection of all the gases and organic compounds

studied. Its response was independent of the emissive detection system and they could be used simultaneously, to give both selective and non-selective chromatograms.

Finally, the emissive detector was used for the determination of metal chelates eluted chromatographically. By monitoring atomic metal emissions this sytem provided highly sensitive and selective detection of all the metal compounds studied.

ACKNOWLEDGEMENTS.

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

I wish to thank my supervisors, Professor T.S. West and Doctor R.M. Dagnall, for their help and guidance throughout this project. I would also like to thank my colleagues for their helpful suggestions and discussions, Miss M. Pinches, with whose help the metal chelates were prepared, and my wife, Michèle, for typing this thesis.

I am grateful to the Science Research Council for the provision of an award under the Award Scheme for Science, Industry and School Teaching.

CONTENTS

INTRODUCTION

I. General

The analysis of mixtures of gaseous and volatile compounds are usually carried out by separation of the components by gas chromatography, followed by their determination using a sensitive detector system. The present study is primarily concerned with the use of a microwave-excited plasma as a detector for gas chromatography.

The chromatographic separation of components of mixtures depends on differences in the distribution coefficients of the components between a stationary and a mobile phase. The term gas chromatography is used (1) to describe all chromatographic methods in which the mobile phase is a gas, and these are generally subdivided into gas-liquid chromatography, which involves the use of a liquid stationary phase (distributed on a solid support), and gas-solid chromatography in which the stationary phase is an active solid.

The technique of gas chromatography appeared first in 1941 when Martin and Synge (2) suggested the possibility of using chromatography to separate components present in the gas phase. However, it

was not until 1952 that the first analytical applications were described by James and Martin (3,4). They used the technique for the separation of fatty acids, which were subsequently determined by automatic titration. Due to the limitations inherent in this method of detection, the general acceptance of gas chromatography as a widely applicable analytical technique was delayed until the development of a simple, practical detector, the katharometer, in 1954 (5). A similar type of detector had previously been used by Phillips (6).

The introduction of the katharometer solved many of the initial difficulties of the technique, and, since this time, the basic design of the apparatus has altered very little, except in the sophistication of the instrumentation. The essential features of gas-chromatographic equipment are shown in Figure I(a). A constant flow of carrier gas is maintained through the injection block, the chromatographic column and the detector. The mixture to be analysed is rapidly injected into the gas stream prior to the column, and the components are eluted after time intervals (retention times) dependent on the flow rate and their relative coefficients of distribution between the stationary phase and the carrier gas at the temperature of the column.

The chromatographic separations possible depend principally on the length and temperature of the

column, the stationary phase, the carrier gas flow rate and the response time of the detector. Highly complex mixtures may often be separated using very long capillary columns in which the stationary phase is coated on the walls of the column (7,8) and a very low carrier gas flow rate is used. The minimum quantity of any particular component that can be determined depends mainly on the detector, and it is essentially the detector which governs the range of concentrations over which a gas-chromatographic separation can be usefully carried out.

II. Detectors in Gas Chromatography

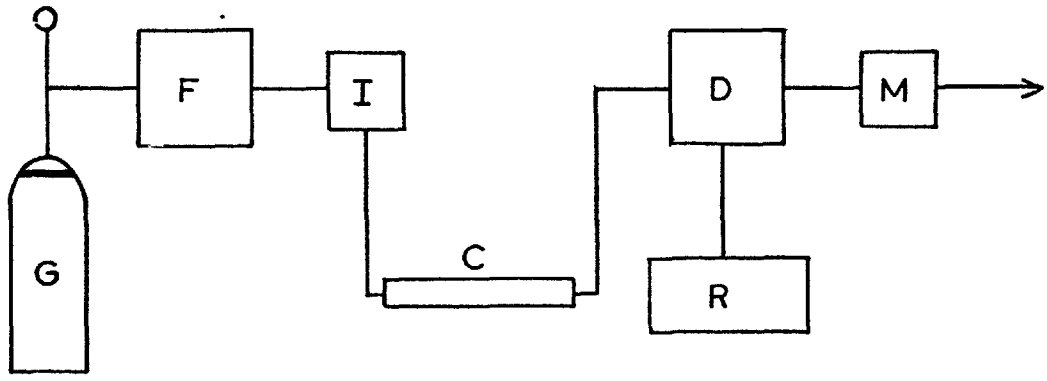
i. Differential and Integral Detectors

The term 'detector' is understood to mean a system which converts the chromatographic result (ie. a carrier gas stream containing various concentrations of other vapours) into a form in which it can be recorded. The record of the response of a detector against time is known as a chromatogram. Detectors may be classified as either differential or integral in type. A differential detector produces a chromatogram which is a record of the variation of the instantaneous concentrations of substances in the gas stream. Ideally, these chromatograms consist of Gaussian-type peaks (Figure I(b)). The chromatogram produced by an integral detector, however, is a record

of the total amount of substance which has passed through the detector, and consists of a step-shaped curve (Figure I(b)).

Ideally, a gas chromatographic analysis should be able to provide both the qualitative and quantitative determination of the individual components in the mixture analysed. Components are most often identified by their retention characteristics. Both absolute values such as retention times, retention volumes (9,10) and relative values of these quantities such as relative retention times (volumes)(10), or Kovats' retention indices (9) are used. These characteristics are more easily determined with a differential detector as the component band centre (peak maximum) used in their measurement can be readily located. In addition, partially resolved and very small peaks are more readily observable.

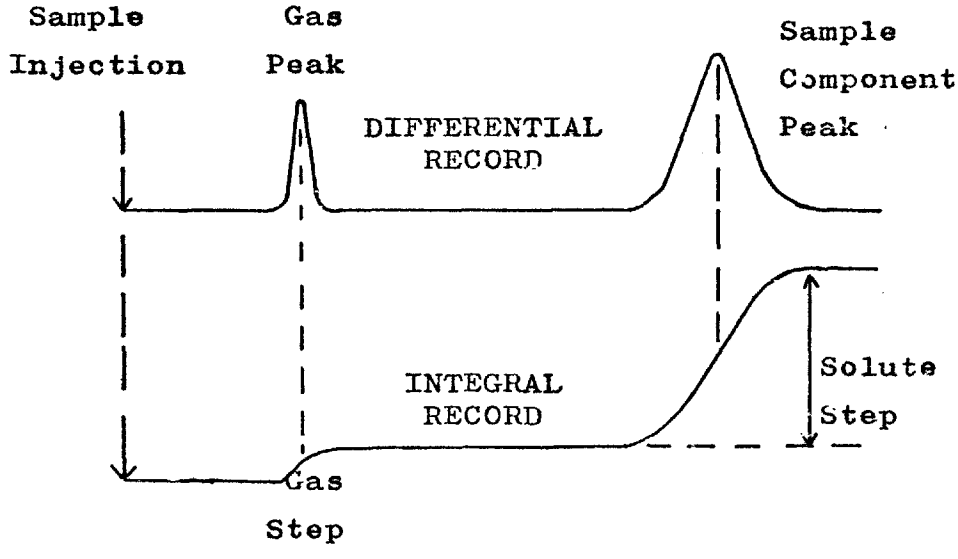
Differential detectors may also be used for quantitative analysis, by measurement of the area under each peak, but integral detectors have the advantage that quantitative estimation only involves step height measurements which are easier and more precise. Therefore, the differential detector is more suitable for qualitative analysis, whereas for quantitative work, in principle, an integral detector is to be preferred. In practice, however, differential detectors are used almost exclusively and integration, if required, is carried out electronically.



G - carrier gas supply
F - flow regulator
I - injection port
C - thermostatted column
D - detector
M - flow-meter
R - read-out

Gas-chromatographic Apparatus

Figure I(a)



Typical Chromatogram

Figure I(b)

ii. Selective Detectors

With mixtures of simple substances retention characteristics often enable the components to be identified, and the use of a detector which responds to all the components non-selectively is adequate. However, in the analysis of complex mixtures the identification of individual components by means of retention data interpretation alone is practically impossible. Selective detectors have therefore been developed.

A detection system is considered selective (11) if the molar response (or relative molar response or response to unit mass) of the detector to a substance A (or group of substances A) differs sufficiently from the response to substance B. In practice, the detector response to the substance being studied (i) is compared with that of a standard substance (r). The selectivity can be expressed as the relative molar response (12) $(RMR)_{ir}$. For a differential detector

$$(RMR)_{ir} = \frac{S_i \, N_r}{N_i \, S_r}$$

where S is the peak area and N is the quantity in moles injected. Hydrocarbon is usually selected as the reference substance. Detector response to it is considered as non-selective. Under these conditions it is suggested (13) that a detector is considered as selective to a substance i if $(RMR)_{ir}$ is greater

than 10. Clearly, if the detector response does not vary linearly with concentration, RMR will also vary with concentration.

A detector which shows selectivity towards a compound or group of compounds can be used to advantage in two ways. It can detect trace amounts of these compounds even when not resolved from relatively large amounts of other compounds and can help to identify unknown peaks obtained on a non-selective detector. Alternative methods of identifying unknown components, which have been used, are post-column trapping (14,15) and pre-column reactors (16) but these are generally less satisfactory, particularly when only sub-microgram quantities of material are involved.

iii. Detector Characteristics.

The requirements of a detector are numerous and varied depending on the particular application for which it is required but some generalizations may be made. A detector should be as versatile as possible; that is, capable of operation over a wide range of temperature, pressure and carrier gas flow rates, and insensitive to random changes in these parameters. Any system that attempts to measure small changes in large values is, in general, unsatisfactory, although such detector systems have been described (17).

In order to avoid peak distortion and limiting the resolution of peaks observed the detector should

have a rapid response time - less than one second (18). The three factors contributing to this are the speed of response of the sensing element or process involved, the detector dead volume (19,20), and the time constant of the associated equipment.

Ideally, a detector should have linear and predictable response to all the compounds to which it responds over the whole range of concentrations encountered in gas chromatography (ie. up to 0.1% in the carrier gas). The predictability could be either on a weight basis or some other stoichiometric property. Thus negligible calculation would be involved in finding the percentage composition of a mixture and absolute quantitative analysis would be possible. However, in practice, very few detectors have a predictable response, and most have a linear response over only a portion of the concentration range. In general, calibration is required for each material at all concentrations. This information can be usually obtained from a single series of measurements. Various methods have been described (21,22,23); the most widely used is the logarithmic dilution method (21).

A detector should have high sensitivity and a wide concentration range over which it can be used. In principle, the maximum possible sensitivity is desirable. In practice, however, the sensitivity is often limited by noise due to such factors as the slight evaporation of the liquid phase from the column

(bleed) and impurities in the carrier gas. In addition calibration becomes increasingly difficult at very low concentrations (24).

The minimum quantity of a substance that can be detected (the limit of detection) is generally taken to be that quantity which will produce a peak twice the height of the noise level (ie. the random variation in background signal). This quantity is clearly dependent on the width and shape of the peak and hence on the chromatographic conditions used. Therefore, for the comparison of detector sensitivities the weight of substance which, if eluted in one second, would give a peak height twice that of the noise is often calculated. Its units are gs^{-1}. An alternative definition in terms of the minimum detectable concentration in the gas stream in millimoles ml^{-1} is also used.

iv. Practical Detectors

This review of detectors is not intended to be exhaustive. In it are described the general types of detector which have been developed for use with gas chromatography. Emphasis is laid on those detectors in most common use, and on detectors with uses similar to those of the detector described in the present work, ie. selective detectors and, in particular, emissive detectors.

The detectors which have been used in gas chroma-

tography may be classified conveniently into four groups according to the basic principles involved in their operation.

1) Non-destructive detectors based on the measurement of changes in the physical properties of the column exit gas stream.

2) Detectors based on ionization or electron absorption phenomena.

3) Spectrometric detectors.

4) Detectors based on chemical or electrolytic phenomena.

1) Non-destructive Detectors Based on the Measurement of Changes in the Physical Properties of the Column Exit Gas Stream.

Katharometer Detector (Thermal Conductivity Detector).

The katharometer is very widely used even though it satisfies few of the criteria of an ideal detector. In the basic katharometer the sensing element is a heated wire mounted in the path of the carrier gas and forms an arm of a Wheatstone bridge. When pure carrier gas is flowing it is balanced by a second wire placed in a reference gas stream. However, when an eluate is present in the carrier gas, the thermal conductivity of the gas is altered and the temperature and hence the resistance of the wire changes. The extent of unbalance of the bridge network is therefore a measure of amount of eluate present.

The sensitivity of the detector is a function of the temperature, the characteristics of the sensing element, the thermal gradient from the element to the cell wall, the thermal conductivity of the carrier gas and the cell geometry (25); consequently katharometer design has been extensively studied (26,27,28). Both thermistors (28-31) and metal wires (usually platinum or tungsten) have been used as sensing elements, but wires are more common owing to the lower stability of thermistors and the difficulty in obtaining matched pairs. Helium and hydrogen have proved to be the best carrier gases due to their high thermal conductivities. Results are obtained which are semi-quantitatively predictable (32,33), but even in the best conditions detector sensitivity is not high (ca. 10^{-8} millimoles ml^{-1}).

The usual cell volume of a katharometer (2ml) is too large for high resolution and use with capillary columns; however, micro-volume versions (down to 3μl) have been designed (34,35). The katharometer can detect all substances including the permanent gases; for quantitative work calibration is required for each substance and its response is sensitive to flow rate and temperature variations. Its operation is simple and it is robust.

Gas Density Balances.

The response of a detector that measures density changes in a gas stream is calculable on the basis

of molecular weights (36). The construction of such a detector for gas chromatography was first described Martin and James (37). It consists of two bridge circuits of tubes arranged so that when the density of the carrier gas equals that of a reference stream no gas flows across a central linkage. Any change in density of the carrier gas results in a gas flow which can be monitored to produce the detector response. This gas density balance is robust, reliable and cheap. The response is predictable, linear (38,39), non-destructive, and flow rate independent. However, the detector is not easy to construct and its major disadvantage is its poor sensitivity. In addition, it requires very careful temperature control.

The Gow-Mac gas density detector, a simplified version of the Martin detector, was designed by Nerheim (39), and is available commercially. Although similar to the Martin detector, its predictability of response is limited (40,41), and its range of linearity significantly less (41). It has been used to calibrate other types of detector (42).

Brunel Mass Detector.

Direct weighing of components in the carrier gas stream has been used as a means of detection (43). Column effluent is fed into a small vessel, containing active charcoal, which is attached to an automatic recording electro-microbalance. Components are quantitatively absorbed by the charcoal giving an

integral response, which is a direct measure of the weight of material present. Absolute quantitative analysis is thus possible (44,45), and this detector has been used to calibrate detectors of unpredictable response (46). Its sensitivity is similar to that of a katharometer. One disadvantage is the need for calibration for the analysis of gases, for which absorption is not quantitative.

Ultra-sonic Detector.

The ultra-sonic detector is based on the measurement of changes in the velocity of an ultra-sonic signal owing to the presence of eluted components in the gas stream. The carrier gas stream is compared to a reference stream, and changes in velocity are observed as phase shifts when the signals from two transducers, one in each gas stream, are compared. With hydrogen as carrier gas detector response to many substances is in agreement with theoretically calculable values (47). Response is linear over five orders of magnitude but is very sensitive to oxygen and nitrogen, and, therefore, even the slightest leak in the system cannot be tolerated.

2) Detectors Based on Ionization or Electron Absorption Phenomena.

Types of Ionization Detector.

Ionization detectors may be classified according to the manner in which ionization is produced :

by thermionic emission (ionization gauge), by radioactivity (ionization cross-section, argon, helium and electron capture detectors), in a flame, by electrical discharge or by photoionization.

Detectors based on the principle of a vacuum ionization gauge suffer from the disadvantages of requiring a high vacuum and of deposits forming on the electrodes, and have, therefore, been rarely used (48,49). In contrast, the range of detectors with a radioactive ionizing source have been widely used. They consist, in general, of an ionization chamber containing the radioactive (β-ray) source, and two electrodes across which a potential can be applied. The current flowing in this electrode circuit is used as detector response. The phenomenon depends on the geometry of the chamber, the potential applied, and the carrier gas used.

Ionization Cross-section Detector.

As the potential across the ionization chamber is increased (to ca. 300 V) the current reaches a steady value, known as the saturation current, dependent on the rate of production of ions in the chamber. This in turn depends on the β-ray source and on the ionization cross-sections of the molecules composing the gas in the chamber. Hence the current depends on the composition of the gas and can be used as a detector response. Hydrogen, with its low ionization cross-section, is preferred as carrier gas. This

detector has many attractive features. The change in current is calculable from the molecular ionization cross-sections of the eluate and carrier gas and agreement with prediction is observed for a number of species (50). The detector response is dependent on temperature and pressure but is linear over a wide range of concentrations. Detector sensitivity is better than that of a katharometer and has been further increased in a micro-version (51,52).

Argon Detector.

This highly sensitive detector was first described by Lovelock in 1958 (53). It differs from the cross-section detector somewhat in its configuration and in the high potential applied (1000-2000 V). Argon is used as carrier gas. The sensitivity of the device is due to the formation of meta-stable argon atoms of high energy (11.7 eV) and relatively long half-life (ca. 10^{-4}s) in the presence of β-radiation (54). This excess of energy can be transferred to organic molecules in the gas by collision processes, and will cause ionization if the ionization potentials of the molecules are sufficiently low. Thus the detector will respond to most organic compounds but not to the permanent gases. Although sensitive, the detector has a very short linear range and requires calibration. In addition, it is easily overloaded and even traces of water seriously affect the response (55); it is

therefore little used.

Two improved versions of the basic detector have been introduced by Lovelock. The micro-version (56) is designed specifically for use with capillary columns. The triode-version (57) encorporates a third electrode to reduce the background ionization current from the argon and gives a better over-all performance.

Helium Detector.

By replacing argon by helium as carrier gas, metastable atoms of sufficient energy (24.5 eV) to ionize all materials except neon are produced (58). The detector formed in this way is extremely sensitive ($10^{-14} gs^{-1}$) but requires very high purity helium to minimize background current. This factor limits its use to the analysis of permanent gases for which it is the most sensitive detector available.

Electron Capture Detector.

This detector developed by Lovelock (59) depends for its operation on the ability of certain molecules to absorb electrons according to the following processes (60) :

$$AB + e^- = AB^- \pm \text{energy}$$

$$AB + e^- = A + B^- \pm \text{energy}$$

In the case of ionization of an inert gas (eg. nitrogen) the only negative particles present are electrons. The probability of the recombination of these electrons with positive ions is low because of their very different velocities (the velocity of

an electron is ca. 10^4 times higher than that of positive ions (61)). However, if an ionized inert gas contains compounds with high electron affinities, some free electrons may be captured by the molecules of these compounds with the formation of negative ions. The velocity of these ions is much lower than that of the free electrons and the probability of combination between negative and positive ions is 10^5-10^8 times higher than that between electrons and positive ions (57). Hence, the presence of a compound able to capture electrons will be indicated by a decrease in the ionization current.

The detector is similar in construction to the ionization cross-section detector but a potential of only a few volts is applied, in order to minimize the acceleration of free electrons. Many carrier gases have been tried (59). One problem is to avoid the detector responding partially as a cross-section or argon detector; to reduce these effects to a minimum nitrogen or a mixture of argon with 5% methane is usually used. To further reduce these unwanted modes of detection a pulse sampling method was introduced (60). In this technique, instead of a d.c. potential, short d.c. pulses are applied to the electrodes. Typical pulse width values are 0.5-1.0 μs with a 100 μs interval, and the pulses have an amplitude of about 30 V. The d.c. pulses are of sufficient duration to allow the capture of electrons but not

sufficient to allow any significant movement of the negative ions. Using the pulse method the effects of variation of temperature (62,63), applied potential (63,64) and carrier gas flow rate (62,65) are reduced and the detector shows better reproducibility (66).

The response of the detector to different types of molecule depends on the probability of electron capture in each case; these probabilities are spread over a range of 10^6 and the detector response is therefore highly selective. The detector is sensitive, and hence selective, to compounds containing halogens (57,60,61), phosphorus and sulphur (67,68), lead (69,70), nitrogen dioxide (63) and nitrates (57), oxygen compounds (particularly quinones), ozone and oxygen (57,71) and also to certain hydrocarbons such as azulene and stilbene (57).

The detector response varies greatly with the structure and number of electron-capturing groups present and is not predictable. The response varies linearly with concentration over a range of ca. 10^3 but tends to drift over relatively short time periods. The detector is, therefore, not very suitable for quantitative work. In addition, there is a relatively small temperature range over which it can be used due to its susceptibility to column bleed and the more rapid deterioration of the radioactive source at higher temperatures. However, these factors are more than compensated for by its very high sensitivity and

selectivity when used for the analysis of traces of electron capturing compounds (e.g. pesticide residues).

Flame Ionization Detector.

The application of a detector using as its basis the ionization of organic materials by a flame was first described by Mc.William and Dewar in 1958 (72). The effluent from a column is mixed with hydrogen and air or oxygen as it passes through a jet and the mixture is burnt in a small flame. A potential of 200-300 V is applied across the flame by means of two electrodes and the current flowing is measured. In practice, the burner jet is one of the electrodes and the other is a wire or grid extending into the tip of the flame. When only pure carrier gas (nitrogen, argon, or helium) is flowing virtually no ionization occurs in the flame and the current in the electrode circuit is very low (10^{-11} to 10^{-12} amps (57)). However, when carbon-containing compounds are present, ionization occurs and the ionization current rises. Despite the poor efficiency of ionization, the detector is very sensitive (responding to ca. 10^{-11} gs^{-1} of many organic compounds) due to the very low background current.

The flame ionization detector (FID) is insensitive to the permanent gases, ammonia, water, carbonyl sulphide and carbon disulphide (73), but responds well to other organic compounds with the exception of organo-metallics. This detector is particularly simple and

elegant and many workers have undertaken detailed studies of its performance (73-77). Its response is linear over a range of 10^6(73,75) and is relatively insensitive to changes in temperature and pressure (78). The response increases generally with higher carbon content of an eluate and for many aliphatic and aromatic hydrocarbons is calculable from the number of carbon atoms and the molecular weight (79,80,81). Tables of relative response factors have been published for a wide range of compounds (82,83), but are dependent on experimental parameters (83,84).

The overall performance of the flame ionization detector approaches the requirements of an ideal detector; it is sensitive, stable, has a small dead volume and a rapid response time. Response is in some cases predictable and its construction is simple and robust (74).

The Alkali Flame Ionization Detector.

The flame ionization detector responds to almost all organic compounds; however, if an alkali metal salt is present in the flame the response to compounds containing certain hetero-atoms is considerably enhanced. This type of detector, known as the alkali flame ionization detector (AFID), was first described by Giuffrida (85) and Karmen (86) and has been investigated in detail by many other workers. However, Brazhnikov et al. (87), who recently

reviewed the literature on this type of detector, concluded that the mechanism of the enhanced detector response still remains unclear. Alkali flame ionization detectors show enhanced response to compounds containing halogens (86,88-90), phosphorus (85,88,89), sulphur (89,91), nitrogen (89,92-95), arsenic (95,96), tin (96), silicon and lead (97). The enhancement is greatest for phosphorus-containing compounds for which the response is 10^3-10^4 times that of a flame ionization detector.

Detectors using either one or two flames have been constructed. The single-flame detector is essentially similar to a FID with an alkali metal salt mounted in it. The salt may be suspended in the flame on a loop or screen (86,96) but better stability was obtained using a compressed salt tip fitted on the jet of the burner (91). The detector response depends on the particular metal salt used. The selectivity for phophorus compounds over the response on a FID is 10^3-10^4 if salts of any of the alkali metals are used (11), while for nitrogen compounds the selectivity is generally 40-100 with all alkali metals except sodium (95). AFID response to halogen compounds is very dependent on detector construction and is negative in some cases (90,98); selectivity is relatively poor. For sulphur compounds the selectivity is only 10 to 20 and using rubidium, caesium or potassium salts the response is negative

(91). Dressler and Janak (91) found that the detector response to monobromo-compounds and chlorobenzenes was proportional to the number of halogen atoms present. A similar proportionallity was found by Aue et al. (99) for the detector response to phosphorus, nitrogen and iodine compounds (positive response) and to chlorine, bromine and sulphur compounds (negative response), using a Rb_2SO_4 pellet. However, attempts to calculate the percentage by weight of heteroatoms in molecules by comparing the AFID response to that of a FID were less successful, giving only poor quantitative agreement.

The double-flame detector (86,89) consists of two flame ionization detectors mounted one above the other, with a screen coated with an alkali metal salt mounted between them. The lower system works as a FID and the combustion products interact with the alkali metal salt before entering the second flame. This produces a highly selective detection system for compounds containing phophorus or halogens (except fluorine), but is not specific; sensitivity to other compounds depends on the lower system and the salt used (96). One disadvantage of this arrangement is that the interaction of the electric fields of the two flame systems results in distortion of performance (100).

Both single and double-flame systems are sensitive and selective. Due to its lower noise the single-flame type is generally the more sensitive but is less selective. The variation of response with concentration

is linear over a range of 10^3-10^4 and also the possibilities of negative or positive response have been used to increase selectivity and to aid in compound identification (90,91,98). However, the response of both types of AFID depend critically on the salt used (92,95,101) and the hydrogen flow-rate (85,86,92) which determines the flame temperature and hence the evaporation of the salt and the magnitude of ionization produced. In addition, the sensitivity decreases with time due to the loss of alkali metal in the flame, although this can be minimised (92) using relatively large reservoirs of the salt. These factors contribute to make a detector system which tends to be unstable and requires frequent recalibration.

Surface Ionization Detector.

The surface ionization detector makes use of an effect described by Kingdom and Langmuir (102). The emission of positive ions of an alkali metal from a heated platinum surface was found to increase in the presence of halogens and in oxygen media. This detector was first used in gas chromatography by Cremer et al.(103) and has been found to be sensitive to halogen compounds (94,103,104) and some organophosphorus and sulphur pesticides (105). In practice, the anode is usually a ceramic tube saturated with a salt and surrounded by a platinum coil. A potential of ca. 400 V is applied between the anode and a collector and the current measured.

Detector response is sensitive (3×10^{-10} g chlorine s^{-1} (103)), selective, and linear over a range of 4-5 orders of magnitude (106). In addition, the response was found to be independent of molecular structure (103). These advantages are outweighed, however, by the instability of the detector response : the sensitivity depends markedly on the age of the anode, the carrier gas flow rate (106), temperature and pressure (103). It also has a relatively high time constant reaching values of 10-20 seconds (103).

Ionization Detectors Involving Electrical Discharges.

Detectors using electrical discharges to produce ionization have found relatively little application. DC glow discharge ionization detectors have been designed by Pretorius (107), Pitkethly (108) and Ryce (109), but in all cases the elctrodes rapidly became contaminated and results were not quantitative. Yamane (110) has described a detector in which the primary electrons are generated by a subsidiary discharge in argon, upstream of the sensing chamber. Some electrons pass into the chamber and the ionization current produced is measured. A limit of detection for cis-butene of 8.9×10^{-11} g s^{-1} was reported. Later modifications (111) using helium for the discharge and miniaturization of the detector resulted in a more linear response. In 1965, Fisher and Mc.Carthy (112) developed a low pressure discharge detector in which a glow discharge is maintained across the gap of a

spark plug by application of 300 V d.c. A sensitivity of 10^{-6} g ml^{-1} for oxygen and carbon dioxide in nitrogen was reported, but its utility is limited because each gas requires a critical setting of the spark gap and applied potential.

A major problem with d.c. discharges has proved to be the deterioration of the electrodes. Arkinar et al. (113-115) have tried to avoid this problem by using an electrodeless discharge in the annulus of an all glass Siemens' ozonizer. The signals appeared as changes in the constant discharge current of the carrier gas (nitrogen) plasma. Sensitivity was a factor of 10 greater than a katharometer and the linearity of response was poor.

Photo-ionization Detectors.

In this type of detector the source of ionization is the intense radiation by a gas discharge maintained separately from the electrodes used to measure the ionization current. Helium, argon, nitrogen or hydrogen are sutable as discharge gases and both d.c. and high frequency excitation have been used (116,117). To maintain the discharge low pressures are usually necessary. This technique was first applied to gas chromatography by Lovelock (118), but has been investigated by other workers (116,117,119,120).

Although in principle the radiation from a helium discharge is sufficient to ionize even the permanent gases, intensive purification of the helium would be

necessary to avoid absorption of the high energy photons by impurities. In practice the detector responds to a similar range of substances as a flame ionization detector. It has a range of linearity of ca. 10^5 (116) and is very sensitive (limit of detection for propane is $5 \times 10^{-13} g\ s^{-1}$).

3) Spectrometric Detectors.

Spectrometric detectors provide both the possibilities of quantitative determination of an eluate and of its identification by means of its electromagnetic or mass spectrum. In addition, by monitoring a particular wavelength or mass number they offer some degree of selectivity. The techniques used are principally mass and emission spectrometry and also ultra-violet and infrared spectrophotometry and spectrofluorimetry.

Mass Spectrometry.

The combination of gas chromatography and mass spectrometry, in which part of the effluent is continually transferred from the chromatographic column to a mass spectrometer, was first described in 1957 (121), and since then has been the subject of extensive study. The amount of effluent which can be introduced into a mass spectrometer is determined by the highest acceptable pressure of the analyser and ion chamber, in which the pressure should not exceed 10^{-5} torr (122).

When capillary columns are used with a gas flow of ca. 1 ml min^{-1} the column outlet can be connected directly to the mass spectrometer ion chamber; with efficient pumping a sufficient vacuum can be maintained (123,124). Direct connection is desirable to minimize dead-space and loss of resolution. However, for columns requiring higher flow rates, which include all packed columns, a method of stream splitting is required so that only a portion of the effluent enters the mass spectrometer. This can be achieved by simply leaking a part of the effluent to the atmosphere (125, 126), however, in order to avoid the consequent loss of sensitivity, a variety of separators have been designed to preferentially remove the carrier gas.

With separators of the Ryhage type, the column effluent streams at high speed through a series of jets (127). Relatively light molecules of the carrier gas, helium, diffuse to the sides of the separator from which they are pumped out while the heavier molecules of the sample continue to another jet. A separator made of sintered glass (128,129) makes use of the easier effusion of carrier gas molecules through the pores of the separator. Teflon (128,130) and organic diaphragm separators (131) make use of the differing permeabilities of carrier gas and eluates. Increases in the concentration of eluates in the carrier gas of ca. 10 may be obtained, and up to ca. 90% of the components entering the separator

may be transferred to the mass spectrometer (128). Helium is used as carrier gas to facilitate separations and because of its low mass, high ionization potential and low ionization efficiency (132).

A mass spectrometer may be used to obtain both quantitative and qualitative information. The mass spectra of most organic molecules do not include a dominant peak corresponding to the molecular weight of the compound, therefore, a complete scan of the spectrum is usually necessary for qualitative information. In general, a portion of the total ion current, which is proportional to the concentration of components present, is used to give a complete chromatogram while the mass spectrum is scanned rapidly and repeatedly throughout the analysis (133,134).

The amount of structural information obtainable from the mass spectra depends on the resolving power of the spectrometer, which in turn limits the scanning time. Scan times of down to 10^{-4} s per mass decade are possible with a time-of-flight spectrometer, which permits determination of mass numbers of the heavier ions to the nearest unit. This is often adequate for the identification of organic ions, however for the determination of the elemental composition of molecules the resolving power required can only be provided by a double focusing instrument with a minimum scan time of 10 s per decade (135). As, ideally, a complete spectrum should be obtained for each peak at its maximum (136) high

resolution studies of sharp peaks are difficult. A further problem arises in the identification of the spectrum produced. The interpretation of mass spectra is still limited and a mass spectrum must often be regarded as a fingerprint which permits identification if it can be found in the files (137). The number of reference spectra is rapidly increasing but it has been found (138) that the spectra vary considerably in detail depending on the instrument and exact conditions used.

Despite these limitations mass spectrometry offers considerable advantages, especially when used in conjunction with a computor. In favourable cases it is possible to detect the parent ion and hence the molecular weight of the compound; fuller structural information can sometimes be deduced. This information is not obtainable for the very small quantities of material used by any other method. Repeated scanning across a chromatographic peak makes it possible to check whether the peak is due to a single component, or, as an alternative, by monitoring a suitable mass number particular types of compound may be determined selectively eg. mass of 43 is characteristic of methyl ketones (124), 91 of alkylbenzenes (139), 208 of alkyl-lead (139). Only small losses of column efficiency have been found compared with a FID (140). These advantages have resulted in the widespread use of mass spectrometry despite the very high cost.

Detector sensitivities of 10^{-12}-10^{-13} g s^{-1} have been reported for particular compounds (124, 141) but, usually, nanogram quantities of components are required in order to obtain useful structural information (135); micrograms of material are often necessary to obtain high resolution spectra (135). One disadvantage of this method of detection is that stationary phase bleed can change the characteristics of the filament of the ionization chamber (142), and so column temperatures as low as possible should be used.

Emissive Detectors.

Flame Photometric Detector.

The flame photometric detector is essentially similar to a flame ionization detector except that, instead of ionization current, emission from the flame is measured. The emission wavelength monitored is selected using a monochromator or filter and recorded via a photomultiplier and amplifier. Hydrogen/air or oxygen flames are usually used with nitrogen or helium as carrier gas.

In the detector, developed in 1966 by Brody and Chaney (143) a hydrogen rich flame is used for the selective determination of phosphorus or sulphur containing compounds. The mixing of the auxiliary gases is critical; the oxygen supply is mixed with the carrier gas stream below the jet and the hydrogen introduced so as to form an envelope of unburnt gas around the flame. Under these conditions, in the

presence of phosphorus and sulphur containing compounds, intense emissions from HPO and S_2 species (144) at 526 nm and 394 nm respectively are obtained above the flame. The flame is screened off and these emissions monitored using narrow band-pass interference filters and photomultipliers.

Sensitivities to phosphorus compounds down to 5×10^{-13}g phosphorus s^{-1} have been reported (143, 145) and sub-nanogram quantities of phosphorus compounds have been determined in the presence of large amounts of non-phosphorus compounds (146). The detector response to phosphorus is linear over a range of 3-4 orders of magnitude and is 10^3-10^4 times greater than that to compounds not containing phosphorus (147), with the exception of sulphur compounds. At the lowest measurable concentrations the selectivity to phosphorus over sulphur is ca. 150 (145) but as the sulphur response increases exponentially with concentration the selectivity falls to only ca. 4 in the range of 100-200 ng (148).

The minimum amount of sulphur which can be determined from the emission at 394 nm is 2×10^{-10}g (149); approximately a factor of 100 worse than for phosphorus at 526 nm. However, as the response to sulphur compounds is approximately proportional to the square of the concentration (148) detector response is similar for microgram quantities of sulphur and phophorus. To take advantage of the relatively greater response

to sulphur at higher concentrations Crider and Slater (150) added sulphur dioxide to provide a sulphur background. They found that a 4 to 8 fold increase in sensitivity could be obtained but the system was slow to return to equilibrium. Emission in the sulphur mode (ie. at 394 nm) was found to be reduced by non-resolved carbonaceous compounds (151,152). Perry and Carter (152) found the quenching effect to be marked - a 50% reduction in response to thiophen resulting from 0.5% of interfering substance. However, Grice et al. (149) found no such effects. Phosphorus-containing compounds produce positive emissions, which are linear with respect to concentration. Therefore, although the selectivity of sulphur to phosphorus is only 40 at the lowest concentrations (145), it rises rapidly to ca. 10^3-10^4 with samples of ca. 100 ng (148).

In the case of compounds containing both phosphorus and sulphur atoms, the simultaneous detection of both the elements can be carried out using two filters and associated optical systems (148,149). This can further be used in conjunction with a FID response; the three responses can be used to help identify compounds. However, the evidence is often inconclusive (149).

Flame photometric detectors can be modified in a similar way to flame ionization detectors by the introduction of metals or metal salts into the flame. Alkali-salt sensitized flames have been used (153-156) for the determination of chlorine, bromine and iodine

compounds by monitoring sodium emission at 589 nm. Nowak and Malmstadt (155) found the detector particularly sensitive to iodine (limit of detection of 2×10^{-11}g methyl iodide) but a factor of 100 less good for chlorine and bromine compounds. Selectivity over nitrogen, fluorine and carbon compounds was also high (ca. 10^4 for iodine, ca. 500 for chlorine and bromine), but phosphorus interfered strongly and the range of linearity was poor. Aue and Moseman (154) found sensitivities (3-5 ng) and selectivities (50-100) to be less good, but were able to use the direction of response (usually positive for iodine and negative for bromine and chlorine) tc help to distinguish between the halogens. Bowman and Beroza (157) used indium to sensitize a flame with similar results and the same workers (157) monitored the emission at 526 nm from a flame burning over a copper gauze. They used the variation of response with different hydrogen flow rates to distinguish between halogens.

A more direct method to differentiate between compounds containing different halogens is to monitor halide emissions from a metal-sensitized flame. Overfield and Winefordner (158) used a two burner arrangement with an indium coated screen between the burners and recorded the indium halide emission from the upper flame. The emissions used were 359.9 nm (InCl), 372.7 nm (InBr) and 409.8 nm (InI). Limits of detection of 5×10^{-10}g for chlorine, 4×10^{-9}g for

iodine and 4×10^{-10} g for bromine compounds were obtained. The ranges of linearity were good (ca. 10^3) and for chlorine and bromine compounds the response per halogen atom was the same within ± 10% for a range of compounds. However, even using very low slit widths (with a 50 fold loss of sensitivity) the selectivity for chlorine over bromine was only 20, and all the halogens (except fluorine) interfered strongly with detector response to bromine and iodine. A similar detector using a single flame with an indium tip has been described (159). Only poor inter-halogen selectivity was achieved and sulphur and phosphorus also interfered.

The flame photometric detector is sensitive and selective for phosphorus and sulphur determinations. It can be modified for halogen determinations, but these are less sensitive and, as in the case of the AFID, the use of additional reactants does not contribute to detector stability.

Use of Emission from Electrical Discharges.

When a compound is introduced into a discharge it is fragmented to atomic and molecular species; these species are excited and emit electromagnetic radiation. The detection of this radiation forms the basis for a range of gas-chromatographic detectors. McCormack et al. (160) evaluated a variety of electrical discharges for the excitation of spectra of chromatographic eluates. High voltage a.c. and d.c. glow discharges, a hollow cathode d.c. discharge and 8- and 2450-MHz electrodeless

discharges were all used to produce the plasma. The intensity of the spectra emitted from the 2450-MHz, microwave, source was found to be significantly higher than that of the other sources, and this type of discharge has therefore been most frequently used.

Microwave-excited plasmas may be maintained in any rare gas, nitrogen or oxygen at low pressures, or in argon at atmospheric pressure. The plasma is normally contained within a quartz tube connected directly to the exit of the chromatographic column and no anciliary gases are required. Much of McCormack's original work (160) was carried out using a helium plasma at low pressures, but this was discontinued due to the complexity of the associated vacuum system and an argon plasma at atmospheric pressure was preferred. With this system emission spectra were obtained for a range of compounds and emissions characteristic of many of the elements present observed. A summary of the results is shown in Table I. Detection limits refer to the hetero-atoms shown in parenthesis in the first part of the table and to the compounds themselves in the second part. Selectivity is defined as the ratio of the response to the named compound to that to n-hexane at that wavelength.

Selectivities vary from very good for methyl iodide to poor for the other halogen compounds. Sensitivities are high for organic compounds but less good for the permanent gases and water. The range of linearity is

Table I.

Compound	Wavelength (nm)	Assignment	Detection Limit (gs^{-1})	Selectivity
$N\text{-}C_6H_{14}$	388.3	CN	2×10^{-16}(C)	-
	516.5	C_2	3×10^{-14}(C)	-
C_6F_6	561.1	?	3×10^{-12}(F)	10
	251.6	Si	5×10^{-10}(F)	20
$CHCl_3$	278.8	CCl	2×10^{-12}(Cl)	20
$CHBr_3$	298.5	?	2×10^{-7} (Br)	10
CH_3I	206.2	I	7×10^{-14}(I)	10^4
$(C_2H_5O)_3PO$	255.5	P	1×10^{-11}(P)	10^2
CS_2	257.6	CS	1×10^{-7}(S)	10^2
CO_2	388.3	CN	1×10^{-7}	
H_2O	308.9	OH	2×10^{-6}	
N_2	336.4	NH or N_2	9×10^{-10}	
O_2	603.7*	CO	4×10^{-9}	

* negative peak

greater than 10^4 for emission from n-nonane at 388.3 nm. but results were not reported for other compounds. Detector response is dependent on the microwave power, the carrier gas flow rate, and the characteristics of the optical system eg. monochromator slit width and resolving power and the photomultiplier used. This system was applied to the analysis of organophosphorus insecticide and iodinated herbicide residues by Bache and Lisk (161,162). The emissions used were the 253.5 nm phosphorus atomic line (yielding sensitivities of ca. 10^{-11}g phosphorus s^{-1}) and the 206.2 nm atomic iodine line (ca. 10^{-10}g iodine s^{-1}).

Further investigations into microwave-excited detectors have concentrated on the use of low pressure plasmas. Bache and Lisk (163,164) used a helium plasma at a pressure of 5-10 torr. They found this arrangement to be more intense than the atmospheric pressure argon plasma, and were able to produce atomic emissions from chlorine, bromine, iodine, phosphorus and sulphur compounds. The sensitivities and selectivities obtained are shown in Table II.

The detector response is, in general, more sensitive than in previous studies, and in some cases more selective, although the selectivities are not directly comparable, the reference substance in one case being hexane and in the other phenanthralene. This detector has been used for the analysis of chloro- and bromo- methyl-dimethylsilyl derivatives of pesticides in the 10^{-7}-

Table II.

Element	Wavelength (nm)	Detection Limit (g element s^{-1})	Selectivity
Br	478.55	1.3×10^{-11}	38
Cl	479.45	4.0×10^{-11}	44
I	533.82	3.4×10^{-11}	38
P	253.57	6.0×10^{-12}	10^3
S	545.38	3.4×10^{-11}	22

10^{-9}g range (165). Moye (166) found that a carrier gas composition of 85% helium and 15% argon at a pressure of 25 torr gave optimum results for phosphorus and halogen compounds.

Dagnall et al. (167,168) investigated in detail the response to sulphur compounds of a low-pressure system using argon or helium as carrier gas. In these studies, unlike those described previously, the column was operated under optimum conditions, at slightly above atmospheric pressure, and the detector at the optimum pressure of between 25 to 35 torr. Characteristic sulphur emissions were observed at 190.0 nm, 191.5 nm (atomic sulphur lines) and 257.6 nm (CS band emission). A detection limit of 2×10^{-10}g sulphur as carbon disulphide, from measurements at 257.6 nm, was reported.

The studies described so far have been confined to

spectral measurements in the visible and ultra-violet; more recently (169), atomic emissions from a helium plasma at a pressure of 2 torr heve been measured down to wavelengths of 120 nm, using a vacuum monochromator and a photomultiplier fitted with a caesium telluride photocathode. The emissions are viewed through a lithium fluoride window. The helium used is purified with a molecular sieve/liquid nitrogen trap, and oxygen (10-100 mtorr) admixed with the helium continuously to prevent the formation of deposits on the window which would result in considerable scatter. The atomic emissions used are 193.1 nm (carbon), 174.3 nm (nitrogen), 182.6 nm (sulphur), 163.4 nm (bromine), and 139.0 nm (chlorine). However, detailed studies were made only for carbon, nitrogen and sulphur compounds.

The range of linearity of detector response is ca. 10^4 and selectivities for nitrogen and sulphur are from 200 to 1000 when compared with carbon compounds, but the general sensitivity of the detector is less by an order of magnitude than those reported in previous studies in the visible and ultra-violet. In addition it has the disadvantages of increased complexity and a large plasma volume (ca. 50cc) which results in a relatively poor response time.

The use of other types of discharge has been reported. Kamada and Kokubun (170) used a 27 MHz high frequency tube, with argon as carrier gas. Good reproducibility, with a range of linearity of two orders of magnitude

was obtained when monitoring molecular emissions due to CS, CCl, and CH species, but sensitivities were relatively poor. Braman and Dynako (171) studied a direct current spectral emission detector; the discharge was maintained at atmospheric pressure in helium between two platinum electrodes. High sensitivities were obtained(10^{-11}-$10^{-14}gs^{-1}$) but these values were enhanced by the use of chromatographic columns at less than $50^{o}c$ to minimise column bleed. Selectivities were less good than those of other emissive detectors. As with the d.c. discharge ionization detectors, contamination of the electrodes again proved to be a problem.

One general limitation of both the flame photometric detector,when operated under hydrogen-rich conditions (172), and the discharges (160) is that they can be overloaded by large (ca. mg) quantities of material and the flame or discharge extinguished; this imposes an upper limit on the working range of the detector. To avoid overloading the detector, solvents may be back-flushed if they elute after the components of interest or, if the solvents elute before, detector initiation can be delayed until after the bulk of the solvent has passed.

Spectrofluorometric Detection.

The compounds leaving the chromatographic column are absorbed by a stream of ethanol, the carrier gas escapes into the air and the ethanolic solution is passed through the flow cell of a spectrofluorometer (173). This detector is clearly only suitable for fluorescing

compounds, and by suitable adjustment of the wavelength detector response can be made almost specific to a given compound. Its sensitivity is also good; the detection limit for p-terphenyl is 4×10^{-10}g. One problem is incomplete quantitivity resulting from the loss of volatile compounds from the ethanol.

Ultra-violet Spectrophotometric Detector.

Separated components are transferred in the stream of carrier gas to the cell of an ultra-violet spectrophotometer. The carrier gas may be hydrogen, nitrogen or any of the noble gases, all of which have negligible absorption at wavelengths higher than 140 nm (174). Detector selectivity depends on the wavelength monitored; eg. aromatic compounds have been determined at 253.7 nm without paraffins interfering (175). Alternatively, the spectrum may be scanned. Kaye and Waska (176) modified a spectrophotometer to scan from 160 to 210 nm in 6 seconds. However, a major disadvantage of the method is the high cost of the equipment required.

Infrared Spectrophotometric Detector.

Direct coupling of a gas chromatographic effluent to an IR spectrometer was first used by Haahti and Fales (177). Considerable selectivity is possible by suitable choice of wavelength used, eg. when determining carbonyl group content at 1739 cm^{-1} the ratio of the sensitivities for acetone and o-xylene was found to be 10^4:1 (178). The principal disadvantages of this detector are its high cost and poor sensitivity. The minimum quantity

required for detection at constant wavelength is 0.01μl (178). Further difficulties occur in the determination of the whole spectrum; in order to achieve fast scan speeds and to observe less intense peaks, detection sensitivity is at least an order of magnitude lower.

4) Detectors Based on Chemical or Electrolytic Phenomena.

Coulometric Detector.

Coulometric detectors consist of three parts : the destructive unit, the titration cell and the coulometer. The compound leaving the chromatographic column passes through the destructive unit where it is either oxidised or reduced to simple inorganic compounds. These compounds pass into the titration cell where they are titrated automatically by appropriate ions. The concentration of the titrant in the titration cell is kept at a constant value by using a variable electric current to produce the titrating agent as it is used up (179). The ions produced in the course of the titration are directly proportional to the amount of a given element in the compound.

By combustion of organic compounds in oxygen at 1000°c carbon dioxide, water, hydrogen chloride, bromine, nitrogen dioxide and sulphur dioxide are produced. If silver ions are used as the titrating agent halogen compounds may be determined selectively (180,181). The minimum detectable amount is 2×10^{-9}g of chloride

(181). Bromo-compounds give a smaller response as bromine is converted into HOBr and HBr and only HBr precipitates silver (181). Some interferences have been observed (180).

Titration of sulphur dioxide is carried out either by bromine (182,185) or iodine (183,184). However, with bromine, nitrogen compounds give a negative response (182). The limit of detection is 10 p.p.b. for hydrogen sulphide (185). For the titration with iodine, the minimum detectable quantity of sulphur is 10^{-8}g (183); large amounts of hydrocarbons and other halogens interfere (161).

Hydrogen sulphide, hydrogen chloride and phosphine are produced under reducing conditions, and absorption methods must be used for specific detection (186). Aluminium oxide is used for the removal of hydrogen sulphide and chloride. A silica gel column removes hydrogen chloride. The relative sensitivities are 2:2:1 for phosphine, hydrogen chloride and hydrogen sulphide respectively using Ag^+ as titrant (186). The sensitivity to mercaptans is 100 times higher than with a katharometer (187) and hydrocarbons and amines give no response (188).

Nitrogen compounds are converted into ammonia by use of a catalyst (Ni-MgO) under reducing conditions and hydrogen ions are used as titrant (189). Acidic gases absorb irreversibly on MgO and very few other basic materials are produced under these conditions.

In quantitative analysis with this detector no empirical calibration factors are required and the amount of the element present can be calculated from Faraday's Laws. The detector response is sensitive and linear; in addition, it is relatively insensitive to hydrocarbons and, hence, can tolerate column bleed and solvent tailing (186). However, against these advantages is set the complicated nature of the whole analytical system. The decomposition and the titration require a certain time and the time constant is therefore higher (2-5s) (182,183) than for conventional detectors. Also, in the determination of nitrogen compounds poisoning of the catalyst gradually results in a loss of quantitativity (189).

Galvanic Detector.

An electrochemical cell consisting of a non-polarisable and a polarisable electrode can be used for the detection of compounds which react with the polarisable electrode. The electrode potential changes and if both electrodes are connected externally a current flows.

This principle is used in the Hersch cell (190) which consists of lead and silver electrodes in a basic electrolyte. The response is specific to oxygen, and under optimum conditions (a flow rate of 20ml/min) the minimum quantity of oxygen detectable is 1.8×10^{-15}g (191). Only organic sulphur compounds have been found to interfere (11).

Bechtold (192) used a cell consisting of

Pt/Ag/AgI/Ag_2S/Pt as a detector for sulphur and halogen compounds. The oxidation products (produced as before) of these compounds react with silver and cause a current to flow. Sensitivities and ranges of linearity are good but no distinction is made between different heteroatoms.

Reaction Coulometer.

In the reaction coulometer (193) the coulometer cell output is maintained at a constant level by feeding to the cell an amount of oxygen equivalent to that which is used during pyrolysis. The amount of oxygen is thus a measure of the quantity of material combusted. Response is calculable and linear but only applicable to compounds containing only hydrogen, carbon and oxygen.

The Electrolytic Conductivity Detector.

After oxidative or reductive decomposition of the compounds eluted from a chromatographic column, the products are dissolved in water and the conductivity of the solution monitored. Under oxidising conditions the detector is sensitive to sulphur and halogen compounds (194,195). The response to carbon is very low due to the inability of carbon dioxide to absorb quickly in water in the course of its passage through the detector and the negligible degree of ionization for that portion which is absorbed (194). Selectivity is 10^4 for sulphur and halogen compounds compared with compounds of carbon, hydrogen, oxygen and nitrogen; the minimum detectable amount of chlorine is $2 \times 10^{-10} gs^{-1}$ (196). Of the

compounds formed under reducing conditions the hydrides of nitrogen, phosphorus, sulphur and chlorine give a response whereas water and hydrocarbons are not detectable (195).

To achieve further selectivity various absorbents are used (195). For the determination of sulphur as sulphur oxides hydrogen chloride is removed by silver on quartz wool, and for chlorine determinations calcium oxide on quartz wool at 800°c removes sulphur oxides. For nitrogen determinations, ammonia is the only base formed, and strontium hydroxide is used to remove acids (194,197).

The response of the electrolytic conductivity detector is relatively little affected by carrier gas flow rate and is linear over two orders of magnitude (194). It is sensitive, and has the advantage that its response to an element is proportional to the weight of that element in any compound. However, initial calibration of the detector is still required and the analytical system is complicated. In addition, its selectivity depends principally on the use of absorbents and therefore many other detectors could be used to determine the reaction products after selective absorption. One example is the determination of oxygen by Kojiima et al. (198). The chromatographic eluates are decomposed on heated platinum in a quartz tube in the presence of excess methane. Sulphur is absorbed on copper, halogens and hydrides of nitrogen and sulphur on sodium hydroxide

and sulphuric acid and the residual gas, CO, is oxidised to CO_2 by iodic acid at 120°c to give iodine which is determined using an electron capture detector.

Polarographic Detector.

A polarographic detector was first used by Janak et al. (199) for the determination of halogens. At a constant voltage of +0.3 V the process was followed by means of the increasing Ti(IV) wave resulting from the reaction of halogens with a solution of Ti(III). For the determination of basic nitrogen compounds the system Ni(II)-pyridine was investigated (200) and a method for carbonyl compounds has also been described (201). Selectivity of polarographic determination is quite high but sensitivity is poor (7×10^{-8} g/ml (200)) and a further disadvantage is the relatively large volume of the detector.

v. Conclusion

The types of detector described in the literature for use with gas chromatography are numerous and no one type has proved satisfactory for all purposes. Owing to differences in design and operating conditions, results obtained from the same type of detector vary considerably and any comparison of different detectors must therefore be of a very general nature. In general, detectors for gas chromatography are required either to provide a complete, non-selective, chromatogram of all compounds eluted from the column, or to be able to selectively

determine a compound or class of compounds in the gas stream in order to facilitate quantitative determination or to obtain further information which would be an aid in identification. Therefore, for comparative purposes detectors will be considered in two groups : non-selective and selective.

Non-selective Detectors.

Ideally, the response of a non-selective detector should be highly sensitive, linear over the concentration range required and predictable, ie. calculable on the basis of some simple property of a compound closely related to its mass. The limits of detection and ranges of linearity for the major non-selective detectors described are shown in Table III. (24).

The response of the gas density balances and the mass detector, are predictable but their low sensitivities limit their usefulness; their major use is for the calibration of other detectors using a stream-splitter. Ultra-sonic and ionization cross-section detectors have been little investigated but have a calculable response to many compounds. Their sensitivities are, however, less than many other non-selective detectors. The flame ionization detector has been widely used for the determination of organic compounds with excellent results and the response can also be calculated for some compounds. Greater sensitivity has been obtained using argon and microwave-excited discharge detectors for organic compounds and the helium detector is the

Table III.

Non-selective Detectors.

Detector	Limit of detection (gs^{-1})	Limit of detection ($mM\ ml^{-1}$)	Linear Range
Katharometer	-	10^{-8}	low
Flame ionization	10^{-11}	10^{-13}	10^{6}
Argon-macro	10^{-13}	10^{-15}	narrow
Argon-micro	10^{-12}	10^{-14}	narrow
Argon-triode	10^{-13}	-	10^{5}
Helium	10^{-14}	10^{-15}	10^{5}
Cross-section	10^{-8}	-	10^{4}
Gas Density : Martin	-	10^{-6}	wide
Gow-Mac	10^{-7}	10^{-6}	10^{3}
Ultra-sonic	-	10^{-11}	10^{5}
Mass	-	$10^{-6}g$	10^{4}
Discharge Spectra	10^{-16}	-	10^{3}
Photo-ionization	10^{-12}	-	10^{5}
Ionization Gauge	-	10^{-8}	10^{4}
Reaction Coulometer	-	10^{-8}	wide

most sensitive detector available for the non-selective determination of the permanent gases. Despite its wide use the katharometer is far from ideal, being neither very sensitive, nor predictable, nor having a wide range of linearity.

Selective Detectors.

Selective detectors play an important part in the success of the gas chromatographic analysis of complex natural mixtures and in the elucidation of the results of difficult separations. The combination of gas chromatography and mass spectrometry must be considered separately from other detection systems as it is the only method available that can provide structural information on compounds present in sub-nanogram quantities. In favourable cases a complete analysis is possible, however, in many other cases the information obtainable is limited, especially if the parent ion is unstable. It is also relatively difficult to use for the determination of hetero-atoms present in compounds. Its high cost, particularly when used with an ancillary computer often results in its use being restricted to problems of identification irresoluble by other methods. Although infrared and ultra-violet spectrophotometry can also provide structural information, their lack of sensitivity usually requires samples to be preconcentrated by trapping.

The other selective detectors respond to particular elements present in an eluate and a summary of the

optimum limits of detection reported in each case are shown in Table IV (11). The electron capture detector also responds to other electron-capturing molecules such as quinoline. Comparisons are even more imprecise with selective detectors because conditions may be optimised differently in order to obtain maximum sensitivity or selectivity (eg. choice of slit width for emissive detectors), and only very limited conclusions can therefore be drawn.

In summary, the electron capture detector is a highly sensitive and selective detector for phosphorus and halogen compounds, particularly for compounds containing more than one of these atoms, but cannot be easily used for identification purposes. The alkali flame ionization detector provides sensitive detection of phosphorus, nitrogen, sulphur and halogen compounds but is particularly sensitive to phosphorus compounds; however, its response tends to be variable and unstable. The flame photometric detector is also particularly sensitive to phosphorus and less sensitive to halogen and sulphur compounds. The microwave-excited emissive detector is highly sensitive to phosphorus, sulphur and halogen compounds. The FPD and the emissive detector have the advantage that they can distinguish between individual halogens and other hetero-atoms and hence provide qualitative information as well as selective sensitivity. However, they both have the disadvantage that they can be overloaded by too high a concentration of organic

Type of Compound	Electron-Capture (moles s^{-1})	Alkali Flame Ionization (g s^{-1})	Surface Ionization (g s^{-1})	Flame Photometric (g s^{-1})	Microwave Emissive (g s^{-1})	Coulometric (g s^{-1})	Galvanic (moles s^{-1})	Electrolytic conductivity (moles s^{-1})
-P	1×10^{-14}	8.3×10^{-12}	-	5×10^{-12}	5.7×10^{-12}	-	-	-
-S	-	1.1×10^{-10}	-	-	3.7×10^{-11}	-	2×10^{-13}	2×10^{-11}
-N	-	2.5×10^{-10}	-	-	-	-	-	-
-Br	8×10^{-14}	2.5×10^{-9}	-	-	1.3×10^{-11}	-	6×10^{-14}	-
-Cl	1×10^{-11}	1.3×10^{-9}	1.5×10^{-10}	-	4.0×10^{-11}	2×10^{-9}	2×10^{-13}	3×10^{-12}
-I	2×10^{-16}	-	-	-	7.0×10^{-14}	-	6×10^{-14}	-

Limits of Detection for Selective Detectors

Table IV

material. The coulometric and electrolytic conductivity detectors are relatively insensitive and both require separate purification techniques to achieve good selectivity. They have the advantage that the response gives a direct measure of the weight of hetero-atom present. The galvanic detector is highly sensitive to sulphur and halogen compounds but does not distinguish between them.

III. The Present Work

Microwave-excited emissive detectors are among the most sensitive and versatile of the selective detectors at present available for gas chromatography. In addition, they show very high sensitivity for the non-selective determination of organic compounds. However, they have been used very little. Their lack of popularity (along with that of other similar detectors) has been attributed (172) partly to the complexity and practical problems associated with the low pressure systems used in most work. The relatively simple atmospheric pressure system has been little studied. Following the initial, very general, survey of its properties by McCormack, Cooke and Tong (160), only its applications in the analysis of residues of iodinated herbicides (162) and organophosphorus insecticides (161) have been reported. No attempt has been made to study in more detail the characteristics of the atmospheric pressure system and the possible range of its applications.

For these reasons an atmospheric pressure microwave-excited plasma was set up for use as a detector for gas chromatography and its properties examined in detail.

The emission spectra produced in the plasma by a wide range of simple organic and inorganic compounds were recorded and the optimum emission wavelengths found were used to determine these compounds as chromatographic eluates. The emissions were monitored using a variety of optical arrangements and electronic read-out systems.

Secondly, a double detector system was set up in which two emission wavelengths could be monitored simultaneously. The relationships between the ratios of appropriate emissions and the inter-element ratios, C:Cl, C:I, C:Br, C:P, and C:S, in the original compounds were studied.

A novel mode of detection, using the measurement of reflected microwave power, was investigated with a view to providing an alternative, non-selective, detection system which could be used in conjunction with the emissive detector.

Finally, the application of the emissive detector to the gas chromatographic determination of volatile metal chelates was studied.

CHAPTER I

AN ATMOSPHERIC PRESSURE MICROWAVE-EXCITED DETECTOR FOR GAS CHROMATOGRAPHY.

I. Emission Spectra

The emission wavelengths used by McCormack et al. (160) in their preliminary studies with an atmospheric pressure microwave-excited emissive detector are shown in Table I (page 36). However, they did not prove completely satisfactory. The emission at 298.5 nm used to determine bromine-containing compounds could not be assigned and gave only poor sensitivity and selectivity. The molecular emissions from CS(257.5 nm) and CCl(278.8 nm) were also less sensitive than the atomic emissions. The CN emission (388.3 nm) used to monitor carbon-containing compounds, although highly sensitive, had the disadvantage that it was dependent on the presence of an impurity, nitrogen, in the gas stream. In addition, Taylor et al. (202), who used a microwave-excited plasma at atmospheric pressure to continuously determine impurity levels in argon, found that atomic carbon emission at 247.9 nm was as sensitive as CN emission for the determination of organic compounds. Therefore, as a preliminary to the present investigation, the emission spectra of a range of simple organic and

inorganic compounds were recorded in order to establish which wavelengths could be used to monitor selectively and non-selectively the passage of the gas-chromatographic eluates into the microwave-excited plasma.

Apparatus

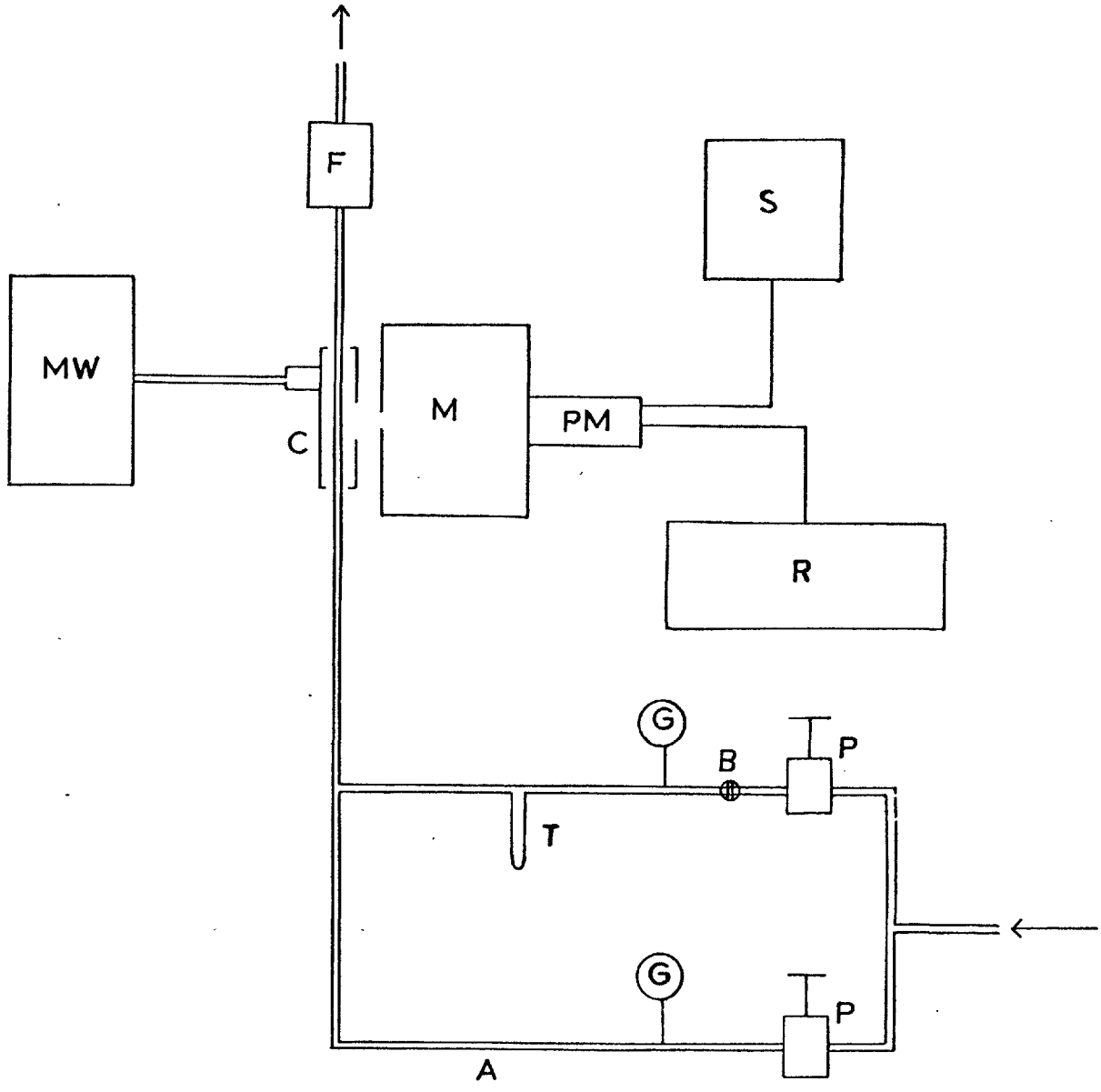
In order to scan the emission spectrum of a compound in the plasma it was necessary to maintain a steady, continuous flow of the vapour of the compound, diluted with argon, into the plasma for periods of ca. 30 min. The apparatus used to achieve this is shown in Figure I,1. This system can be divided into three sections :

1) the section up-stream of the plasma, which provided a continuous flow of argon and sample vapour,
2) the microwave section, which produced the plasma,
3) the detection system, which monitored and recorded the electromagnetic radiation from the plasma.

1) The Sample Dilution System

The carrier gas, argon, was split into two streams, which were regulated by pressure controllers (Watts type 15-2, 0-175 KN m^{-2}) and measured by pressure gauges (0-210 KN m^{-2}). Two capillary restrictors were included in the gas lines to enable the controllers to work under optimum conditions (ca. 80-170 KN m^{-2}).

In order to obtain a suitable concentration of sample vapour in the argon entering the plasma one gas stream flowed across the top of a 6-mm o.d. glass tube nearly



MW - microwave power supply
C - microwave cavity
F - flow-meter
M - monochromator
PM - photomultiplier
T - sample tube
S - power supply
R - read-out
G - pressure gauge
P - pressure controller
A - dilution line

APPARATUS FOR THE DETERMINATION OF SPECTRA

Figure I,1

full with the sample under investigation. To increase the concentration of sample vapour the tube could be warmed with a water or oil bath but with the more volatile compounds (eg. carbon, disulphide, acetone) it was found necessary to cool the tube in ice to keep the vapour concentration sufficiently low. In addition, the second gas stream was used to dilute the mixture of argon and sample vapour. The flow rates of the two streams could be adjusted independently by means of the pressure controllers until a suitable sample vapour concentration was obtained. The total flow rate, measured with a bubble flow-meter, was kept between 2.0 and 4.0 lh^{-1}, the range of flow rates normally used in gas chromatography.

When the spectra of gaseous samples were investigated the sample tube was replaced by a connection to a cylinder or aerosol can of the gas, via a pressure control valve and a needle valve. By means of these valves a suitable mixture of the gas with argon could be produced.

2) The Microwave System

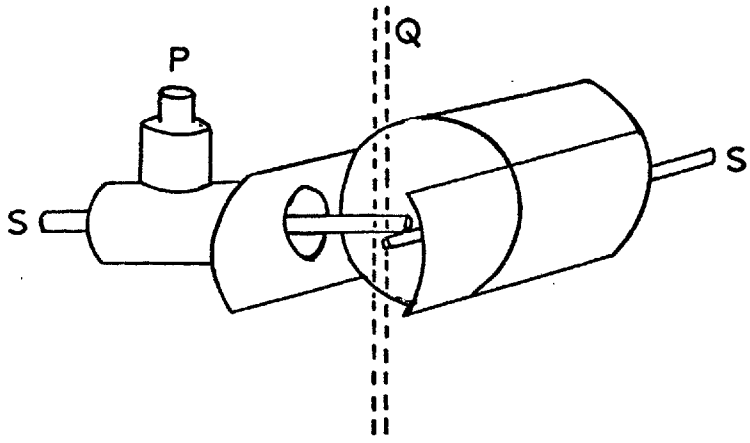
The mixture of argon and sample vapour from the sample dilution system passed directly into the detector tube which consisted of a ca. 200 mm length of transparent quartz tubing surrounded by a microwave resonant cavity. In order to produce a discharge within the tube power was supplied to the cavity from a 2450-MHz generator (Electro-Medical Supplies, Great Portland Street, London,

W.1, Microton 200, giving a maximum output of 200 W) coupled to a reflected power meter. The discharge was initiated using a high frequency vacuum tester and was adjusted for maximum stability, maximum intensity of emission and minimum reflected power by optimising the the position of the quartz tube and the setting of the tuning stub on the cavity. When a compound was introduced into the discharge plasma it was fragmented. The fragments were excited and caused to emit electromagnetic radiation.

The three types of cavity used during the present study are shown in Figure I,2. They all have, in common, a co-axial connection to the microwave generator, viewing apertures and tuning stubs, which enable the coupling of the microwave power with the discharge tube to be optimised. They differ in the length, intensity and stability of the discharge they were able to produce in the quartz tube.

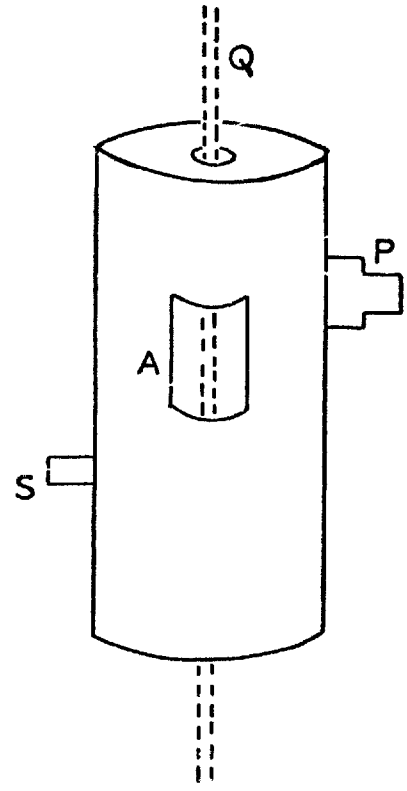
The $\frac{1}{4}$-wave Evenson-type cavity (2a) (E.M.S. model 214L) produced a discharge ca. 60 mm long with a very intense central region. This type of cavity had the advantages that the emissions from the plasma it produced were particularly intense and that, due to its open construction, the whole length of the plasma could be viewed. However, it was relatively unstable; the optimum settings of the tuning stubs and the position of the quartz tubing in the cavity were very critical and required periodic adjustment.

The discharge obtained in a $\frac{3}{4}$-wave cavity (2b) was

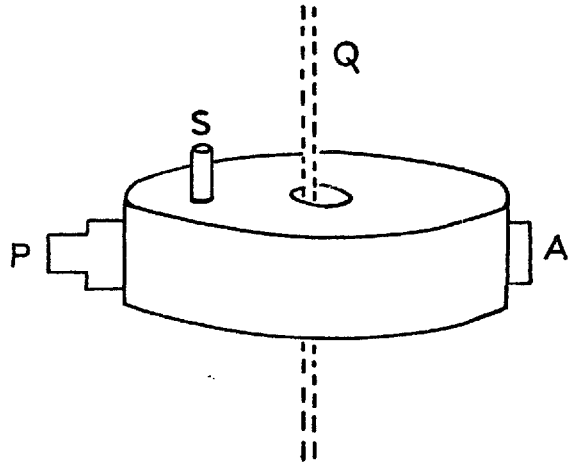


(a) $\frac{1}{4}$-WAVE EVENSON-TYPE

S - tuning stub
P - power connection
A - aperture
Q - quartz tube



(b) $\frac{3}{4}$-WAVE



(c) $\frac{1}{4}$-WAVE FORESHORTENED RADIAL LINE

MICROWAVE CAVITIES

Figure I,2

longer (ca. 80 mm), slightly less intense and more stable than that in a $\frac{1}{4}$-wave cavity. Neither the position of the tube in the cavity nor the setting of the tuning stub were critical and no adjustments were necessary during operation.

The $\frac{1}{4}$-wave foreshortened radial line cavity (2c) (E.M.S. model 211L) proved inferior to the other cavities and was little used. The discharge it produced was less stable and shorter than those obtained with both the other cavities and of intermediate intensity.

The detector was arranged so that the quartz tube was held vertical and extended ca. 100 mm on each side of the cavity centre so that the argon discharge plasma was formed completely within the tube. The upper end of the tube was connected via polythene tubing to a 500-ml bottle and thence to the atmosphere. This arrangement was used to reduce the possibility of plasma noise caused by draughts and/or air diffusion at the top of the quartz tube.

Quartz tubing was used because it is transparent to both ultra-violet and microwave radiation and softens at higher temperatures than other glasses. The narrower the quartz tubing used, the more intense was the emission from the plasma. However, with tubing of 1-mm i.d., local hot-spots developed with relatively high microwave powers ($\geqslant$150W). The 2-mm i.d. quartz tubing gave a decrease in emission of ca. 30% compared to the 1-mm tubing, but negligible overheating. Both sizes of tubing

were used in these spectral studies but no qualitative differences in the resultant spectra were observed.

Similarly, the continuous spectra obtained using all three types of microwave cavity were qualitatively the same. The results described are those produced with the more stable discharge in a $\frac{3}{4}$-wave cavity which was later used for the gas-chromatographic determinations.

Argon was used throughout as carrier gas. Attempts to admix helium with the argon, even at concentrations of less than 1%, resulted in a very unstable plasma which was readily extinguished.

One of the fragments formed by the decomposition of organic compounds in the plasma was free carbon. If the proportion of organic vapour in the carrier gas was too high carbon was deposited on the walls of the quartz tube. The build-up of carbon deposits (carbonization) reduced the intensity of the emission reaching the detection system. In addition, as microwaves are absorbed by carbon, local hot-spots developed, the plasma became distorted and ultimately the plasma was extinguished. Similar problems occurred with sulphur and phosphorus compounds, however these hetero-atoms were generally present in much lower concentrations than carbon. The discharge may also be quenched by the presence of high concentrations (ca. 1% by weight) of compounds in the carrier gas. Consequently, in order to obtain representative spectra from a stable plasma it was necessary to regulate the concentration of

sample vapour in the argon gas stream using the sample dilution system.

3) The Dectection System

Emissions from the argon plasma at wavelengths from 200 nm to 600 nm were monitored using a Beckmann DU monochromator fitted with an EMI 9601B photomultiplier which was supplied at 1 KV from a Brandenburg PM 2500R power supply. The readout consisted of a microammeter and a Servoscribe potentiometric recorder. For spectral studies at wavelengths belcw 200 nm a Hilger and Watts type D330 monochromator, flushed with argon and fitted with an EMI 6256S photomultiplier, was used. The photomultiplier was operated with a Brandenburg 472R high voltage supply at a potential of 1.25 KV and its output was measured directly using a Servoscribe recorder. The microwave cavity was mounted with its viewing aperture as close as possible to the entry slit of the monochromator being used and the monochromator slit width was set to the minimum width with which clear spectra could be obtained (ca. 0.02 mm).

Procedure

In order to determine the spectrum of each compound the sample was placed in the sample tube (T) and the plasma iniated using only pure argon from line A. The position of the quartz tubing and the tuning of the cavity were optimised and the emission spectrum of the plasma

was scanned in order to ascertain the intensity of background emissions present. Tap B was opened and the flow of argon over the sample tube slowly increased. The gas flow through A was reduced proportionally to keep the total flow rate approximately constant. The temperature of the sample tube was adjusted until a suitable increase in emission at one of the major bands (CN, NH or OH) was obtained. The emission spectrum of the plasma was then scanned at microwave powers of 50 W, 100 W and 150 W.

After the spectral studies on each compound had been completed the sample tube was removed and the steel tubing between the tube and the detector flamed to ensure that no condensates remained. The quartz tubing was also changed.

Results

The emission spectra produced by a wide range of simple organic compounds, nitrogen, hydrogen, water, oxygen and carbon monoxide in a microwave-excited plasma were recorded at wavelengths from 200 nm to 600 nm. In addition, the spectra of nitrogen and sulphur-containing compounds were recorded down to 170 nm.

1) Background Emissions

A typical spectrum obtained from an argon plasma is shown in Figure I,3. The principal emissions were argon atomic lines in the region between 390 nm and

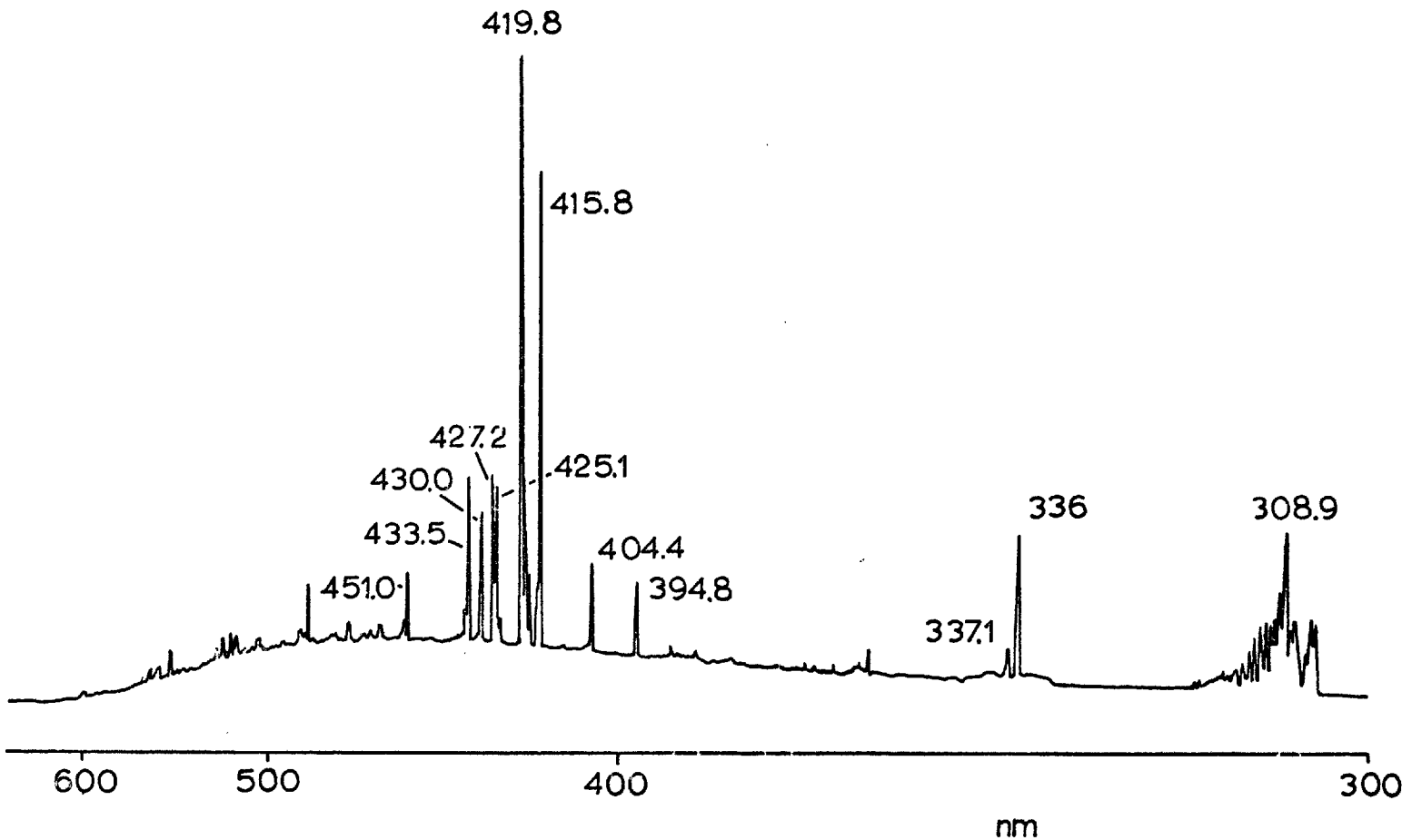


Figure I.3

BACKGROUND EMISSION SPECTRUM

and 500 nm, N_2 and NH bands at 337.1 nm and 336.0 nm and OH bands around 308.9 nm. No emissions were observed at wavelengths shorter than 300 nm.

The presence of background emissions considerably limited the analytical utility of other emissions which they overlapped due to the inherent variability of the background and the greater associated noise. In addition, background emissions were found to decrease during the passage of other compounds through the plasma, making the quantitative evaluation of measurements at these wavelengths very difficult.

Without changing the carrier gas, background argon emissions were unavoidable, however, by passing argon slowly over anhydrous magnesium perchlorate and granular titanium metal at ca. 800°c the nitrogen and hydroxyl emissions could be reduced to such an extent that they could only just be distinguished from the background noise. Nevertheless, in practice, traces of water and nitrogen in the sample (and, later, to a much greater extent, on the column) always resulted in the presence of some background emission. The purification system was therefore not used in further studies so as to keep the detector as simple as possible.

2) Carbon-containing Compounds

The spectrum of propane is shown in Figure I,4. Carbon monoxide and all the organic compounds examined gave the same emissions from carbonaceous species :

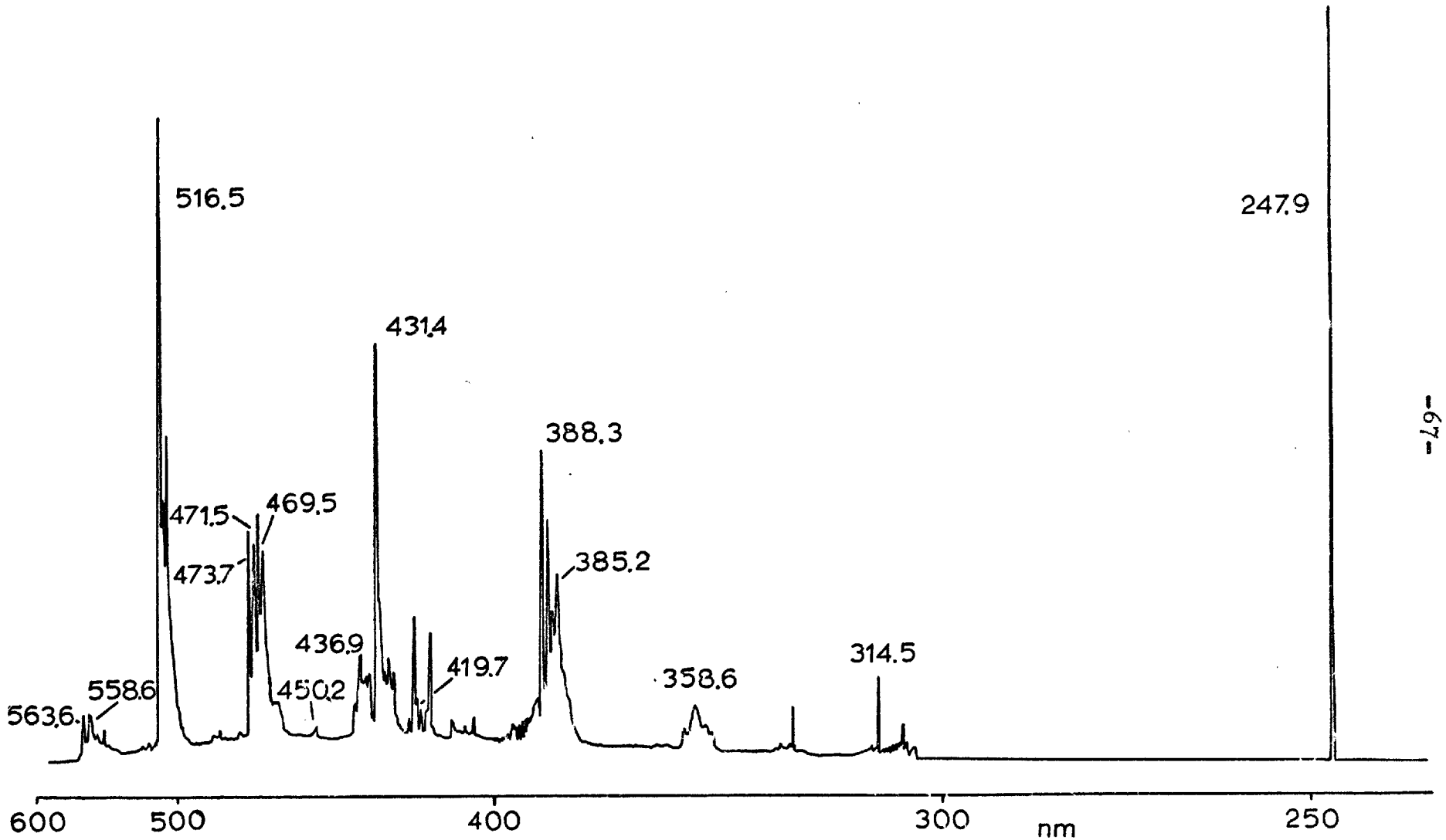


Figure 1.4 EMISSION SPECTRUM OF PROPANE

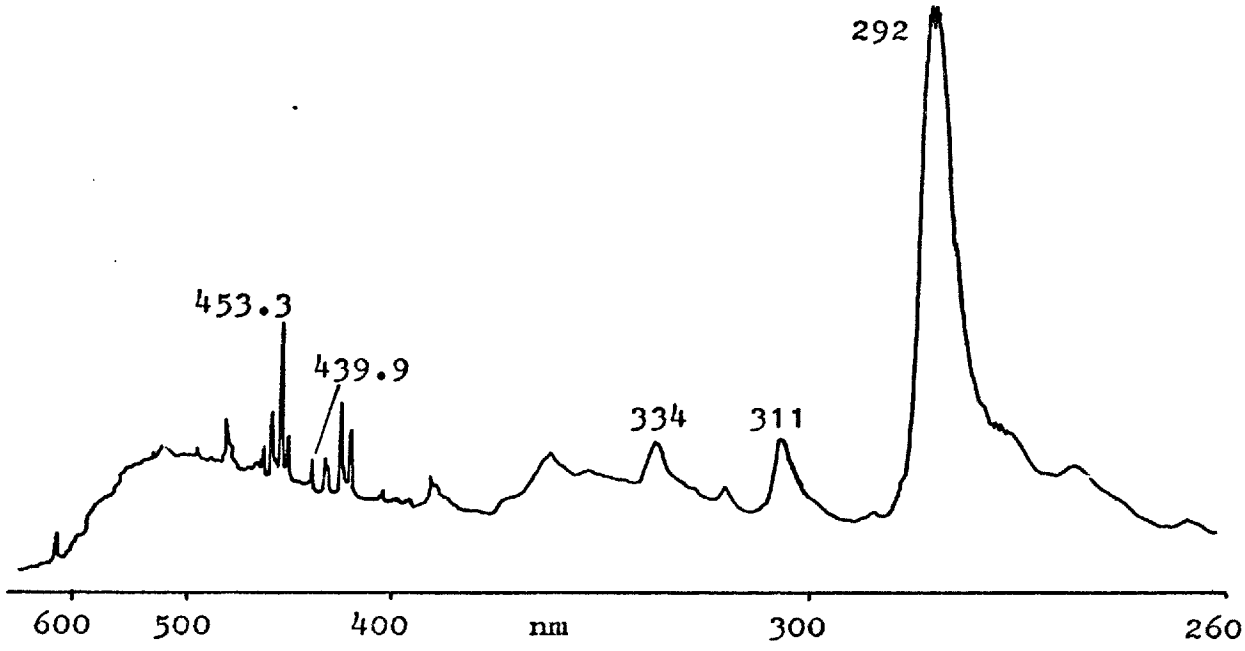
247.9 nm (atomic carbon); 358.6 nm, 388.3 nm, 419.7 nm, 421.6 nm, 450.2 nm and 494.9 nm (CN); and 385.2 nm, 436.9 nm, 469.7 nm, 471.5 nm, 473.7 nm, 516.5 nm, 558.6 nm and 563.6 nm (C_2). In addition, an emission at 193.1 nm (atomic carbon) was observed in all the spectra of carbon-containing compounds which were scanned in that region. Compounds also containing hydrogen gave CH emissions at 314.5 nm and 431.4 nm. No qualitative differences were observed between the spectra at different microwave powers.

3) Halogen-containing Compounds

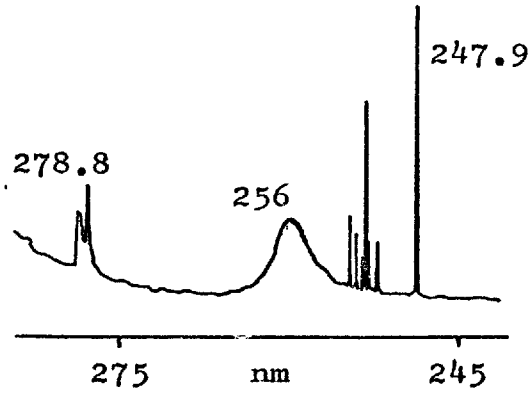
In addition to the emissions listed above the spectra of n-propyl iodide and ethyl iodide showed only one extra emission - an intense line at 206.2 nm (atomic iodine).

In the spectra of chloroform and carbon tetrachloride obtained using a microwave power of 50 W a broad band at 256 nm was observed in addition to a smaller emission at 278.8 nm and the normal carbon emissions (Figure I,5b). Characteristic emissions of chlorine-containing compounds have been reported (160) at 278.8 nm (CCl), however, the emission at 256 nm, which was identified as a Cl_2 band (203),had not previously been observed in a microwave-excited discharge. Its intensity was considerably reduced at a power of 100 W and it was not distinguishable from background noise at 150 W.

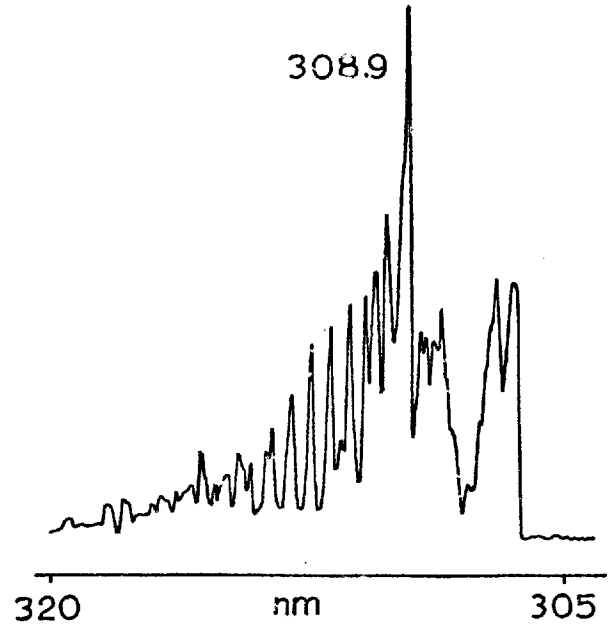
Bromoform and n-propyl bromide gave only one character-



(a) BROMINE VAPOUR



(b) CHLOROFORM



(c) WATER

EMISSION SPECTRA

Figure I,5

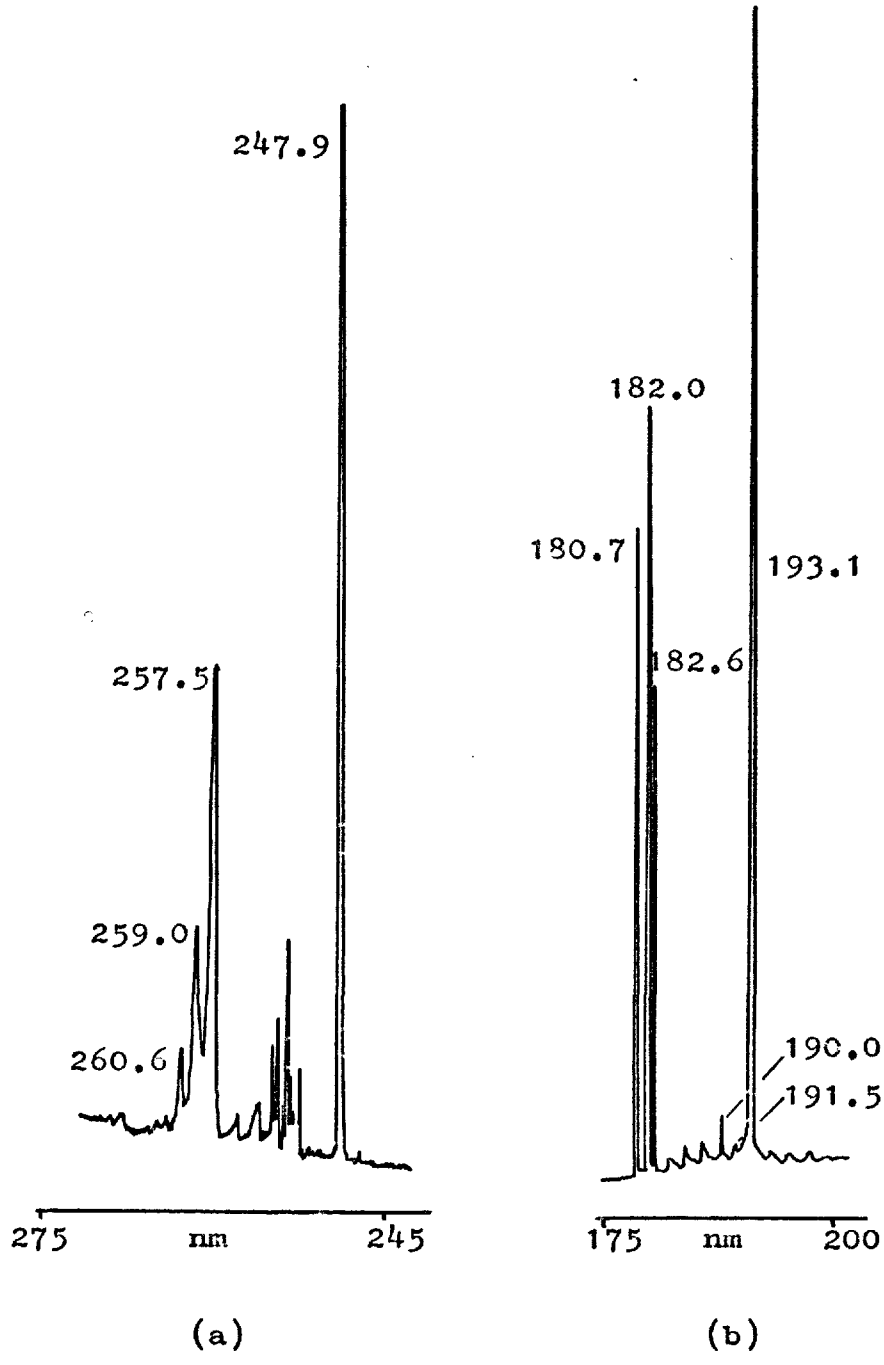
istic emission, a band at 292 nm, which had not been reported during previous studies. Its assignment as a Br_2 band emission (203) was supported by the spectrum of Br_2 vapour as shown in Figure I,5a. The strongest of the series of broad bands was again at 292 nm. The weaker bands at 311 nm and 334 nm were also assigned as Br_2 bands and those at 453.3 nm and 439.9 nm as BrO bands (203). The intensity of the Br_2 emission at 292 nm was found to decrease at higher microwave powers.

4) Sulphur- and Phosphorus-containing Compounds

Only one emission characteristic of tri-n-butyl phosphate and tri-methyl phosphite was observed, the phosphorus atomic line at 253.5 nm.

McCormack et al. (160) used CS emission at 257.5 nm to monitor sulphur-containing compounds and this emission band was observed in the spectrum of thiophen (Figure I,6a) and carbon disulphide, along with weaker CS bands at 259.0 nm and 260.6 nm. The additional emissions observed between 250 nm and 253 nm were assigned as atomic silicon lines at 250.7 nm, 251.4 nm, 251.6 nm, 251.9 nm, 252.4 nm and 252.9 nm. These emissions can also be seen in the spectrum of chloroform (Figure I,5b).

The CS bands were generally very weak and, as no other characteristic emissions were observed between 200 nm and 600 nm, the spectrum of thiophen from 170 nm to 200 nm was scanned. Atomic sulphur lines at 180.7 nm, 182.0 nm, 182.6 nm, 190.0 nm and 191.5 nm were recorded as well as



EMISSION SPECTRUM OF THIOPHEN

Figure I,6

the strong atomic carbon line at 193.1 nm (Figure I,6b). The intensity of the emissions at these wavelengths decreased rapidly with the formation of carbon deposits and at high microwave powers.

5) Other Compounds

Water vapour caused an increase in the background emission bands around 308.9 nm (Figure I,5c) and in the hydrogen atomic line at 486.1 nm. Hydrogen itself also gave emission at this wavelength.

The spectrum of an argon plasma containing nitrogen is shown in Figure I,7, with assignments of the principal band heads. However, in the spectra of diethylamine and acetonitrile the most intense N_2 bands at 357.6 nm, 380.5 nm and 389.4 nm, if present, were masked by CN emissions at 358.6 nm and 388.3 nm, which were particularly intense. The only characteristic emissions recorded were those at 337.1 nm (N_2 and NH) and 336.0 nm (NH). No emission at the atomic nitrogen lines at 174.3 nm and 174.5 nm (204) could be observed, but this may have been due to atmospheric absorption of radiation at these wavelengths.

No emissions could be obtained for oxygen. Its only effect on the spectrum was to decrease all background emissions. The spectra of alcohols, ethers and ketones also showed no additional emissions to those of carbon and hydrogen compounds.

EMISSION SPECTRUM OF NITROGEN

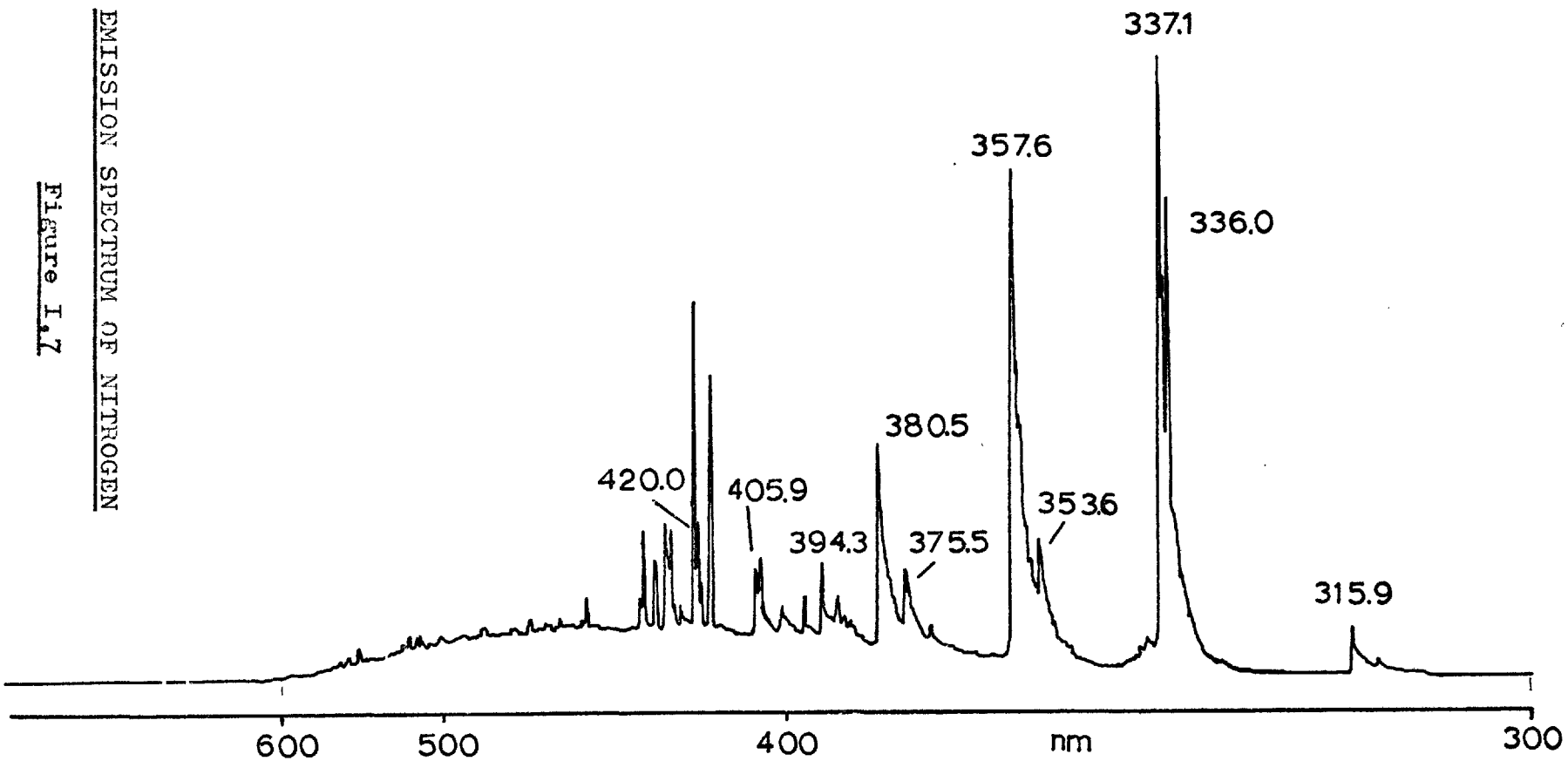
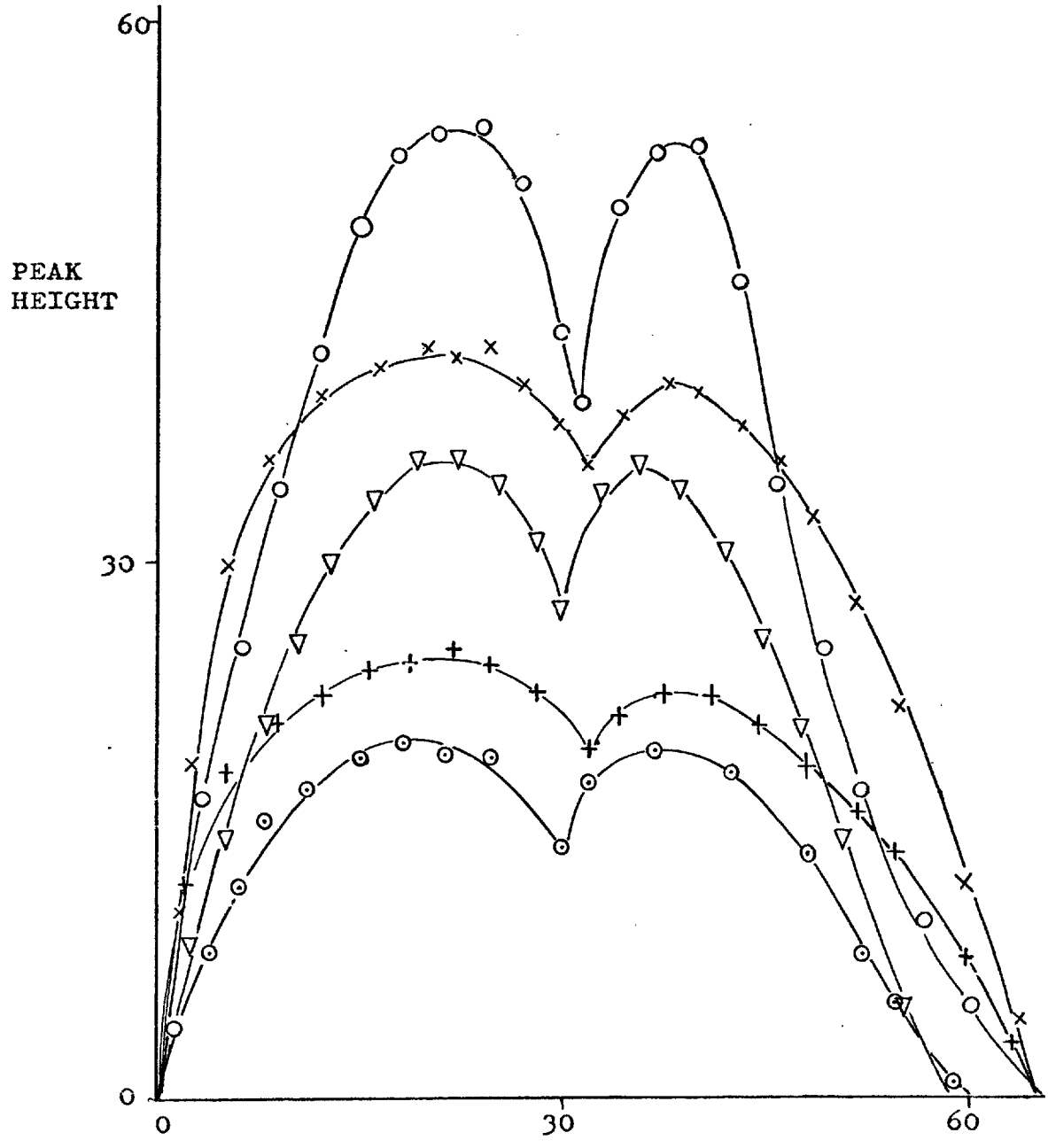


Figure I.7

6) Variation of Emission Intensities with Position in Plasma

The length of plasma viewed by the Beckmann DU monochromator was ca. 15 mm, whereas the total length of the plasma was 60-80 mm. To optimise the positioning of the monochromator it was necessary to determine from where in the plasma the emissions were most intense. The following procedure was used. A $\frac{1}{4}$-wave Evenson-type cavity was set up to enable the whole length of the plasma to be monitored. The vertical height of the viewing slit of the monochromator was reduced to ca. 1 mm by a horizontal slit. Sample vapour was passed continuously into the plasma. The cavity, and hence the plasma, was moved vertically by means of a rack and pinion and the intensity of the emissions was measured at intervals of 3 mm along the length of the plasma.

The variations of emissions with position were measured in this way at 247.9 nm (C_2H_5I, $CHCl_3$), 256 nm ($CHCl_3$), 206.2 nm (C_2H_5I), 253.5 nm ($(CH_3O)_3P$) and 292 nm ($CHBr_3$). The results are shown in Figure I,8. The emissions of all species were most intense around the central zone of the plasma. The decrease of all intensities in the exact centre was presumably due to the gap in the plasma which could be seen near the central electrodes when using this type of cavity. With a $\frac{3}{4}$-wave cavity the plasma showed no such gap.



o - 247.9 nm (C_2H_5I)
⊙ - 253.5 nm ($(CH_3O)_3P$)
∇ - 206.2 nm (C_2H_5I)
× - 256 nm ($CHCl_3$)
\+ - 292 nm ($CHBr_3$)

VARIATION OF PEAK HEIGHT WITH POSITION IN PLASMA

Figure I.8

Conclusions

With the exception of oxygen-containing compounds, characteristic emissions were observed for all the types of compound studied. They are summarised in Table I,1. The principal emissions not previously observed in the spectra of atmospheric pressure microwave-excited plasmas are the sulphur atomic lines and the molecular Cl_2 and Br_2 bands. The presence of these molecular bands and other bands, such as those of C_2 and CN in the spectrum of chloroform, indicated that considerable recombination of species occurred in the plasma and that, therefore, no structural information could be deduced from the observation of the emission of any particular species. Accordingly, the operational conditions of the detector were optimised to make the detector response, as far as possible, independent of compound structure and dependent only on the weight of elements present. This would be analytically very useful, in that the direct calculation of the weight of an element present in an unknown eluate would be possible.

The emissions of both atomic and molecular species were most intense around the centre of the plasma and it was therefore concluded that the use of the centrally placed viewing apertures of the $\frac{3}{4}$-wave cavity would not result in any loss in sensitivity. Owing to its long-term stability this type of cavity was used throughout the gas-chromatographic determinations.

Table I.1.

Principal Emission Wavelengths.

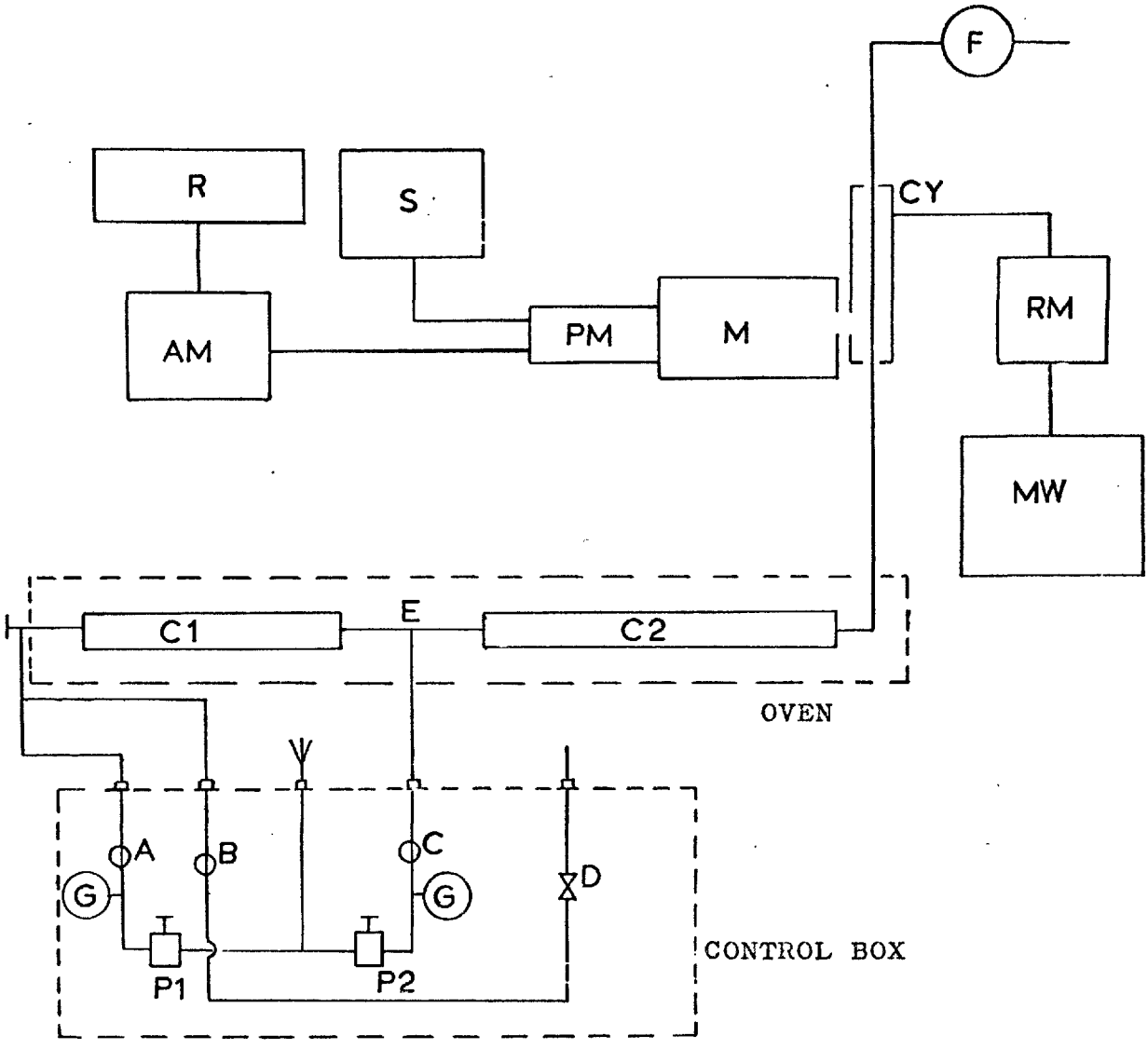
Type of Compound	Emission Wavelength (nm)	Assignment
- C	193.1	C
	247.9	C
	388.3	CN
	516.5	C_2
- Cl	256	Cl_2
	278.8	CCl
- Br	292	Br_2
- I	206.2	I
- P	253.5	P
- S	180.7	S
	182.0	S
	182.6	S
	257.6	CS
- N	337.1	N_2 or NH
	336.0	N_2 or NH
H_2O	308.9	OH

II. Gas-Chromatographic Determinations

Experimental

The experimental arrangement is shown in Figure I,9. The microwave system was the same as that used for the determination of spectra. A $\frac{3}{4}$-wave cavity was used throughout. The detection system was also very similar; the only modification made was the use of a small, low resolution, grating monochromator (Rank Precision Industries Ltd., London, Type D292) fitted with a EMI 9601B photomultiplier during initial studies on carbon-containing compounds. In later work, owing to the need for higher resolution, the Beckmann DU and the Hilger and Watts D330 monochromators were again used.

The sample dilution system was replaced by a Pye Model Series 104 Chromatograph. The katharometer supplied with the instrument was removed and the column connected to the quartz tube of the detector by means of stainless steel tubing and brass connections. Liquid sample solutions were injected, using 5 μl and 10 μl syringes, directly onto the top of the column. Attempts to purify the argon carrier gas prior to the injection point were abandonned after it was found that the column was the greatest source of background emission. In addition to the argon, nitrogen and hydroxyl emissions observed previously, CN bands at 388.3 nm and 358.6 nm were also observed in the background. The emission at 388.3 nm was particularly intense.



R - recorder
AM - amplifier
S - power supply
PM - photomultiplier
M - monochromator
G - pressure gauge
D - needle valve
F - flow-meter
CY - cavity
RM - reflected power meter
MW - microwave power supply
C1,C2 - columns
P1,P2 - pressure controllers
A,B,C - taps

GAS-CHROMATOGRAPHIC APPARATUS

Figure I,9

For the determination of relatively involatile compounds a 3-mm diameter column of Chromosorb 101, 1m in length (Column C) was used. The compounds were dissolved in a solvent, such as ethanol or methanol, which was eluted prior to the components of interest. To avoid excessive carbonization of the detector tube the plasma was initiated only after the solvent had been eluted (ca. 30 s).

For volatile compounds solvents with long retention times were used. The analysis time was limited by use of the back-flushing system shown in Figure I,9. Columns 1 and 2 were Porapak S, 6-mm diameter columns of ca. 0.3 and 0.7 m length, respectively. (This combined column arrangement is subsequently referred to as Column S). With taps B and C closed and tap A open, the system functioned normally and a sample injected travelled through both columns. After the individual components to be resolved had passed through the T-piece (E) connecting the two columns, taps B and C were opened and tap A was closed. The pressure at E was adjusted by control valve P_2 and the needle valve D so that the gas flow through the second column and the plasma was unchanged. The solvent, still in column 1, was then back-flushed at ca. twice the previous flow rate and ejected. Hence, as soon as the sample peaks were recorded the flows could be reversed and a further sample injected.

Results

1) Carbon-containing Compounds

Three main emissions had been observed for all carbon-containing compounds, viz. atomic carbon at 247.9 nm, C_2 at 516.5 nm and C_2 and CN emission at 385-389 nm. No distinction between the C_2 band emission at 385.2 nm and the CN band emission (band head 388.3 nm) was possible with the low resolution (D292) monochromator used. Each emission region was evaluated for quantitative work with mixtures of ethyl iodide, benzene, acetone and ethanol.

Column S at 140° resolved, with base-line separation, a mixture of 790 p.p.m. ethanol and 790 p.p.m. acetone in toluene (retention times 3.15 min, 4.20 min and ca. 16 min, respectively, at a flow rate of 3.0 lh^{-1}). The system was switched to back-flush after 2.20 min and back to normal operation after 6 min. The monochromator wavelength control was optimised for maximum emission by repeated sample injection (1 μl) with a Hamilton syringe held in a Shandon multi-injector. The microwave power was also optimised for maximum emission intensity and the noise level at each setting was recorded. Further comparative and confirmatory results were obtained with 630 p.p.m. carbon disulphide in n-butanol at 150° (retention times 60 s and ca. 4 min, respectively).

A similar series of measurements were made with a

mixture of 1940 p.p.m. ethyl iodide and 440 p.p.m. benzene in ethanol; 1 μl injection volumes were used with Column C at 132°c. The solvent was eluted first, with a retention time less than 90 s, after which the plasma was initiated. The retention times for ethyl iodide and benzene were 3.30 min and 4.35 min, respectively.

The results of these investigations are summarised in Figures I, 10, 11, 12 and 13. The optimum monochromator slit width of 0.1 mm was used throughout. The maximum signal : noise ratios obtained are shown in Table I,2. The most sensitive emission characteristic of carbon-containing compounds was that due to atomic carbon at 247.9 nm. In addition, this emission had the advantages that its intensity varied relatively little with microwave power at 70-80 W (the optimum power settings) and that background emission from the plasma at this wavelength was low.

With these relatively low microwave power settings overheating of the quartz tubing was no longer a problem and 1-mm i.d. tubing was therefore used in all subsequent determinations.

The effect of carrier gas flow rate variation on emission at 247.9 nm was measured for the ethyl iodide-benzene mixture and the solution of carbon disulphide in n-butanol. The flow rate was measured immediately before and after recording each emission peak; the peak areas were approximated by triangulation. The linear

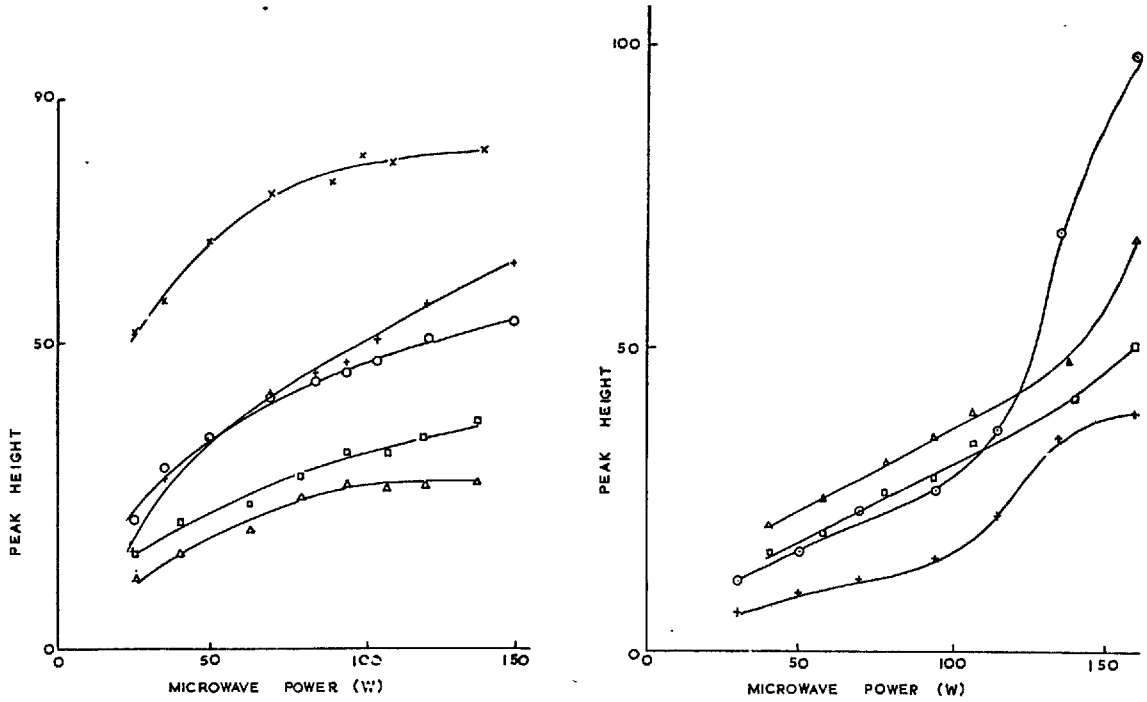


Fig. 10 Variation of peak height with microwave power for atomic carbon emission at 247.9 nm. (×) Carbon disulphide, (+) benzene, (○) ethyl iodide, (□) acetone, (△) ethanol.

Fig. 11 Variation of peak height with microwave power for C_2 emission at 516.5 nm. Symbols as for Fig. 10

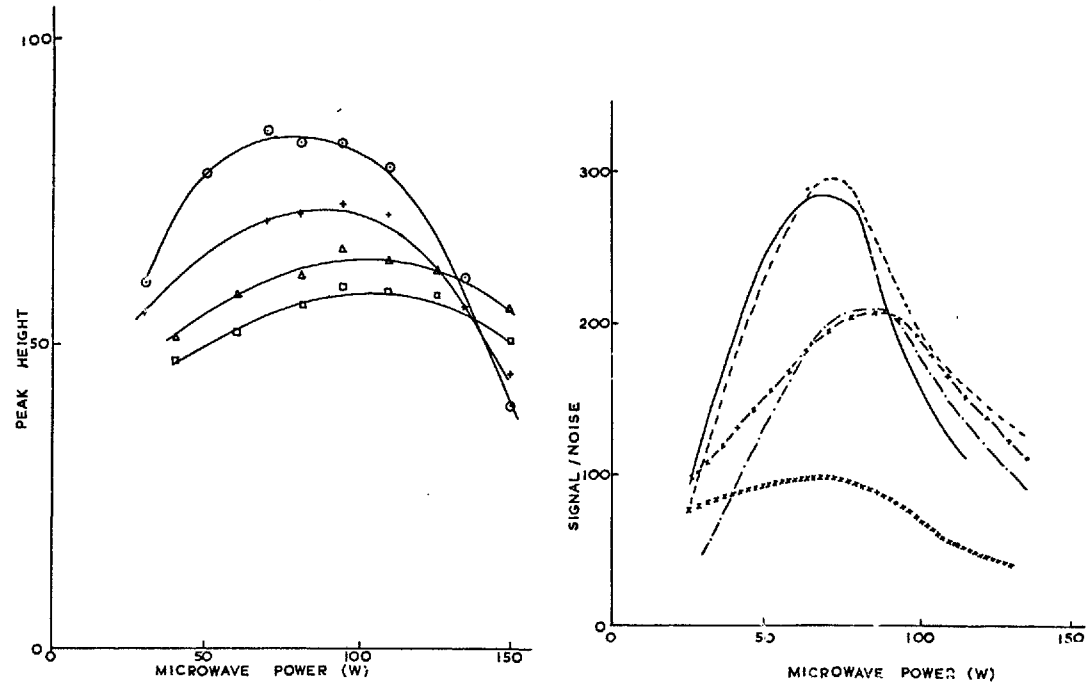


Fig. 12 Variation of peak height with microwave power for C_2/CN emission at *ca.* 388 nm. Symbols as for Fig. 10

Fig. 13 Variation of signal-to-noise ratio with microwave power. (———) Benzene, (---------) ethyl iodide, (×–×–×) acetone, (–·–·–·–) ethanol, (× × ×) carbon disulphide.

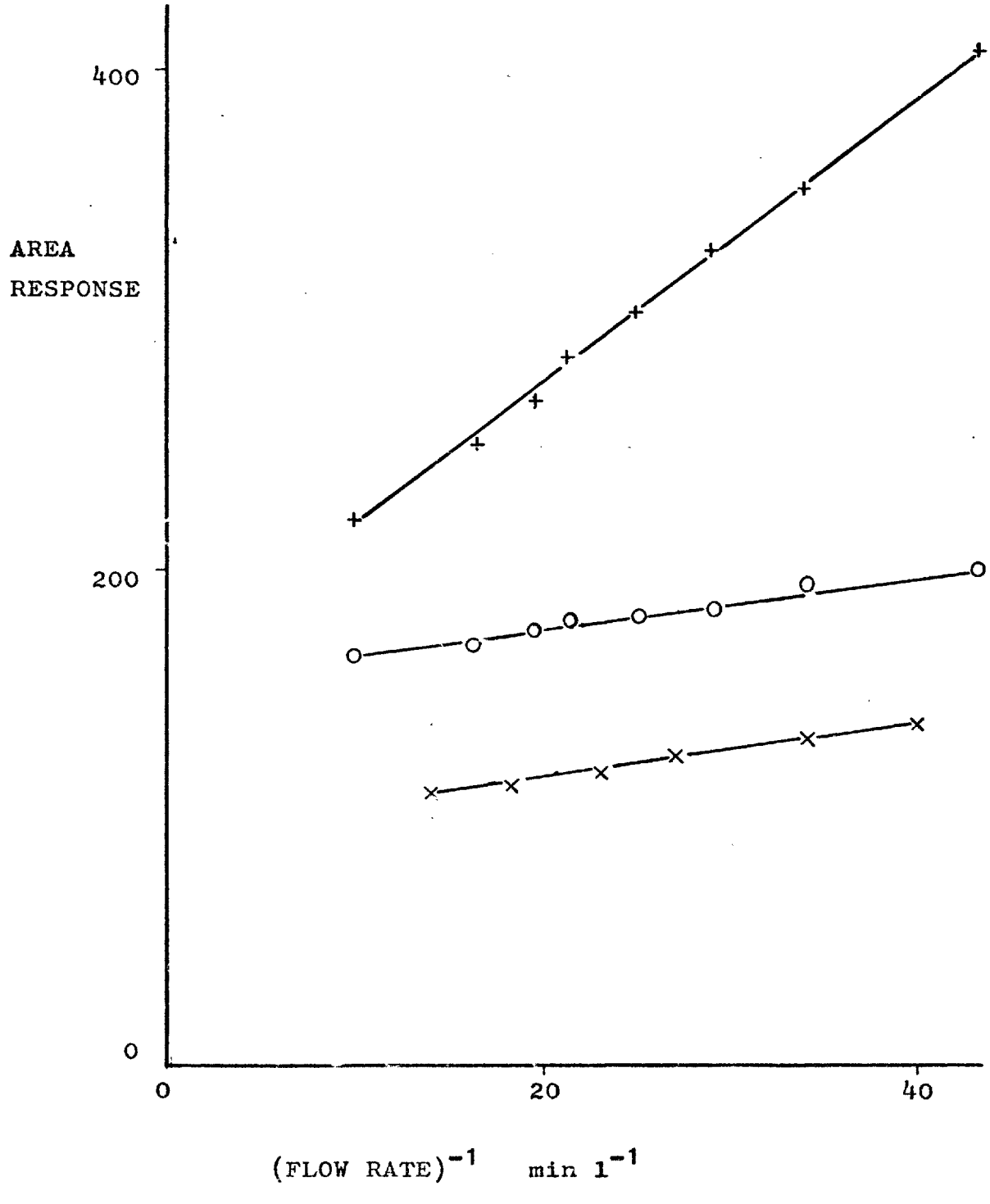
Table I,2.

Maximum Signal : Noise Ratios.

Compound	Atomic C 247.9 nm	C_2 516.5 nm	C_2/CN 385-389 nm
Ethyl iodide	290(70)[a]	39(50)	120(160)
Benzene	280(72)	32(60)	49(160)
Acetone	205(80)	83(54)	71(160)
Ethanol	210(85)	74(63)	52(160)

[a] The figures in brackets represent the applied microwave power in W.

increase of peak area with decrease in argon flow rate (Figure I,14), which was also shown by all the emission species studied, may be correlated with linearly increasing residence time for the species in the plasma. The noise did not vary appreciably with flow rate, hence as low a flow rate as possible, compatible with a convenient retention time would give the maximum sensitivity. A flow rate of 3 lh^{-1} was generally used.



VARIATION OF AREA RESPONSE WITH RECIPROCAL OF FLOW RATE

Figure I,14

Table I,3 shows the limits of detection (signal : noise = 2), linear ranges, sensitivities (ie. limits of detection expressed in terms of gs^{-1}) and analytical conditions for various carbon-containing compounds. These results were all obtained using 1-mm quartz tubing, a microwave power of 70 W and the Beckmann DU monochromator with a slit width of 0.1 mm. The limits of detection at 247.9 nm expressed in g carbon s^{-1} are the same within ± 3% for all compounds with the exception of carbon tetrachloride and chloroform. The approximate independence of the response at this wavelength from structural variations and from the presence of hetero-atoms in the original compound is illustrated in Figure I,15. This shows a plot of detector response against weight of carbon injected in the form of a wide range of organic compounds.

2) Halogen-containing Compounds

Ethyl iodide was examined alone and in admixture with benzene in ethanol at 206.2 nm (atomic iodine) and at 247.9 nm (atomic carbon) with a microwave power level of 80 W. When a low-resolution monochromator (D292) was used, the relative sensitivity for equal weights of the two compounds was 50:1 in favour of ethyl iodide. Further experiments with a higher resolution Beckmann DU monochromator (slit width 0.1 mm) gave a relative sensitivity of 500:1. Because of the low noise level at 206.2 nm (compared with that at

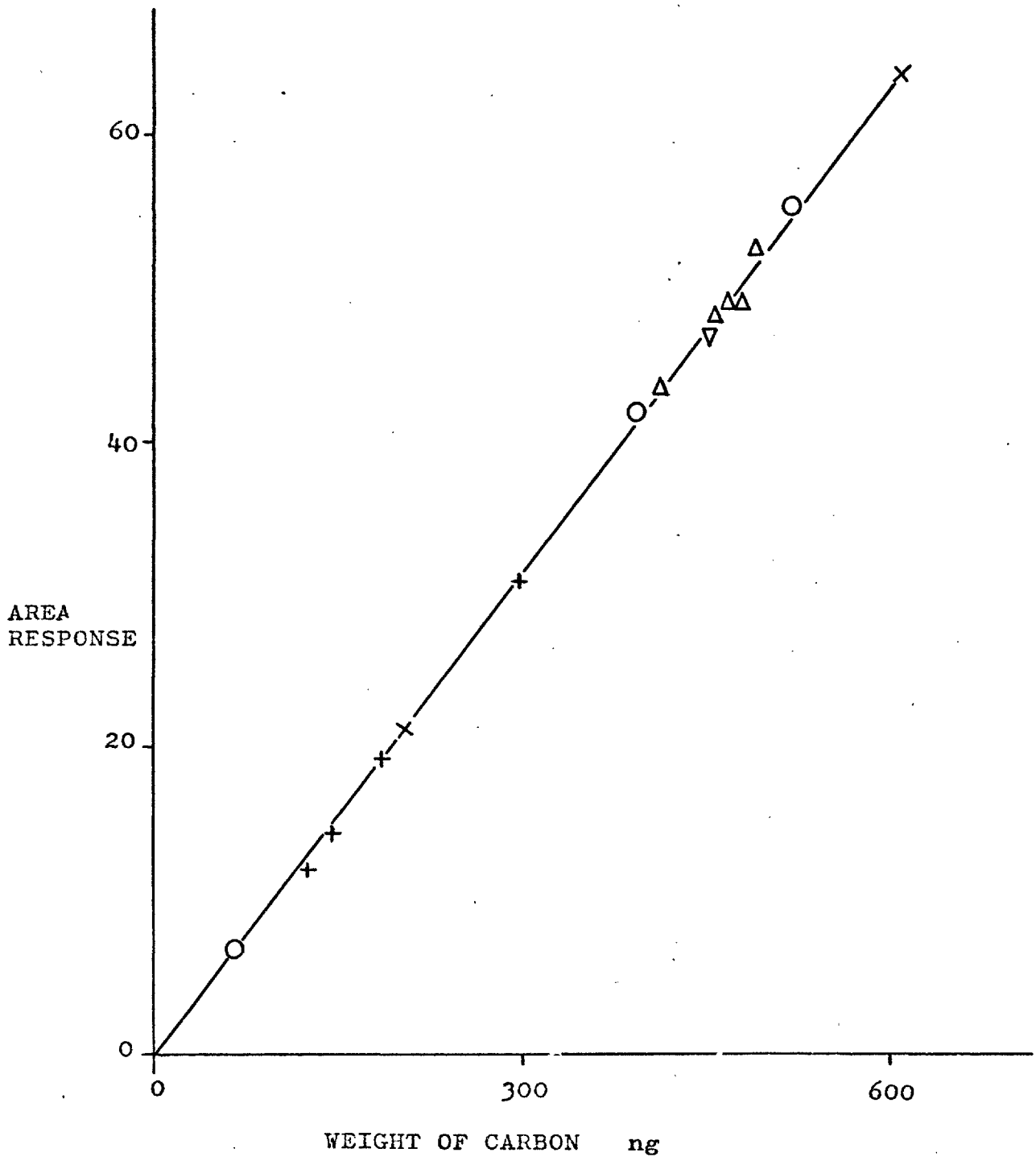
TABLE I,3

EMISSION CHARACTERISTICS OF SOME CARBON-CONTAINING COMPOUNDS

Compound	*Emission (nm)*	*Column*[a]	*Solvent*	*Column temperature (°)*	*Retention time (min)*	*Limit of detection (ng)*[b]	*Sensitivity* $\cdot 10^{-11}$ *g C sec*$^{-1}$	*Linear working range*
Carbon disulphide	247.9	S	Toluene	150	1.06	23.4	1.88	$>10^2$
Acetone	247.9	S	Toluene	150	4.00	7.3	1.88	$>10^3$
Methanol	247.9	S	Toluene	150	1.53	17.8	1.95	$>10^2$
Ethanol	247.9	S	Toluene	150	2.50	7.9	1.91	$>10^3$
sec-Propanol	247.9	S	Toluene	150	4.05	10.9	1.91	$>10^3$
n-Propanol	247.9	S	Toluene	150	4.30	12.7	2.00	$>10^3$
Benzene	247.9	C	Ethanol	140	3.90	6.0	1.90	$>10^3$
Toluene	247.9	C	Ethanol	150	3.30	4.0	1.90	$>10^3$
Ethyl iodide	247.9	C	Ethanol	125	3.85	31.0	1.96	$>10^3$
	206.2	C	Ethanol	125	3.85	22.4	—	$>10^3$
n-Propyl bromide	247.9	C	Ethanol	125	3.50	25.4	1.91	$>10^3$
	292	C	Ethanol	125	3.50	163.0	—	$>10^2$
Dichloromethane	247.9	S	Toluene	150	3.35	98.0	1.88	$>10^2$
	278.8	S	Toluene	150	3.35	*ca.* 5,000	—	—
Chloroform	247.9	C	Methanol	150	1.40	30.4	2.06	$>10^3$
	256	C	Methanol	150	1.40	41.6	—	$>10^3$
Carbon tetrachloride	247.9	C	Methanol	150	2.20	103.0	2.10	$>10^2$
	278.8	C	Methanol	150	2.20	*ca.* 4,000	—	—
	256	C	Methanol	150	2.20	96.0	—	$>10^2$

[a] C denotes Chromosorb 101; S denotes Porapak S.

[b] Limit of detection defined as signal:noise=2.



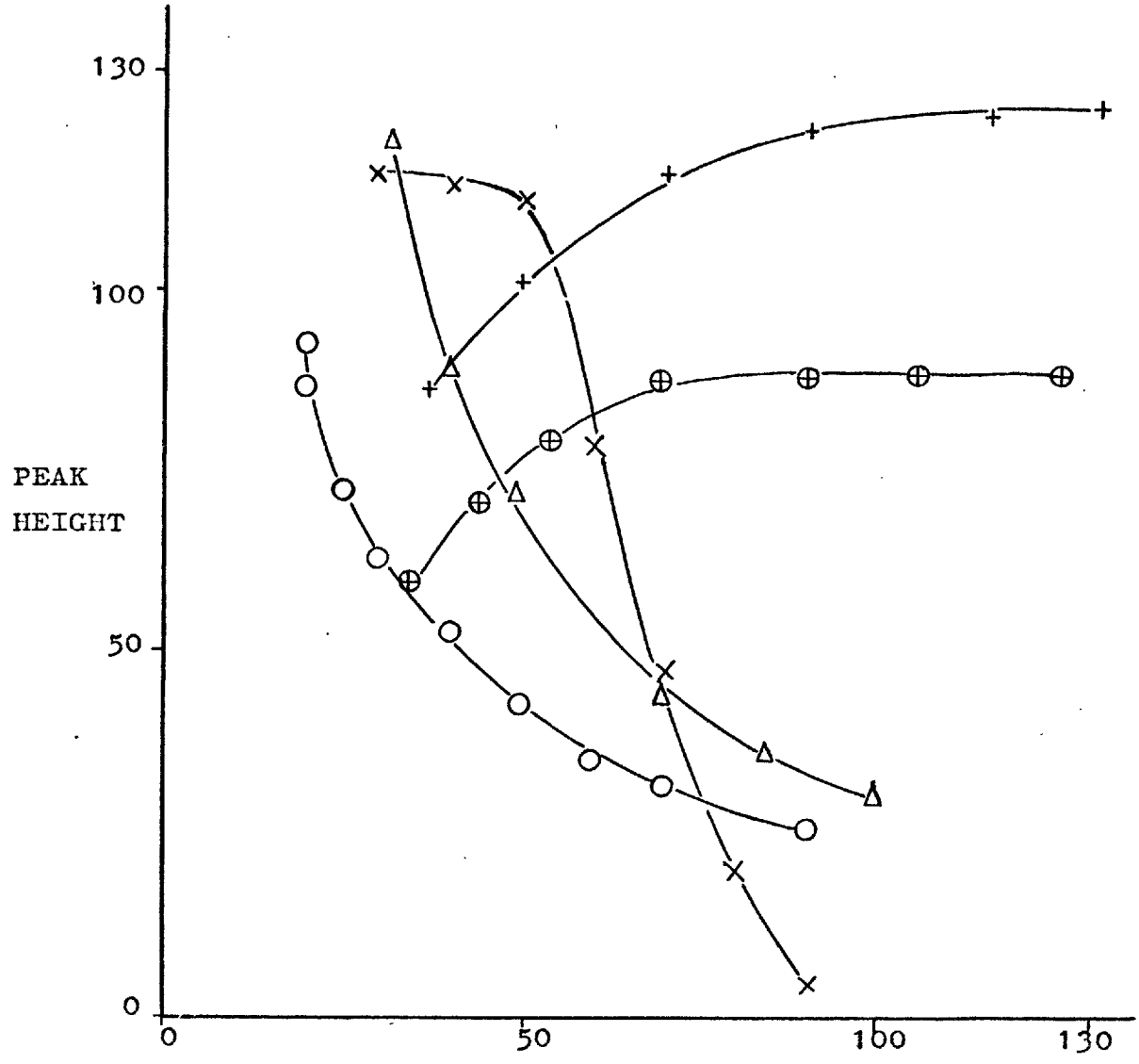
VARIATION OF AREA RESPONSE WITH WEIGHT OF CARBON INJECTED

Figure I.15.

247.9 nm), this emission line proved the most sensitive for the determination of ethyl iodide. The response at this wavelength varied linearly with concentration over a range of greater than 1000 and showed a similar variation with microwave power to that at 247.9 nm (Figure I,16).

In contrast to carbon emission at 247.9 nm Cl_2 emission at 256 nm from 1 μl injections of a solution of 177 p.p.m. chloroform in methanol was found to decrease markedly at higher microwave powers (Figure I,16). This phenomenon may indicate an increased breakdown of the molecular species with increasing microwave power. The log-log plot of detector response against concentration of chloroform injected was linear over three orders of magnitude, with a gradient of 2.04. A gradient of 2.0 would be expected if the rate of formation of Cl_2 molecules by the combination of two chlorine atoms was the factor limiting Cl_2 emission.

Background carbon emissions at 256 nm varied approximately linearly with carbon concentration and increased somewhat at higher microwave powers. Therefore the selectivity of Cl_2 emission over carbon decreased with decrease in concentration and increase in microwave power. For an injection of 177 p.p.m. chloroform the selectivity was 25 over an equal weight of toluene at a power of 70 W and 71 at 50 W. The limits of detection at 50 W were 4.4×10^{-9} g chlorine s^{-1} for carbon tetrachloride and 4.6×10^{-9} g chlorine s^{-1} for chloroform.



o - 292 nm ($CHBr_3$)
Δ - 256 nm ($CHCl_3$)
⊕ - 206.2 nm (C_2H_5I)
× - 182.0 nm (C_4H_4S)
\+ - 253.5 nm ($(CH_3O)_3P$)

VARIATION OF DETECTOR RESPONSE WITH MICROWAVE POWER

Figure I,16

Only microgram quantities of methylene chloride and carbon tetrachloride could be detected at 278.8 nm (CCl emission).

Br_2 emission at 292 nm showed characteristics very similar to those of Cl_2 emission in respect to variations with microwave power (Figure I,16) and concentration. The gradient of the plot of log response against log concentration was 1.94. The selectivity of response for 1 μl of a solution of 430 p.p.m. n-propyl bromide in ethanol was 109 over toluene and the limit of detection was 2.5×10^{-9} g bromine s^{-1}.

The limits of detection, linear ranges and analytical conditions used for various halogen compounds are shown in Table I,3.

3) Phosphorus and Sulphur Compounds

Detector response at 253.5 nm (atomic phosphorus emission) was determined using tri-n-butyl phosphate which was eluted after 1.70 min from Column C at 230°c at a flow rate of 2.7 lh^{-1}. Emission at this wavelength proved somewhat less sensitive to tri-n-butyl phosphate than at 247.9 nm but showed similar characteristics (Figure I,16). The response was linear over a concentration range of three orders of magnitude. The selectivity over an equal weight of toluene was 21. The sensitivity was 3.0×10^{-10} g phosphorus s^{-1}.

Detector response at the atomic sulphur lines and at the CS band emission were compared using repeated

1 µl injections of a 1060 p.p.m. solution of thiophen in methanol on Column C at 132°c. The Hilger and Watts D330 monochromator with a slit width of 0.05 mm was used. The results are shown in Table I,4.

Table I,4.

Wavelength (nm)	Species	S:N	Selectivity*
180.7	S	481	108
182.0	S	586	116
182.6	S	329	56
190.0	S	34.1	3.1
191.5	S	18.5	1.7
193.1	C	235	-
257.4	CS	41.0	12

* Over equal weight of pentane.

The sulphur atomic line at 182.0 nm was the most sensitive and selective emission characteristic of sulphur-containing compounds observed. Emission at this wavelength decreased very markedly at high microwave powers (Figure I,16). The optimum power setting

was 40 W. The response varied linearly over a concentration range of 500, however, at higher concentrations the response levelled-off, possibly due to the formation of deposits. The limit of detection was 4.0×10^{-11} g sulphur s^{-1}.

4) Water and Oxygen-containing Compounds.

Solutions of water in sec-propanol were used to determine the detector response at 308.9 nm (OH emission). Correction was made for the blank water level in the propanol. Water was eluted after 60 s at 153°c on Column S. The response was linear over the concentration range of 200 measured. A power of 50 W proved optimum. The limit of detection was 2×10^{-8} g water s^{-1} but this was limited by the background OH emission which appeared to arise principally from column bleed. All other materials gave negative peaks at this wavelength, presumably due to suppression of the OH background emission. The negative peaks due to oxygen and nitrogen were proportional to the intensity of the OH background. It had been hoped to use 308.9 nm for the selective determination of oxygen-containing compounds, however, even alcohols gave negative peaks at this wavelength under all conditions.

5) Nitrogen-containing Compounds

Diethylamine and acetonitrile gave positive responses at 336.0 nm and 337.1 nm (N_2 and NH bands), however, so

also did the other hydrogen-containing compounds monitored at this wavelength, including hydrocarbons and alcohols; the only exception was water. Compounds which did not contain hydrogen (carbon tetrachloride, carbon monoxide and carbon dioxide) gave negative peaks dependent on the level of background emission. These results indicated that NH was being formed by the combination of hydrogen, from any hydrogen-containing compound broken down in the plasma, with background nitrogen present in the argon. The increase in sensitivity for diethylamine over pentane at 337.1 nm was only a factor of 2. Therefore, unless nitrogen impurities could be removed, these emissions could not provide selective determination of nitrogen-containing compounds.

6) Analysis of Gases

For gas analysis, a Pye Chromatographic Valve fitted with a 5-μl internal sample loop was used. Gas samples were obtained in pure form and as calibrated dilutions in nitrogen (EDT Supplies Ltd., London). The gases were available in push-buttoned aerosol cans and could be readily interfaced with the sample injection system. The gases used were CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, C_4H_8, C_2H_2, CO, CO_2, O_2 and N_2.

Column S was used at 150° (for C_2, C_3 and C_4 compounds) and at 50° (for C and C_2 compounds). The argon carrier gas flow rate was held at 1.5 lh^{-1} and all measurements were made using the D292 monochromator

set to monitor emission at 247.9 nm. The microwave power was 70 W. The response of the detector system was found to be very similar for all hydrocarbons studied; an average limit of detection of 7.6×10^{-11} g carbon s^{-1} with a maximum variation from this of 8.5% was obtained. No difference in response was found for saturated or unsaturated species and there was no change in area response with increase in column temperature. Each series of hydrocarbons, eg. C_2, C_3, C_4 compounds, gave an approximately linear response over the concentration range investigated; the maximum difference between the curves was 8.5%.

The limit of detection for carbon dioxide was 8.0×10^{-11} g carbon s^{-1} at 247.9 nm and 1.6×10^{-10} g carbon s^{-1} at ca. 193 nm. The corresponding limits of detection for carbon monoxide were 7.7×10^{-11} g carbon s^{-1} and 4.3×10^{-11} g carbon s^{-1}.

Nitrogen could be measured at 336 nm (N_2 and NH band emission). Under the conditions used above, oxygen is not separated from nitrogen and causes a negative interference. Separation was achieved on a 2-m molecular sieve column at -40° and the limit of detection for nitrogen was then 1.5×10^{-11} g nitrogen s^{-1}. The signal : noise ratio was independent of microwave power. The selectivity at this wavelength to nitrogen was not calculated as it was dependent on the background emission. As described in the preceeding section all hydrogen-containing compounds except water gave

a positive response. Therefore, unless all nitrogen-containing impurities could be excluded, high selectivity would not be possible.

Oxygen is one of the few gases which cannot be directly determined in a microwave-excited plasma. Its negative interference, particularly at argon, nitrogen and OH emission wavelengths could be used for its detection. However, this response is non-selective.

7) Interferences

Interferences with the response of this detector to a particular eluate may arise in any of three ways :

a. Distortion of the plasma by a large excess (greater than 10^{-6} gs^{-1}) of another eluate.
b. Spectral emissions from other species at the wavelength being monitored.
c. Suppression or enhancement of emission by another substance present in the plasma.

Overloading of the plasma affects all emissions and must be avoided. It imposes an upper limit on the working range of the detector. Attempts to extend the range by admixing a secondary flow of argon with the effluent stream from the column prior to the detector were unsuccessful; at high flow rates the plasma was more stable but extensive carbonization still occurred. One method of extending the upper limit of the detector, the use of a plasma extending above the top of a quartz tube, is described in Chapter II. Two alternative

methods, back-flushing and delayed initiation of the plasma, used to overcome the problems of carbonization and overloading with regard to the solvent have already been described. Both proved satisfactory.

The principal element that interfered spectrally is carbon which gave rise to a large number of emitting species (C_2, CN, CH, C). The measurement of the detector response to some carbon compounds at the major emission wavelengths has been described. A summary of the selectivities of the atomic emissions used is shown in Table I,5.

Table I,5.

Element	Wavelength (nm)	Limit of Detection (g/sec)	Selectivity
C	247.9	1.9×10^{-10}	-
I	206.2	1.0×10^{-10}	1000
S	182.0	4.0×10^{-11}	460
P	253.5	3.0×10^{-10}	150
Cl	256	4.5×10^{-9}	
Br	292	2.5×10^{-9}	

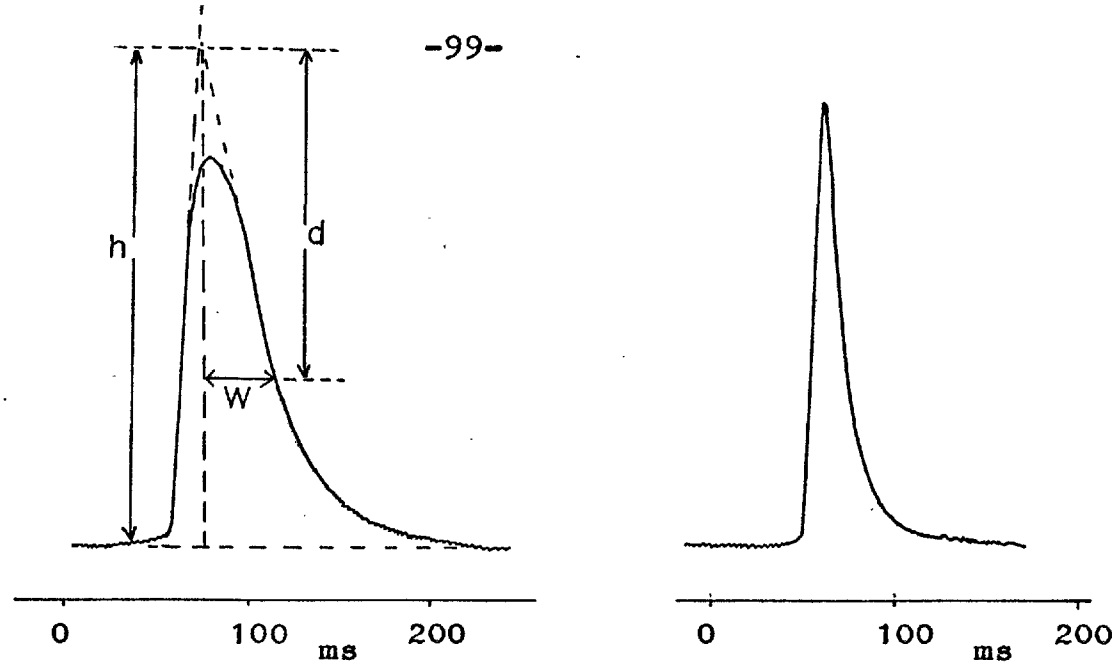
These selectivities are given as the ratio of response per gram-atom of the element to the response per gram-atom of carbon. The interferences from other emissions were found in all cases to be less than those from carbonaceous species.

The elution of excesses of carbon-containing compounds (usually the solvent) with a component of interest was not found to produce any enhancement or suppression of detector response, except at concentrations sufficient to cause distortion of the plasma or severe carbonization. Negative interferences were observed only when a wavelength at which there was considerable background emission was being monitored.

8) Response Time of the Emissive Detector

An important parameter of any detector is its response time. Too slow a response time (more than 1 s) will reduce the resolution possible and may lead to peak overlap and distortion. Detectors with long response times cannot be used with capillary columns.

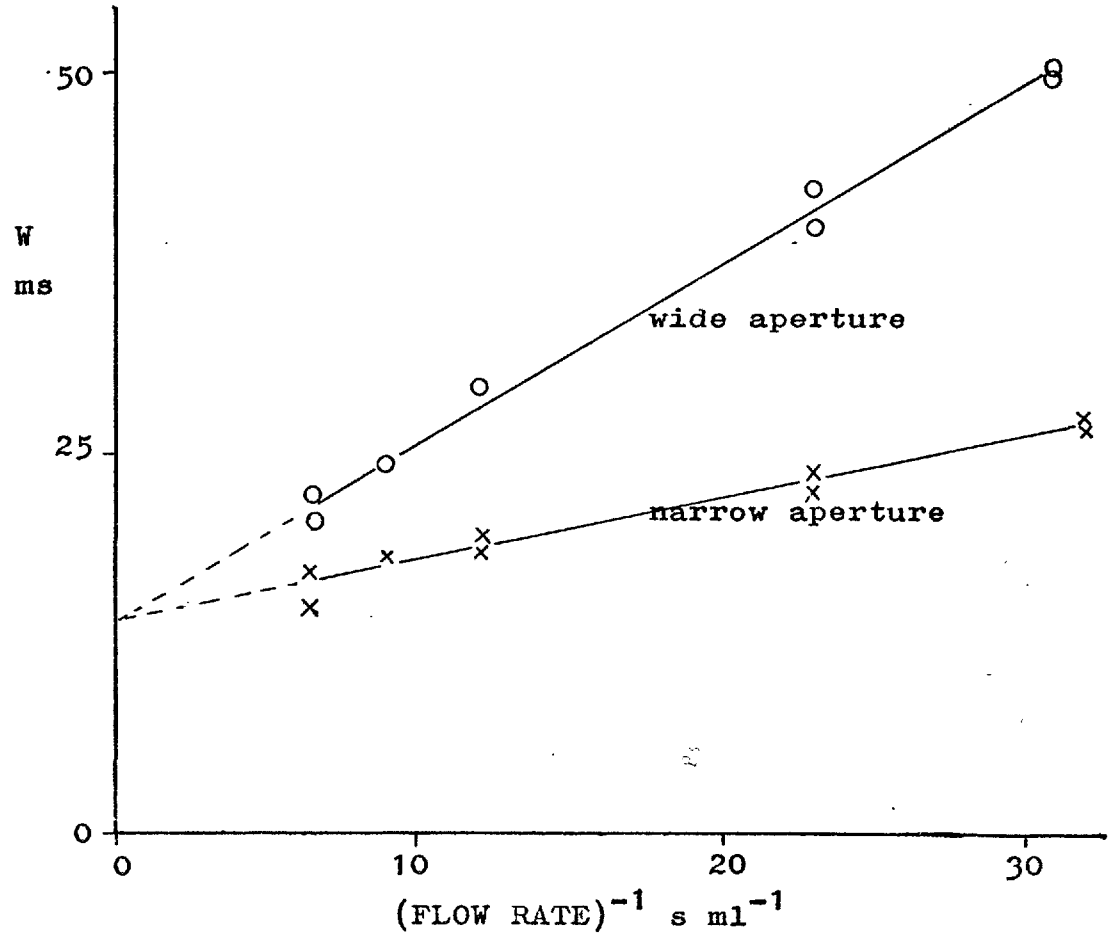
The response time of the microwave emissive detector was measured by a method applied by Chowdhury and Korasek (31) to a katharometer. An instantaneous signal is applied and the detector response is recorded. The response time of the detector (T) is given by the time taken for the response to fall to 1/e of the applied signal (W in Figure I,17a, where d = 0.63 h).



(a) Response to 1μl air at 1.82 lh^{-1}, wide aperture.

(b) Response to 1μl air at 5.45 lh^{-1}, narrow aperture.

Figure I,17



VARIATION OF RESPONSE TIME WITH RECIPROCAL OF FLOW RATE

Figure I,18

An injection cap was fitted into a T-piece just below the 1-mm i.d. detector tube. The Beckmann DU monochromator was set to monitor 336.0 nm and 1 μl injections of air were made. In order to avoid interference from the small pressure wave which accompanied insertion of the syringe needle the syringe was filled beyond the 1 μl mark, the needle inserted, the plunger pushed in to the mark and, after 20 s allowed for the plasma to re-equilibrate, the sample was injected, A very sharp peak was produced. The Servoscribe recorder proved too slow to follow the photomultiplier response adequately and an oscillograph (S.E. Laboratories, Type 3006, fitted with a B160 recording galvanometer), with a response time of ca. 2 ms, was used. A series of peaks were recorded at various argon flow rates using two different length viewing apertures (5 mm and 15 mm). W (Figure I,17a) was measured in each case, and plotted against the reciprocal of the flow rate (Figure I,18). The response time of the detector at infinitely fast flow rate was obtained by extrapolating to a reciprocal flow rate of zero.

A response time of 14.0 ms was obtained for both apertures but this may have been the limit set by the injection technique. Identical results were produced by propane monitored at 247.9 nm. The gradients of the lines in Figure I,18 are in agreement with the times taken for the sample to travel the length of the plasma viewed, as calculated from the flow rate and the bore

of the tubing. Using the Servoscribe recorder a value for W of ca. 0.8 s resulted, independent of flow rate. Therefore, the response time of the detector was not greater than 14 ms and in practice is limited by the recorder used. The dead-volume of the detector is also very small. With 1-mm i.d. tubing and a viewing aperture of 15 mm flow rates of down to 0.05 lh^{-1} could be used before exceeding the limit on the response time set by the recorder (0.8 s).

Conclusions

The optimum emission wavelengths for each element, the limit of detection (in g element s^{-1}) and the selectivity of the atomic emissions over carbon (expressed as the ratio of responses per gram-atom) are shown in Table I,5 (page 97). The detector provided sensitive and fairly selective determination of carbon-, phosphorus-, sulphur-, chlorine-, bromine- and iodine-containing compounds. In addition, water and nitrogen could be determined from their emissions at 308.9 nm and 336.0 nm respectively. At 247.9 nm (atomic carbon emission) the sensitivities for all the compounds investigated were directly proportional to the weight of carbon in the compounds, and independent of structure.

The linear working range of the detector was approximately three orders of magnitude and was limited at higher concentrations by overloading of the plasma and carbonization. The area response at all wavelengths

increased linearly with the reciprocal of the carrier gas flow rate and the detector was therefore most sensitive at low flow rates. The response time of the detector was limited by the recorder used at flow rates over 50 $ml h^{-1}$.

The limits of detection reported here are sometimes not as low as those reported by previous workers; this may be explained by the nature of the read-out system used. An advantage of the photoemissive system is that the limit of detection may be lowered by increasing the solid angle of measurement or the photomultiplier gain. Various modifications to the detection system are described in Chapter II.

CHAPTER II

MODIFIED EMISSIVE DETECTOR SYSTEMS.

Introduction

The emissive detector system described in Chapter I consisted of a microwave-excited plasma maintained in a quartz tube, a monochromator for selecting particular wavelengths from the electromagnetic radiation emitted from the plasma, a photomultiplier to convert and amplify the intensity of emission at those wavelengths into a current and an amplifier and potentiometric recorder to record the resultant signal as a d.c. voltage change. The sensitivity and selectivity of such a detector system are clearly dependent on the nature of the components used. In addition to improvements in the quality of any of the components, various, more fundamental, modifications may be made.

The initial method of amplifying and recording the photomultiplier output consisted simply of passing the current from the photomultiplier through a variable resistance and recording the potential drop across the resistance, via a backing-off unit, on a potentiometric recorder. This system was replaced by two alternatives : a d.c. amplifier / integrator and a photon counting system.

Furthermore, with high frequency modulation of the microwave power applied to the resonant cavity the output from the photomultiplier was recorded via an a.c. amplifier. Finally, two, more basic, modifications were made to the detector. The emission from a plasma was viewed using a solar-blind photomultiplier without a monochromator and a system was set up in which a plasma extended above the top of a quartz tube.

I. d.c. Amplification and Integration

A simple amplifier / integrator designed and built in this laboratory (205) was used to monitor the output of the Beckmann DU monochromator and 9601B photomultiplier. The unit operated as an amplifier with a gain of x 10 or as an integrator with a gain of x 1; both outputs were connected to a Servoscribe potentiometric recorder. Prior to integration the background d.c. level was backed-off using two potentiometers and any further drift compensated by trimming the zero.

Detector response with this arrangement was studied using solutions of ethanol in n-butanol and mixtures of hydrocarbons in nitrogen. Atomic carbon emission at 247.9 nm was monitored. The gas mixtures were particularly suitable for integration because the dilutant, nitrogen, was rapidly and completely eluted; the baseline therefore returned quickly to a steady level. As the limits of detection obtained using the integrator were more dependent on the drift of the baseline than on the

short-term noise a stable baseline was essential for high sensitivity.

The amplifier gave a similar response to that of the microammeter used previously. The integrator eliminated the need for area measurement for quantitative work but proved slightly less sensitive than the amplifier. In addition, it proved more difficult to unambiguously distinguish small sample steps near the limit of detection from the background drift of the integrator. Some comparative results between the amplifier and integrator are shown in Table II,1. The slit widths used are shown in parenthesis.

Table II,1.

Compound	Limit of Detection (ng)			Peak Width (s)
	Amplifier	Integrator	Photon Counting	
Acetylene	1.7 (0.1)	2.3 (0.1)	2.0 (0.1)	9
Ethanol	5.6 (0.04)	8.0 (0.04)	14.4 (0.02)	16

II. Photon Counting

Photon counting involves the digital measurement of the current pulses resulting at the anode of a photomultiplier from photon impact at the photocathode. Provided that the rate of photo-electron emission and the frequency response of the measurement are such that individual current pulses are resolved, then the measurement gives a direct digital integration of the intensity of radiation on the photomultiplier. This method has been used in this laboratory (206-208) for the detection of transient signals in emission and fluorescence spectrometry, to which it is best suited. The limitation of photon counting lies in the counting of high photon emission levels, which requires a very high frequency response and a counter with a sufficiently large store. A microwave-excited plasma is not an ideal source for photon counting owing to the high level of its background emission, particularly at wavelengths longer than 300 nm. Broad gas-chromatographic peaks also present a problem in that they require long counting periods (ca. 30 s) leading to overloading of the counter.

Photo-electron pulses from the photomultiplier were amplified by a wide-band a.c. amplifier with a bandwidth of 0.6-6 MHz (AIM Electronics, Cambridge, type ACA powered by module PSU 101) and counted by a frequency meter (Venner Electronics, Kingston-upon-Thames, type TSA 6636/3) capable of 40 MHz operation and having a 6 digit readout. Atomic carbon emission at 247.9 nm was

again monitored. To obtain usuable counts with broad peaks monochromator slit widths of 0.02 mm or less were necessary, resulting in a loss of sensitivity.

The retention time and the time period (t seconds) during which a component passed through the plasma were first measured using a d.c. read-out system. Then, with the next injection three counts of t seconds were taken, one immediately prior to the arrival of the component peak, one during the passage of the peak and the third immediately afterwards. The component count was obtained by subtracting the mean of the first and third counts from the second. The limit of detection was taken as the smallest change in the total count which could be repeatedly distinguished from the random variation of the count. This was found, in practice, to be approximately twice the standard deviation in the background count.

Some comparative results are shown in Table II,1 for ethanol and acetylene. Despite its inherent unsuitability photon counting proved only slightly less sensitive in these cases than d.c. measurement. However, for broader peaks the need to reduce the slit width still further caused considerable losses in sensitivity. In addition, photon counting had the major disadvantages that prior information on the retention time and width of peaks was required in order to set correctly the counting period and that it could not be used to measure partially resolved peaks or peaks with variable backgrounds. For these reasons photon counting was not considered a suitable method for recording the response of this detector.

III. Electronic Modulation of the Microwave-excited Plasma.

Electronic modulation of microwave-excited electrodeless discharge lamps has been used to increase the signal : noise ratio in analytical measurements (209). The application of the same method to the plasma detector system used in the present studies was investigated.

The modulator used was a function generator (Hewlett Packard Model 3310A) capable of generating various waveforms of different frequencies (1×10^{-4} - 5×10^{6} Hz) and amplitude (0-35 V peak to peak). The modulation amplifier was a modified prototype modulation unit (Evans Electroselenium Ltd., Halstead, Essex) used as a voltage amplifier. The microwave generator (Evans Electroselenium Ltd. Model 245) was current stabilized and modulation of the magnetron output was provided by injecting the modulation waveform at the error-sensing point of the stabilizing element of the magneton power supply.

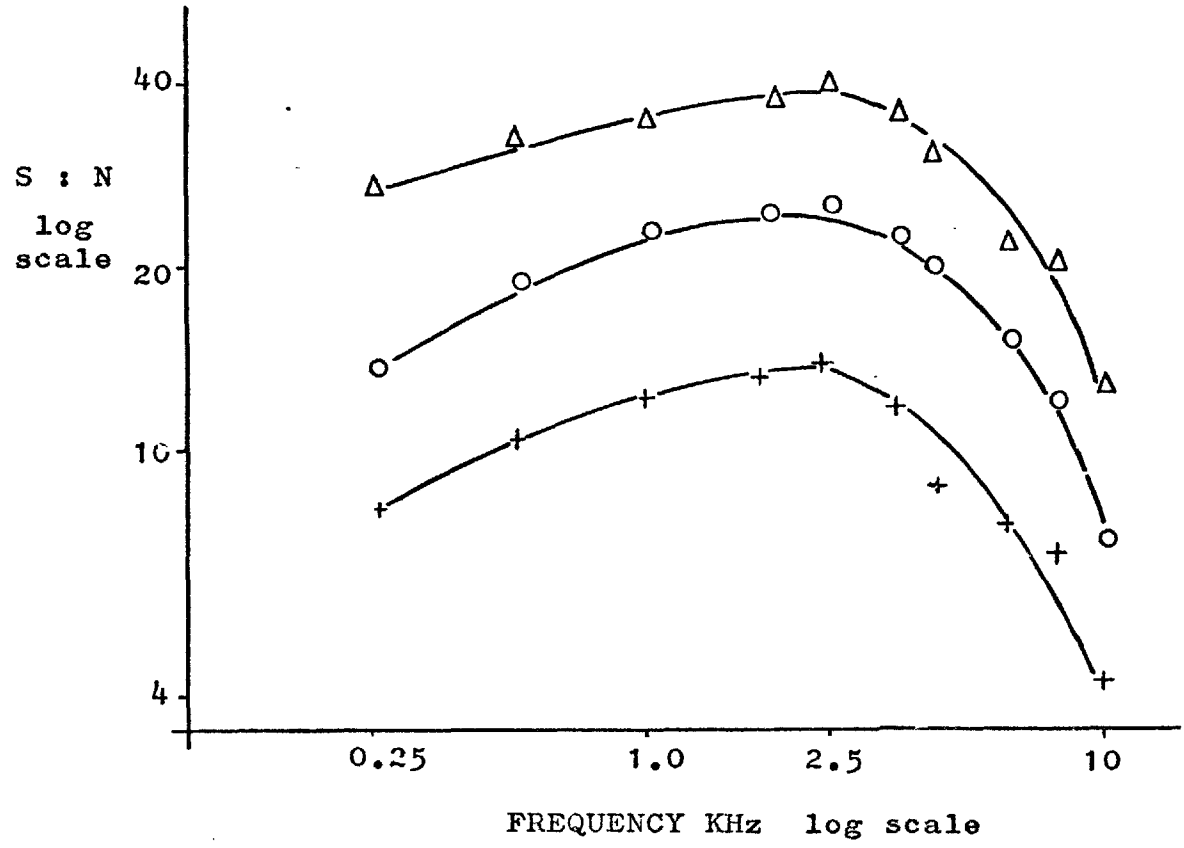
The same $\frac{3}{4}$-wave resonant cavity, 1-mm i.d. quartz tubing, Beckmann DU monochromator and photomultiplier were used. The signal from the phctomultiplier was amplified by a low-noise wide-band preamplifier, a wide-band amplifier and a variable-frequency, narrow-band amplifier (AIM Electronics Ltd., Model PSD 122A) which was phase-locked to the modulator.

Mixtures of hydrocarbons in nitrogen were used to compare the response of the detector in this mode of operation to that with d.c. amplification. It was first

established by repeated injections of 2.5% methane in nitrogen that the d.c. measurement of emission from the plasma was unaffected by modulation at frequencies over 1 KHz. The two detection systems could therefore be compared directly using a modulated plasma. The signal : noise ratios for a mixture of 0.46% ethane, 0.76% propane and 0.43% n-butane in nitrogen were measured over a range of modulation frequencies using phase-sensitive a.c. detection. The results are shown in Figure II,1. A modulation frequency of 2.5 KHz was therefore used. The signal : noise ratio for all the gases was found to increase linearly with increase in the degree of modulation, as shown in Figure II,2, and the maximum degree of modulation (ca. 75%) was used. Some comparative results obtained under these conditions are shown in Table II,2. a.c. phase-sensitive detection of the modulated plasma was on average a factor of 5.8 more sensitive than direct d.c. detection.

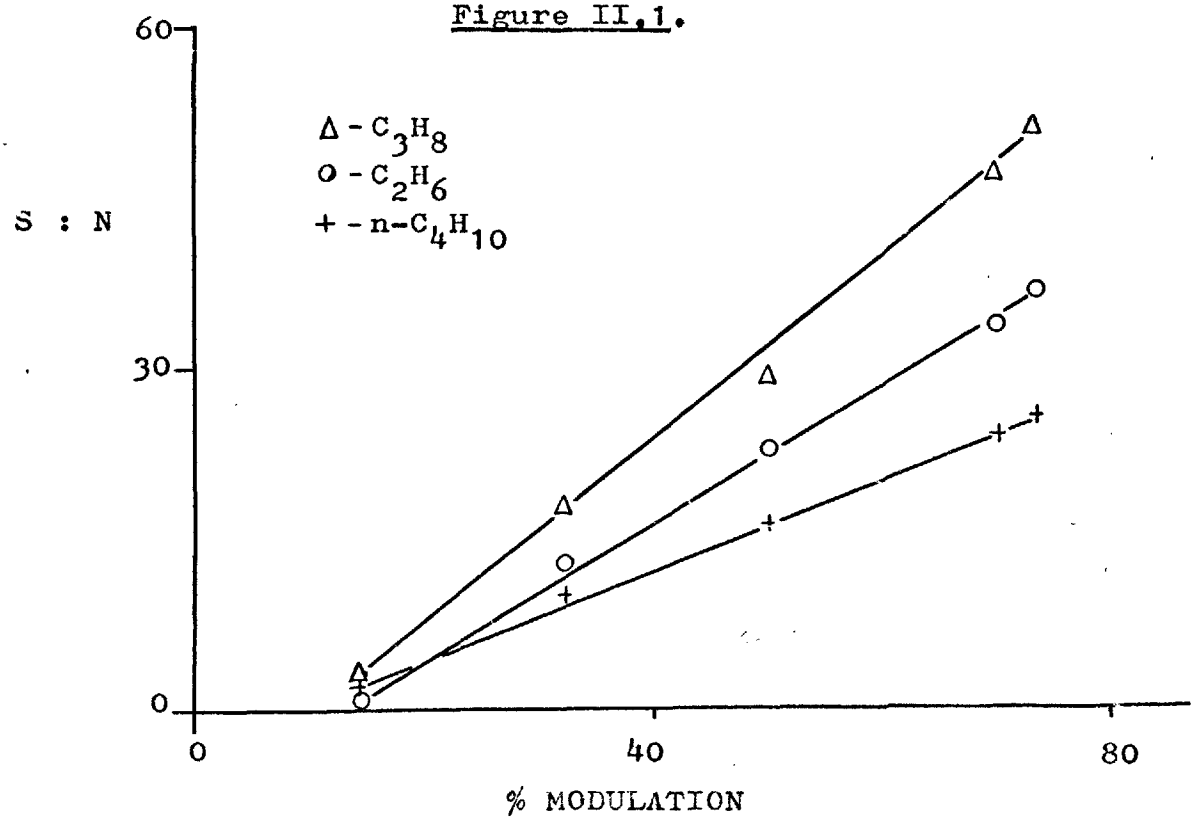
Table II,2

Compound	Limit of Detection (g carbon s^{-1} x 10^{-10})	
	d.c. Amplifier	a.c. phase sensitive detection
C_2H_6	2.40	0.39
C_3H_8	2.36	0.40
$n\text{-}C_4H_{10}$	2.32	0.41



VARIATION OF S : N WITH MODULATION FREQUENCY

Figure II,1.



VARIATION OF S : N WITH % MODULATION

Figure II,2

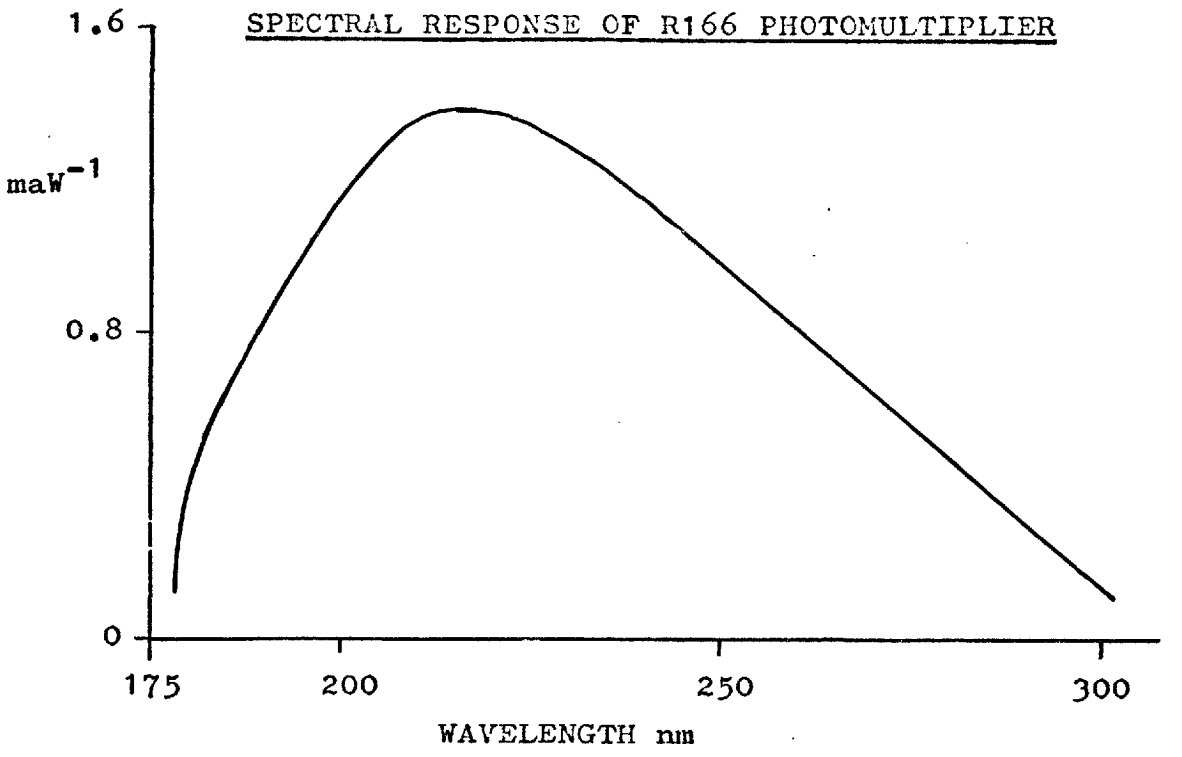
IV. Non-selective Detection of Organic Compounds.

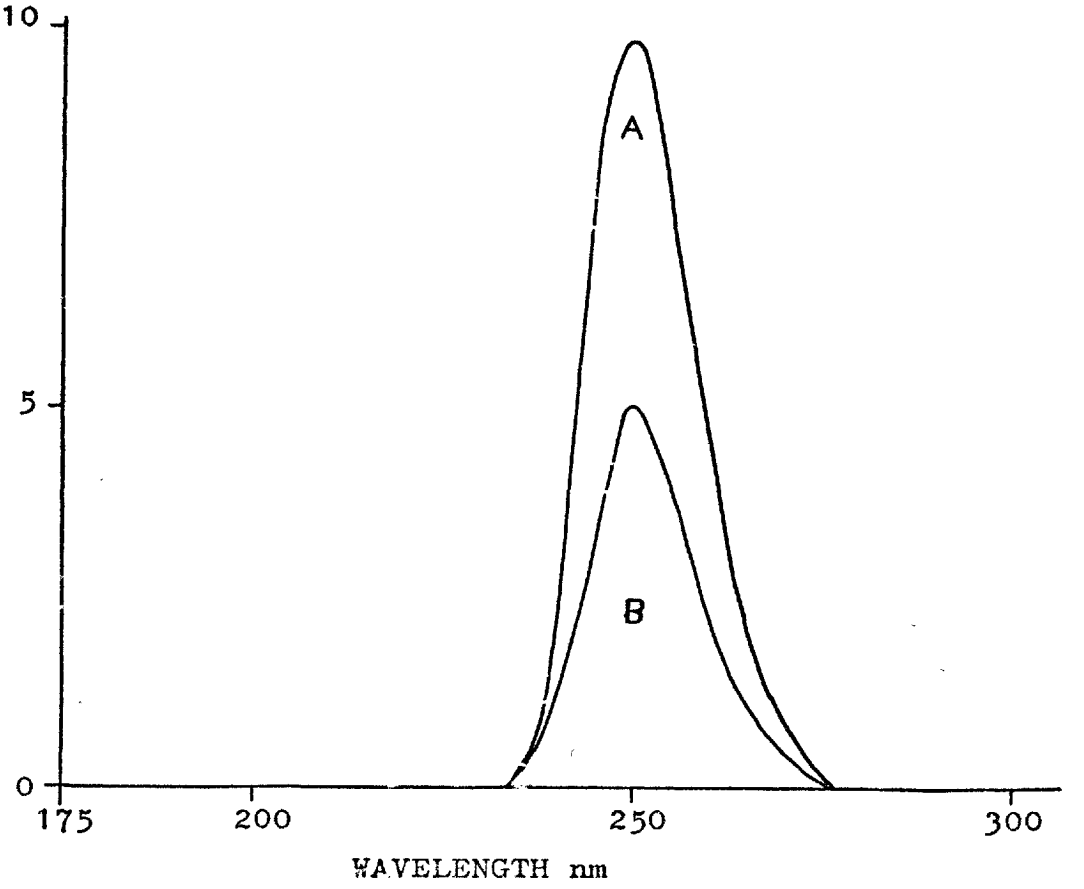
One possible limitation on the sensitivity of the emissive detector system is the comparative low level of radiation reaching the photomultiplier through the monochromator. The emission from a microwave-excited plasma was therefore monitored directly using a solar blind photomultiplier (Hamamatsu TV Company Ltd., Japan, HTV R166) in order to determine whether a significant gain in sensitivity was possible. The spectral response of this photomultiplier is shown in Figure II,3. A photomultiplier with very low response to visible light was required in order to avoid problems of high background and rapid deterioration of the photomultiplier. Even with this photomultiplier it was necessary to reduce the viewing area to ca. 0.8 mm^2 by means of a light shield.

The photomultiplier, used in conjunction with the d.c. amplifier, was mounted on the opposite side of the plasma to the Beckmann DU monochromator system (B) used previously, as shown in Figure II,5, so that both detector systems could be used to record emissions simultaneously. This arrangement had the advantage that the responses of the two systems could be compared directly without the need to calibrate the samples used. Both photomultipliers were supplied at 1 KV from the same power supply.

The monochromator (B) was set to monitor atomic carbon emission at 247.9 nm and the linearity of response of

Figure II,3

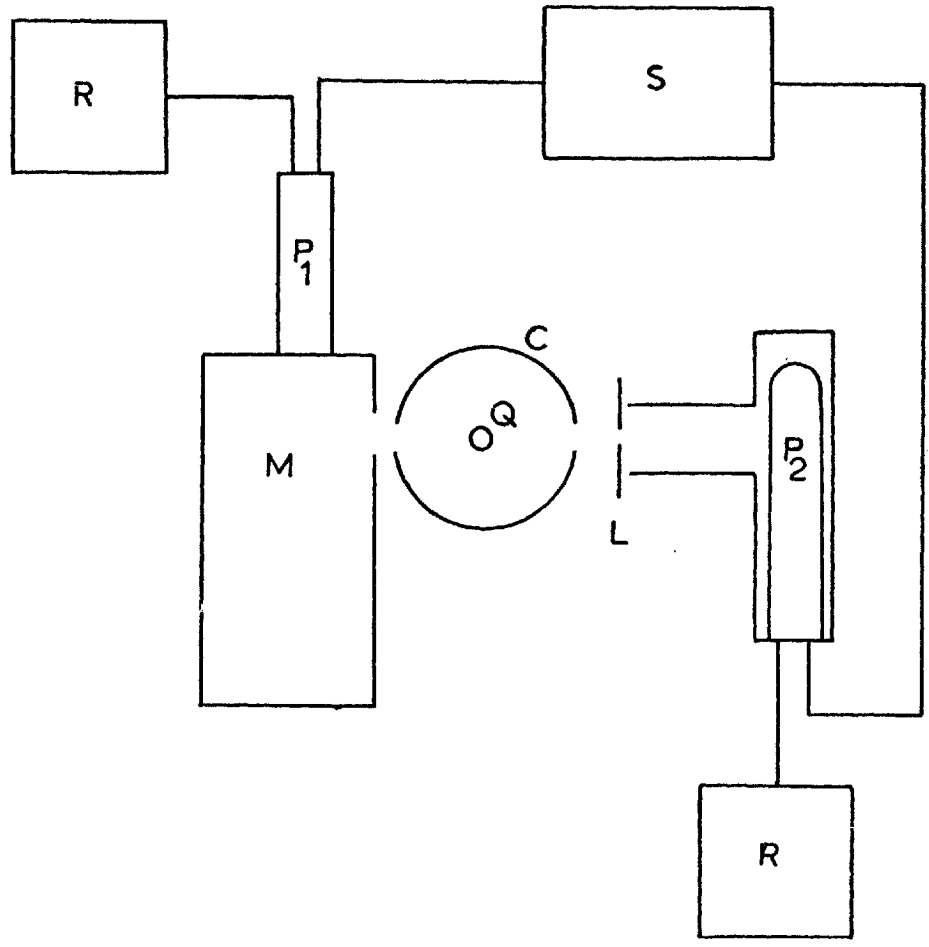




(A) SPECTRAL RESPONSE OF R166 PHOTOMULTIPLIER AND FILTER

(B) SPECTRAL BAND-PASS OF FILTER

Figure II,4



R - read-out
M - monochromator
S - power supply
C - cavity
P_1 - 9601B photomultiplier
P_2 - R166 photomultiplier
L - light shield
Q - quartz tubing

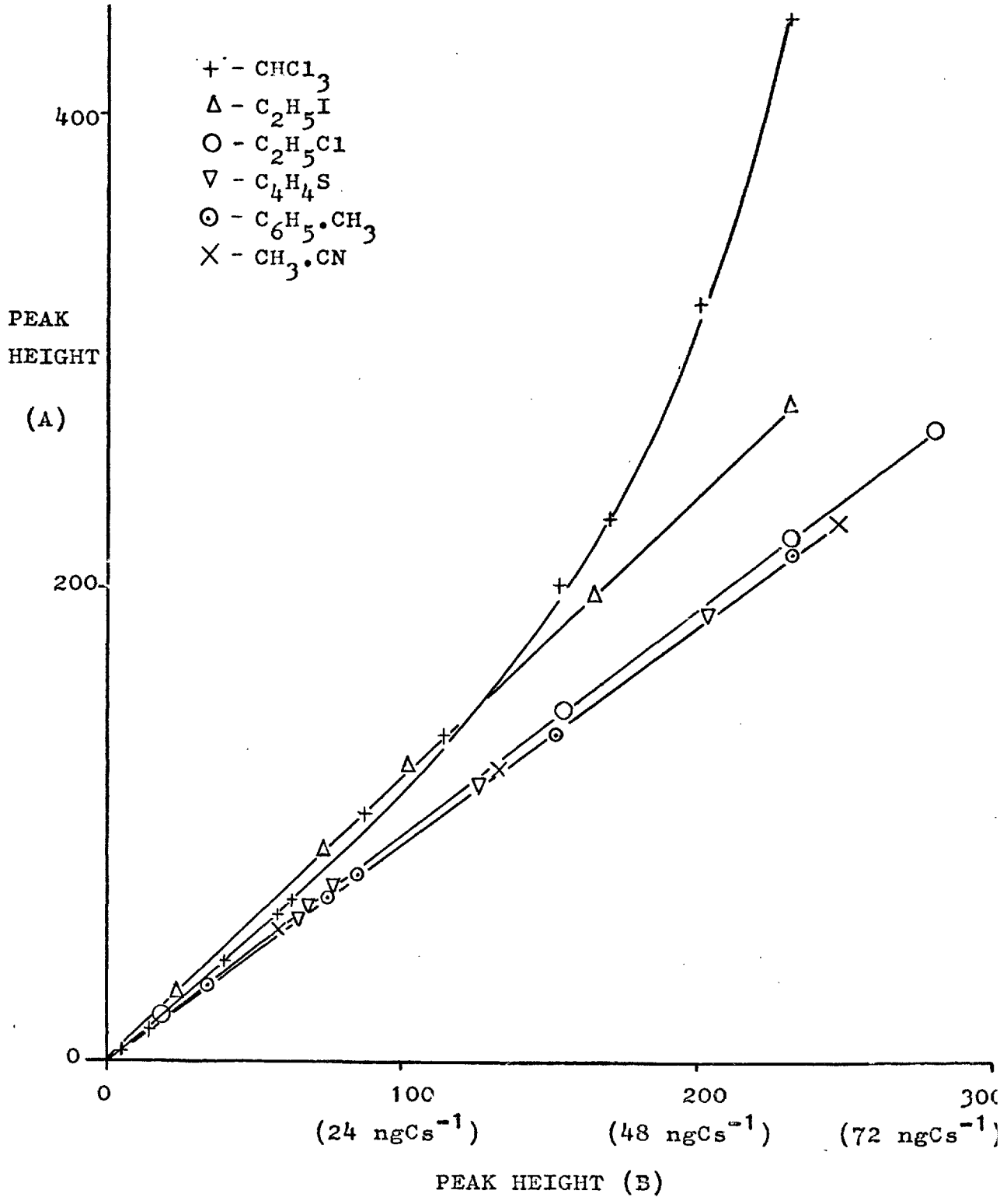
DOUBLE DETECTOR ARRANGEMENT (from above)

Figure II.5

the direct-viewing system (A) to a range of organic compounds was measured by injecting small quantities (from ca. 10^{-8} g to 10^{-5} g) of each compound onto Column C at 150°c. The emission peaks were recorded simultaneously on both detector systems and a graph of peak height on A against peak height on B was plotted (Figure II,6). The response of system B at 247.9 nm to all the compounds used had previously been found to be linear and proportional to concentration. Therefore, a linear plot in Figure II,5 shows that the response of system A was also linear. In addition, as the sensitivities in g carbon s^{-1} of all the compounds on system B at 247.9 nm were the same (within ± 4%), the abscissa can be represented approximately in ng carbon s^{-1} as shown. Therefore, similar gradients indicate similar sensitivities in g carbon s^{-1} on system A.

The results were as might be expected. The sensitivities of the response of system A to most compounds were similar, indicating that atomic carbon was the major emission observed. The exceptions were ethyl iodide, which also gave atomic iodine emission at 206.2 nm (linear) and chloroform with a major component from Cl_2 emission at 256 nm (non-linear). Ethyl chloride also showed a slightly increased gradient.

The sensitivity of the direct-viewing system was measured by determining its response to solutions of toluene in the normal way. A limit of detection of 8×10^{-12}g carbon s^{-1} was obtained. Its response to 5μl



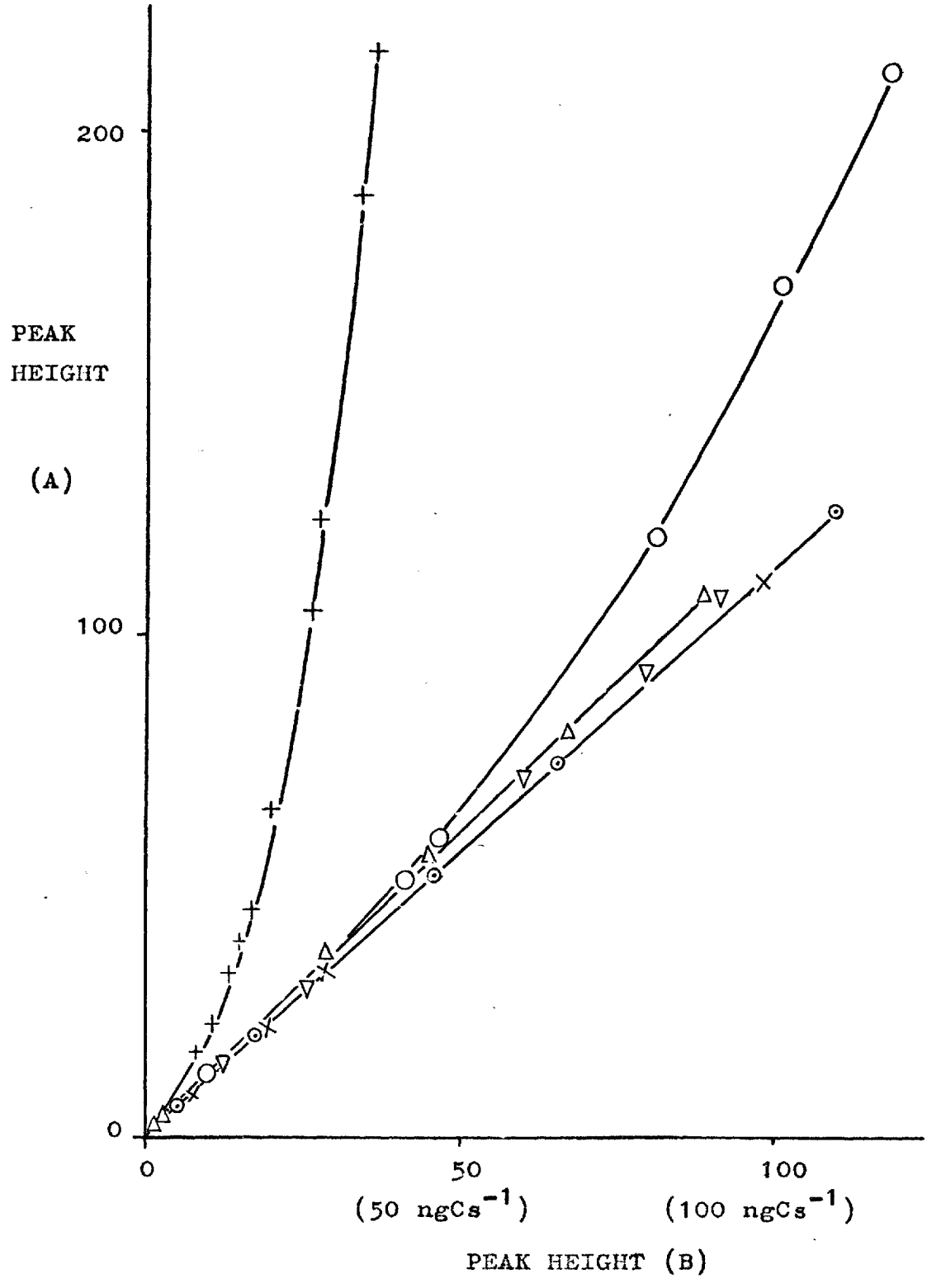
SIMULTANEOUS RESPONSES OF THE R166 PHOTOMULTIPLIER DETECTOR (A) AND THE EMISSIVE DETECTOR AT 247.9 nm (B)

Figure II,6

of 1% CO was 2.7 times that to 5 μl of pure nitrogen and 8.7 times that to pure oxygen (negative peak) as compared with ratios of 18.5 and 12.3 respectively on system B.

In order to reduce response to emissions other than that at 247.9 nm an interference filter with a maximum transmittance (10%) at 250 nm and a band-pass of 25 nm was fitted over the window of the solar-blind photomultiplier. The spectral band-pass of the filter and the response of the combined filter and photomultiplier (as calculated from the literature) are shown in Figure II,4. A series of measurements similar to those described for system A was carried out with the filter system. The results are shown in Figure II,7. The overall effect was little different; the deviations of chloroform and ethyl chloride were more marked while that of ethyl iodide was considerably reduced. The limit of detection for toluene was 9×10^{-12}g carbon s^{-1}. The detector responded equally to 1% CO and pure nitrogen. Water also gave an increased negative interference.

For the non-selective determination of carbon-containing compounds, direct monitoring of plasma emission with a solar-blind photomultiplier was found to provide a viable alternative to the use of a monochromator set to monitor atomic carbon emission at 247.9 nm. Its response to non-chlorine-containing compounds was linear over a similar range (ca. 10^3) and was more sensitive but somewhat less selective. The use of a broad band-pass filter was found to offer no advantages.



Symbols as for Figure II,6

SIMULTANEOUS RESPONSES OF THE R166 PHOTOMULTIPLIER AND FILTER DETECTOR (A) AND THE EMISSIVE DETECTOR AT 247.9 nm (B)

Figure II,7

V. The 'Open' Plasma Detector.

An alternative form of microwave-excited plasma detector, with an argon plasma extending above the top of a 2-mm quartz tube, has been used in other studies in this laboratory (205). It has the advantage that no carbon deposition or devitrification of the tubing is possible. A discharge under these conditions could only be maintained with the more efficient $\frac{1}{4}$-wave Evenson-type cavity which created an intense localized field immediately above the top of the tube. Further, it was necessary to use a relatively high carrier gas flow rate (ca. 120 lh^{-1}) which is not generally compatible with gas-chromatographic applications. Hence an auxiliary argon flow was mixed with the main chromatographic flow at the base of the detector tube.

The characteristics of this system were studied using the D292 monochromator set to monitor atomic carbon emission at 247.9 nm and 1 μl injections of a 7.8% solution of carbon disulphide in butanol. Carbon disulphide was eluted after 0.67 min on Column S at 175°c. The effects of variations of microwave power and total flow rate were similar to those on the enclosed plasma detector. However, presumably because of the high flow rate used, the limit of detection for carbon disulphide was only 4.0×10^{-9} g carbon s^{-1}, a factor of ca. 50 less good than the original system. The linear range was still greater than 10^3 and extended to samples of over 1 mg. The plasma was not extinguished by solvents.

Allied to its freedom from the problems of carbonization this form of the microwave-excited plasma detector proved robust but relatively insensitive.

CHAPTER III

USE OF THE MICROWAVE-EXCITED EMISSIVE DETECTOR FOR THE QUANTITATIVE MEASUREMENT OF INTER-ELEMENT RATIOS.

Introduction

The wide range of selective detectors described for use in gas chromatography has been outlined in the Introduction (pages 9-53). In general, these detectors have been used to provide more sensitive detection for particular types of compounds, to enable the determination of such compounds in the presence of high background and to obtain qualitative information on hetero-atoms present in the chromatographic eluates. Very few attempts have been made to determine the quantitative ratios between the elements present in an eluate despite the fact that this information would enable a much more conclusive identification of a compound to be made. Many detectors highly suited to sensitive, selective detection are unsuitable for this purpose. Most can only be used to determine one element at a time and some also have an unpredictable response or enhance the response of more than one element (eg. electron-capture detectors).

In principle, emissive detectors are best suited to the suimultaneous determination of several elements; ideally, the emission at each selected wavelength should be structure independent and characteristic of the element in question. However, in practice, the only determination of emission ratios reported is that of Bowman and Beroza (148). They used a flame photometric detector to view the chemiluminescent emission from HPO and S_2 species above a hydrogen-rich hydrogen / air flame and measured the ratio of P : S emission. The ratios were found to be in the range 5.2 to 6.0 for PS compounds, 2.8 to 3.3 for PS_2 compounds and from 1.7 to 2.3 for PS_3 compounds. Sulphur was found to interfere with the phosphorus emission and the ratio showed some dependence on compound structure.

Although the microwave-excited emissive detector is potentially well suited to this type of investigation no studies on atomic ratio determinations (with this form of detector) have been reported. Therefore, a double detector system was set up and used to measure the ratios of chlorine, bromine, iodine, phosphorus and sulphur emission to carbon emission for a range of simple compounds. The factors which affect these ratios were also measured and the potential of this technique for the determination of inter-element ratios was assessed.

Apparatus

The experimental arrangement used was similar to that shown in Figure II,5 (page 113). The microwave system was modified by the use of a narrow, water-cooled $\frac{3}{4}$-wave microwave cavity. Two apertures on opposite sides of the cavity were used for viewing the plasma in conjunction with a Beckmann DU monochromator fitted with a 9601B photomultiplier (EMI Electronics Ltd) and a low resolution monochromator (Rank Precision Industries Ltd. Type D292) fitted with a R166 solar-blind photomultiplier (Hamamatsu TV Co. Ltd., Japan). Both photomultiplier tubes were operated from the same high voltage power supply (Brandenburg PM 2500R) at a potential of 1 KV. During later work on S:C and Br:C ratios, the D292 monochromator was replaced by a Hilger and Watts type D330 monochromator fitted with a 6256S photomultiplier which was operated with a Brandenburg 472R high voltage power supply at a potential of 1.25 KV. The responses of the two photomultipliers were recorded simultaneously on Servoscribe chart recorders using two independent electronic read-out systems.

A 0.7 m column of 3-mm stainless steel tubing packed with Chromosorb 101 was used throughout this work. Injections were made directly onto the column and argon was used as the carrier gas.

Procedure

In the investigation of each group of compounds one

of the monochromators was set to the emission wavelength of atomic carbon (247.9 nm) and adjusted for maximum signal using repeated injections of butane. The other monochromator was set to a suitable wavelength to record the emission characteristic of the particular hetero-atom (eg. 206.2 nm for iodine) and optimised using a compound with a relatively high proportion of that atom (eg. methyl iodide).

The two detection systems responded simultaneously to an eluate passing through the plasma, and the ratio of the responses was taken as the ratio (R) of the peak heights (P) on the two chart recorders (eg. P_I at 206.2 nm and P_C at 247.9 nm). Peak heights are in arbitrary units as it was only the variation of R with different compounds which was studied. The effect of the variation of microwave power on R for each group of compounds was investigated and the optimum power selected.

The variation of R with concentration was measured by injecting a series of small quantities (from ca. 10^{-8}g to 10^{-5}g) of each compound. The exact quantity injected was not important because previous studies had shown that the atomic carbon emission was linear with respect to concentration for all the compounds investigated over the concentration range used; hence, P_C was taken as a measure of the concentration of each compound present.

Results

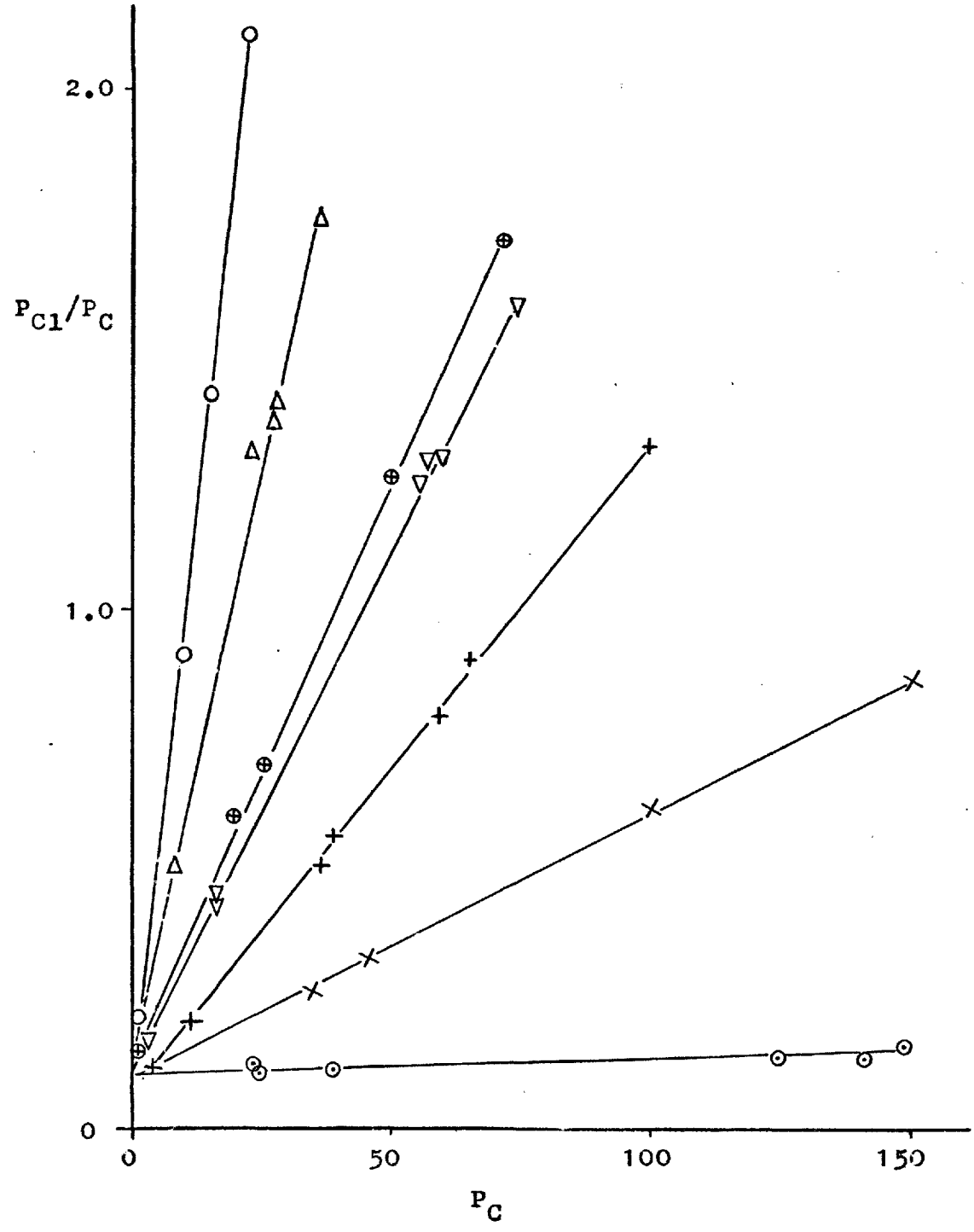
1) Chlorine / Carbon Ratio

The D292 monochromator (slit width 0.5 mm) was set to 247.9 nm and the Beckmann monchromator (slit width 0.1 mm) to 256 nm (Cl_2 emission band). An oven temperature of 150°c and a carrier gas flow rate of 2.07 lh^{-1} were used. The effect of microwave power on R (P_{Cl}/P_C) was studied using chloroform and trichloroethylene. The ratio of the ratios $R_{CHCl_3}/R_{C_2HCl_3}$ was found to be constant above ca. 50 W, and a microwave power of 70 W was used for further studies.

The following compounds were studied (retention times in minutes are shown after each compound) carbon tetrachloride (2.21), chloroform (1.77), dichloromethane (0.92), trichloroethylene (2.87), tetrachloroethylene (6.42), ethyl chloride (0.50), chlorobenzene (10.17) and 1:2-dichloroethane (2.64).

All the compounds showed a linear variation when R was plotted against P_C and all exhibited approximately the same intercept (Ro) on the R axis, equivalent to R for a compound containing no chlorine (Figure III,1).

It was also found that the plot of log (dR/dP_C) (ie. log of the gradient) against log r, where r is the empirical formula ratio of chlorine to carbon for each compound (eg. r = 3 for $CHCl_3$) is linear with a gradient of 2.08. Alternatively, a plot of log $R-R_o$ for all compounds, at any one value of P_C, against log r gives



VARIATION OF P_{Cl}/P_C WITH P_C

Figure III.1

the same gradient (Figure III,2).

The above results can be explained from the fact that the chlorine emission is a Cl_2 band emission. Let P_x be the peak height due to emission species x and (x) be the instantaneous concentration of x in the plasma.

If P_x is proportional to (x) then :

$$P_C = K_C\ (C)$$

and $$P_{Cl_2} = K_{Cl}\ (Cl_2)$$

Now if : $$(Cl_2) = K_1\ (Cl)^2$$

then $$P_{Cl} = K_{Cl}K_1\ (Cl)^2 + P_o$$

Where P_{Cl} is the total emission at 256 nm and P_o is the emission at that wavelength due to non-chlorine-containing species.

and
$$R = \frac{P_{Cl}}{P_C}$$
$$= \frac{K_{Cl}K_1}{K_C}\ \frac{(Cl)^2}{(C)} + \frac{P_o}{P_C}$$
$$= K_2\ \frac{(Cl)^2}{(C)} + R_o$$

For a compound of the type CCl_r, r is equal to the ratio of total chlorine to total carbon (where the totals are expressed in gram-atoms). If (C) $\propto$ total carbon and (Cl) $\propto$ total chlorine,

then
$$r = \frac{\text{total chlorine}}{\text{total carbon}}$$
$$= K_4\ \frac{(Cl)}{(C)}$$

and
$$R = R_o + K_5 r^2 (C)$$
$$= R_o + K_6 r^2 P_C$$

Therefore, for any compound of constant r

$$R = R_o + K_7 P_C$$

and for all compounds

$$\frac{dR}{dP_C} = K_6 r^2 + \frac{dR_o}{dP_C}$$

R_o was found experimentally to be independent of P_C, therefore $\frac{dR_o}{dP_C} = 0$

and $$\log \left[\frac{dR}{dP_C}\right] = 2 \log r + \log K_6$$

Furthermore, for all compounds, at any one value of P_C

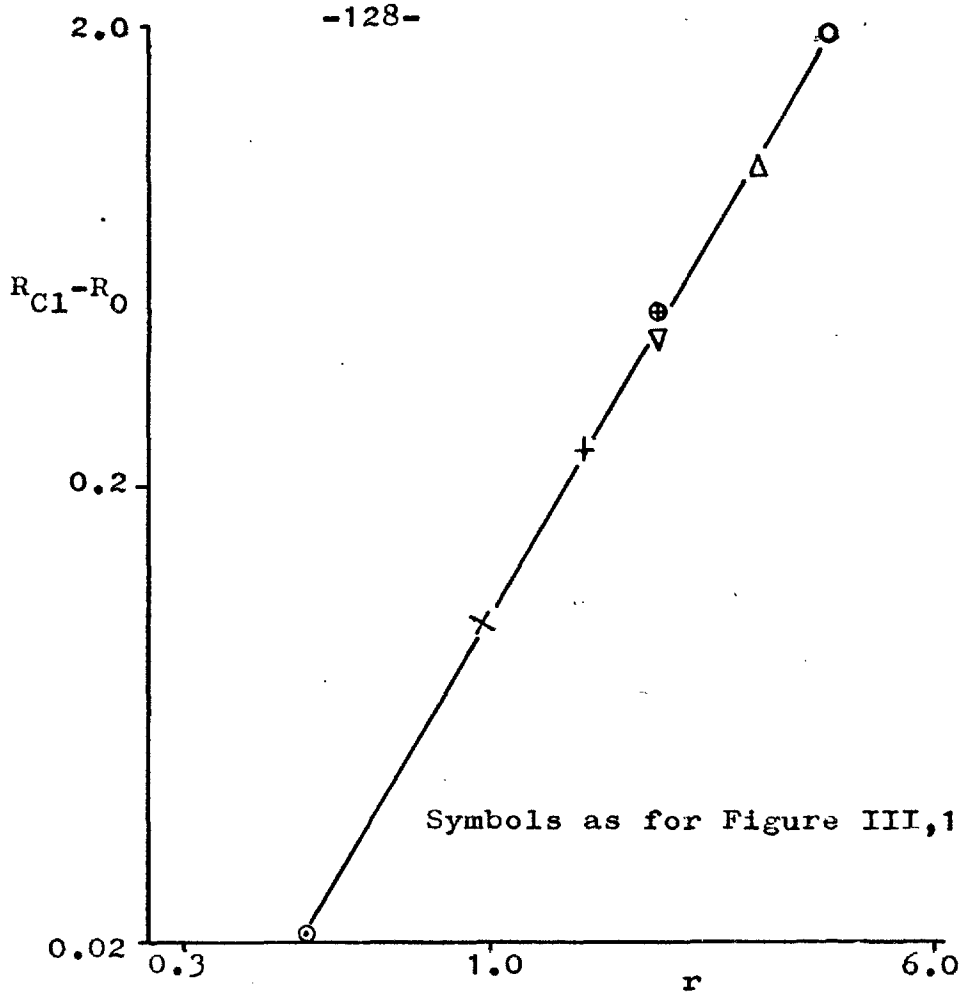
$$R = R_o + K_8 r^2$$

and $$\log \left[R-R_o\right] = 2 \log r + \log K_8$$

Hence a plot of R versus P_C for any compound should be linear and plots of $\log\left[\frac{dR}{dP_C}\right]$ and $\log\left[R-R_o\right]$, at constant P_C, against log r should be linear with gradients of 2.

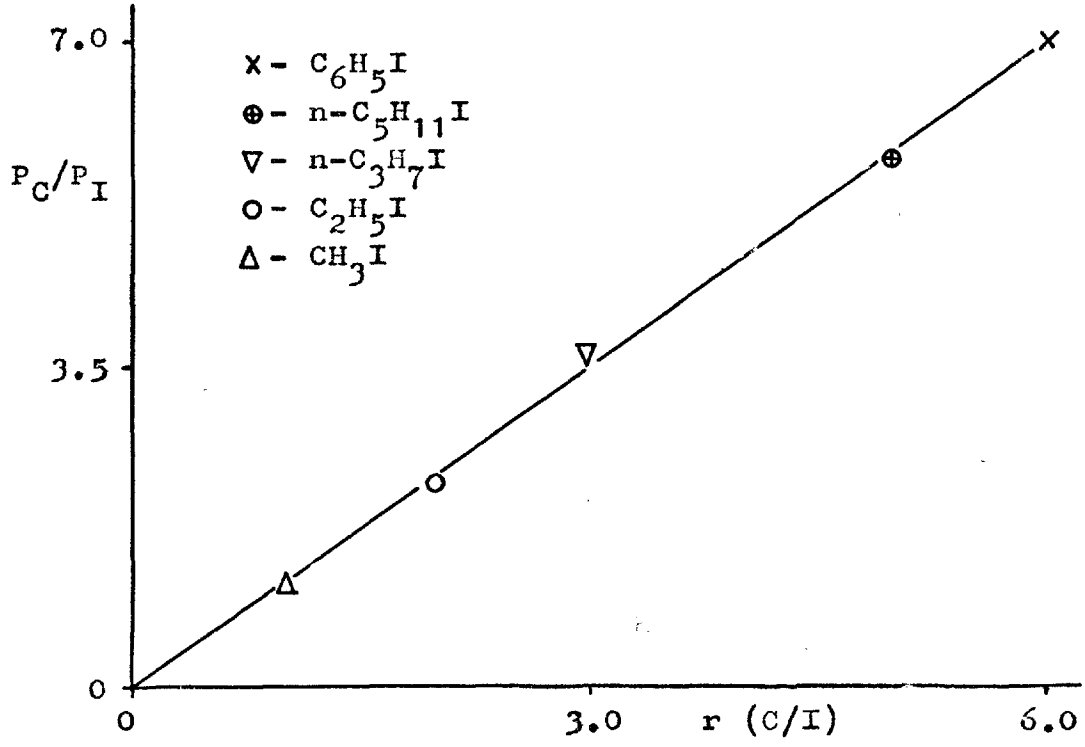
2) Iodine / Carbon Ratio

The Beckmann monochromator was set to monitor the iodine atomic line at 206.2 nm. A temperature of 160°c and a carrier gas flow rate of 3.8 lh^{-1} were used. The ratios of iodine to carbon emission for ethyl iodide and methyl iodide were found to be constant at microwave powers greater than 60 W, and a power of 70 W was again used. The following compounds were studied : methyl iodide (0.38), ethyl iodide (0.72), n-propyl iodide



LOG-LOG PLOT OF $(R_{Cl}-R_O)$ AT CONSTANT P_C AGAINST r

Figure III.2



VARIATION OF P_C/P_I WITH r (C/I)

Figure III.3

(1.35), amyl iodide (6.20) and iodobenzene (15.0). For all these compounds the ratio P_C/P_I was found to be independent of concentration and carrier gas flow rate. The ratio of peak heights P_C/P_I plotted against the theoretical carbon to iodine ratio (r) is shown in Figure III,3. The plot is linear with a maximum deviation from linearity of 4%. If P_I (I), then $\frac{P_C}{P_I} \propto \frac{(C)}{(I)} \propto r$ for a compound of the type C_rI, and a linear plot of P_C/P_I against r would be expected

3) Phosphorus / Carbon Ratio

The major phosphorus emission was the atomic line at 253.5 nm and hence the Beckmann monochromator was set to monitor this wavelength.

As before, 70 W microwave power was found to be optimum. Unlike in the previous studies, one set of conditions could not be established to obtain convenient retention times for all the compounds studied. The following conditions were used : temperature 150°c and flow rate 3.3 lh^{-1} for trimethylphosphite (0.66), triethylphosphite (0.90) and trimethylphosphate (0.95); temperature 230°c and flow rate 2.7 lh^{-1} for triethylphosphate (0.80) and tributylphosphate (1.70); and temperature 270°c and flow rate 2.4 lh^{-1} for triphenylphosphate (6.0).

For each of these compounds the ratio of the peak heights for phosphorus and carbon emissions was found to be independent of concentration and carrier gas flow rate. The graph of P_P/P_C against the theoretical ratio

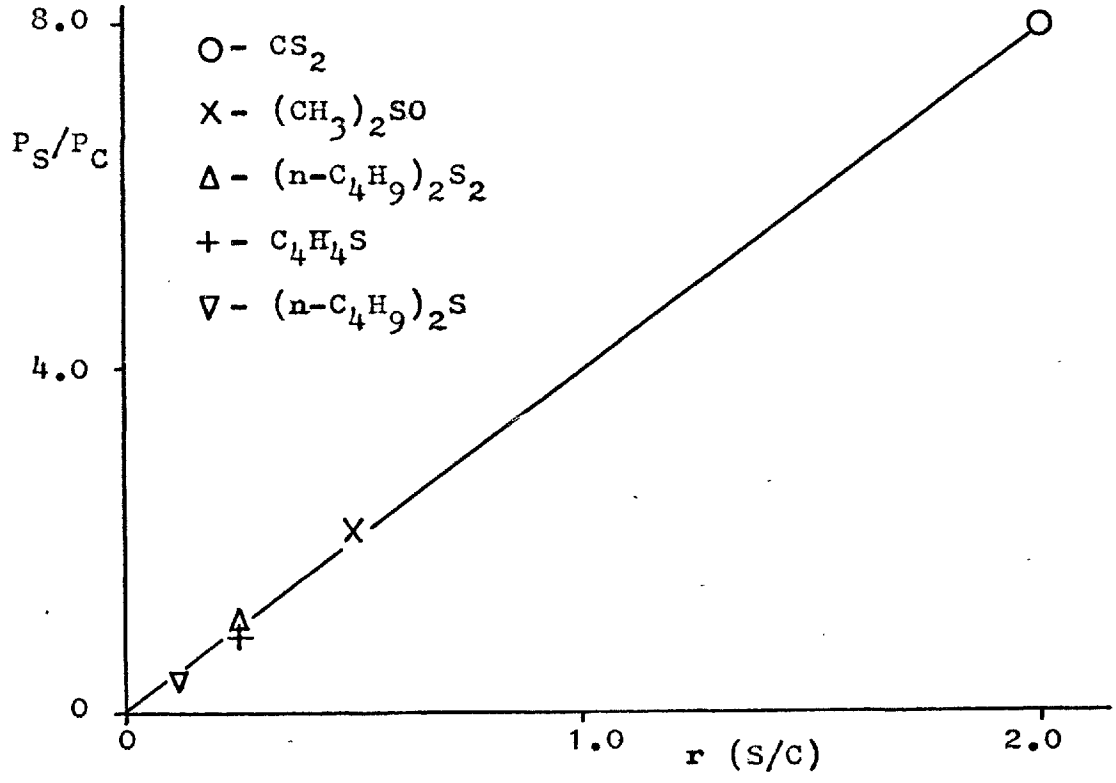
is shown in Figure III,4. The maximum deviation from linearity is 8%.

4) Sulphur / Carbon Ratio

The D330 monochromator was set to the atomic sulphur line at 182.0 nm and was puged with argon. The Beckmann monochromator was set to 247.9 nm. In this instance 50 W microwave power was found to be optimum because the sensitivity of the atomic sulphur emission decreased rapidly at higher microwave powers. A flow rate of 3.3 lh^{-1} and an oven temperature of 200°c were used. The compounds studied were carbon disulphide (0.48), dimethylsulphoxide (2.92), thiophen (0.65), dibutylsulphide (1.33) and dibutyldisulphide (4.50). Again for each of these compounds R (P_S/P_C) was found to be constant over a wide range of concentrations and flow rates. However at high concentrations (ca. 10^{-5}g) the value of R tended to decrease, particularly for compounds with a high carbon content. This was probably due to carbon depositing on the walls of the detector tube which would particularly reduce the sulphur emission in the far ultra-violet region. The graph of P_S/P_C versus the theoretical ratio shows a maximum deviation from linearity of 5% (Figure III,5).

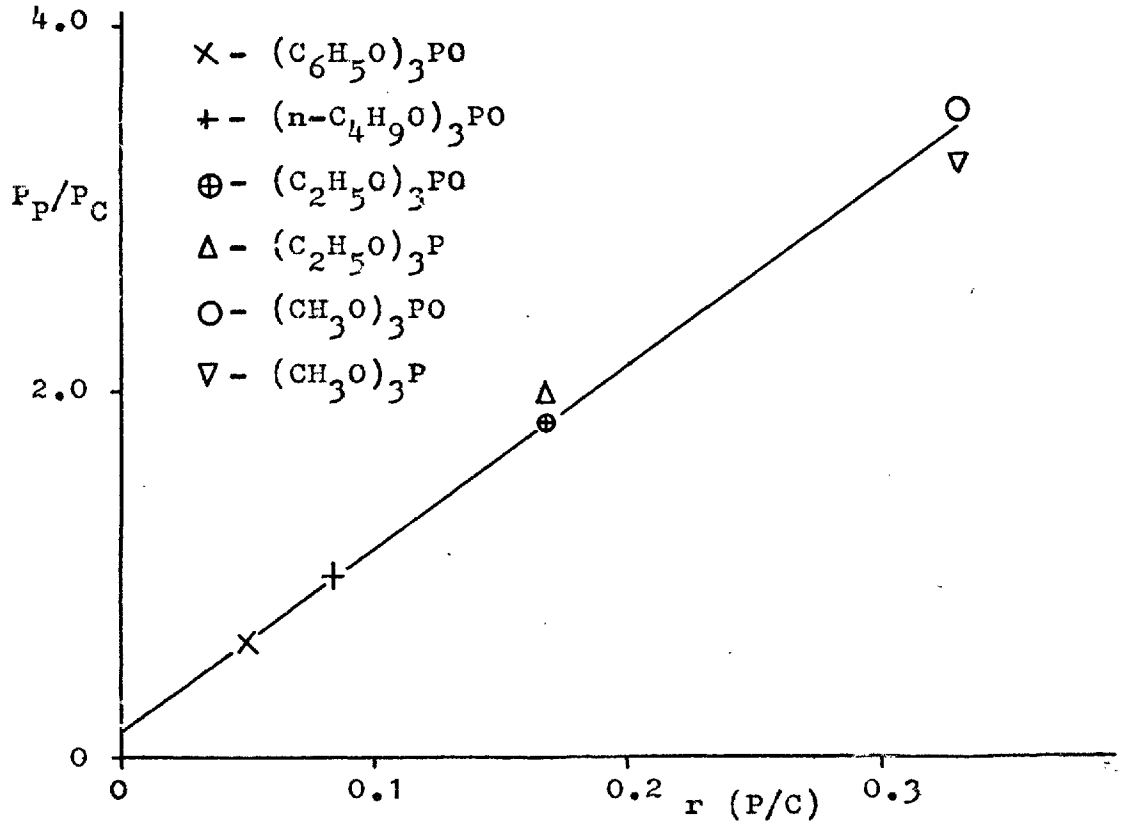
5) Bromine / Carbon Ratio

The D330 monochromator was set to monitor a Br_2 band emission at 292 nm. A microwave power of 70 W was found to be optimum and a column temperature of 170°c and a



VARIATION OF P_S/P_C WITH r (S/C)

Figure III.5



VARIATION OF P_P/P_C WITH r (P/C)

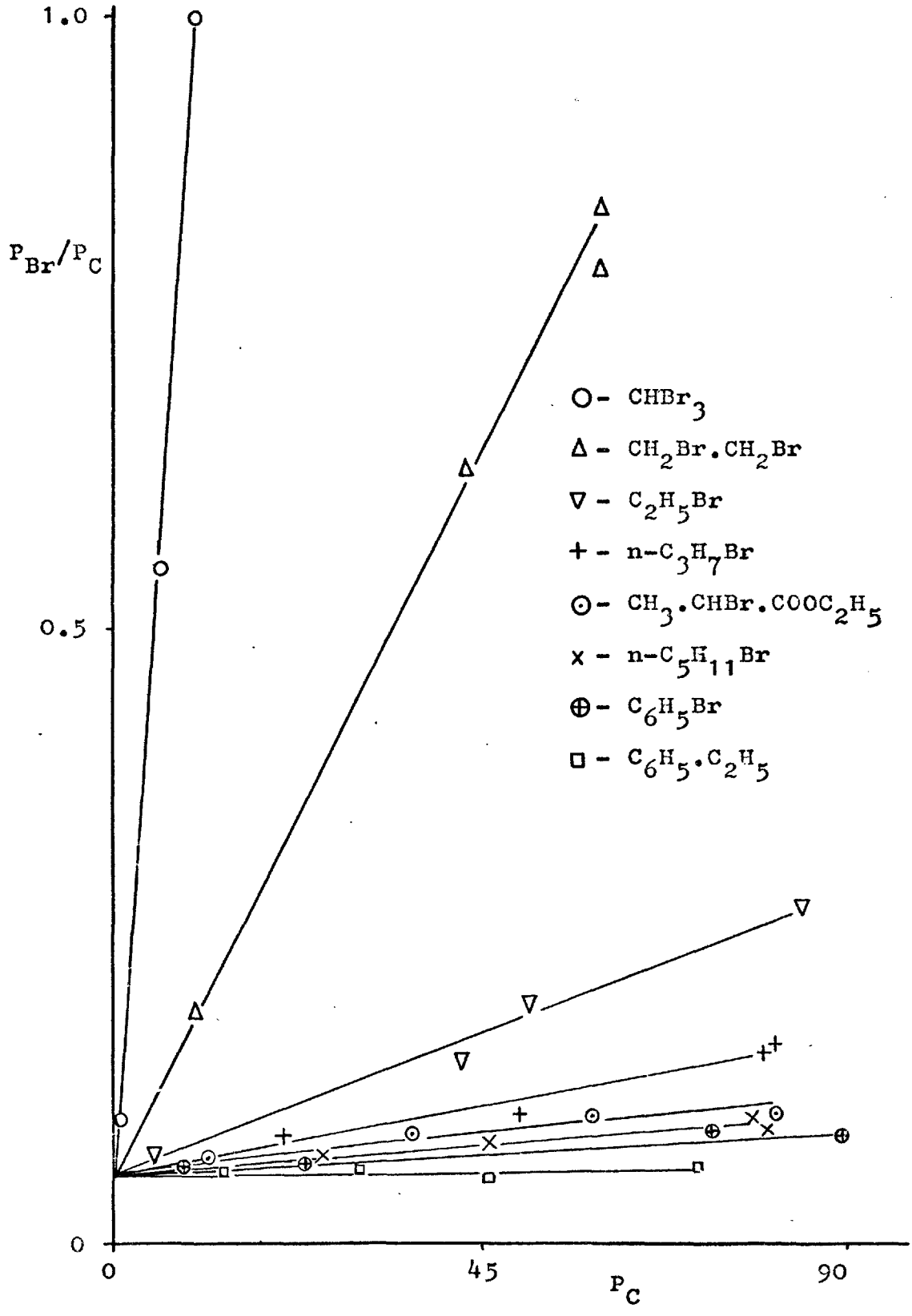
Figure III.4

carrier gas flow rate of 3.3 lh^{-1} were used. The compounds studied were bromoform (5.00), bromobenzene (6.45), ethyl-2-bromopropionate (6.75) dibromoethane (2.57), n-amyl bromide (2.30), ethyl bromide (0.55) and n-propyl bromide (1.04).

The results were similar to those obtained for chlorine. All the compounds showed a linear variation when R was plotted against P_C with approximately the same intercept on the R axis (Figure III,6). When the logs of the gradients of these slopes were plotted against the logs of the theoretical bromine / carbon ratios a straight line with a gradient of 1.96 was obtained (Figure III,7).

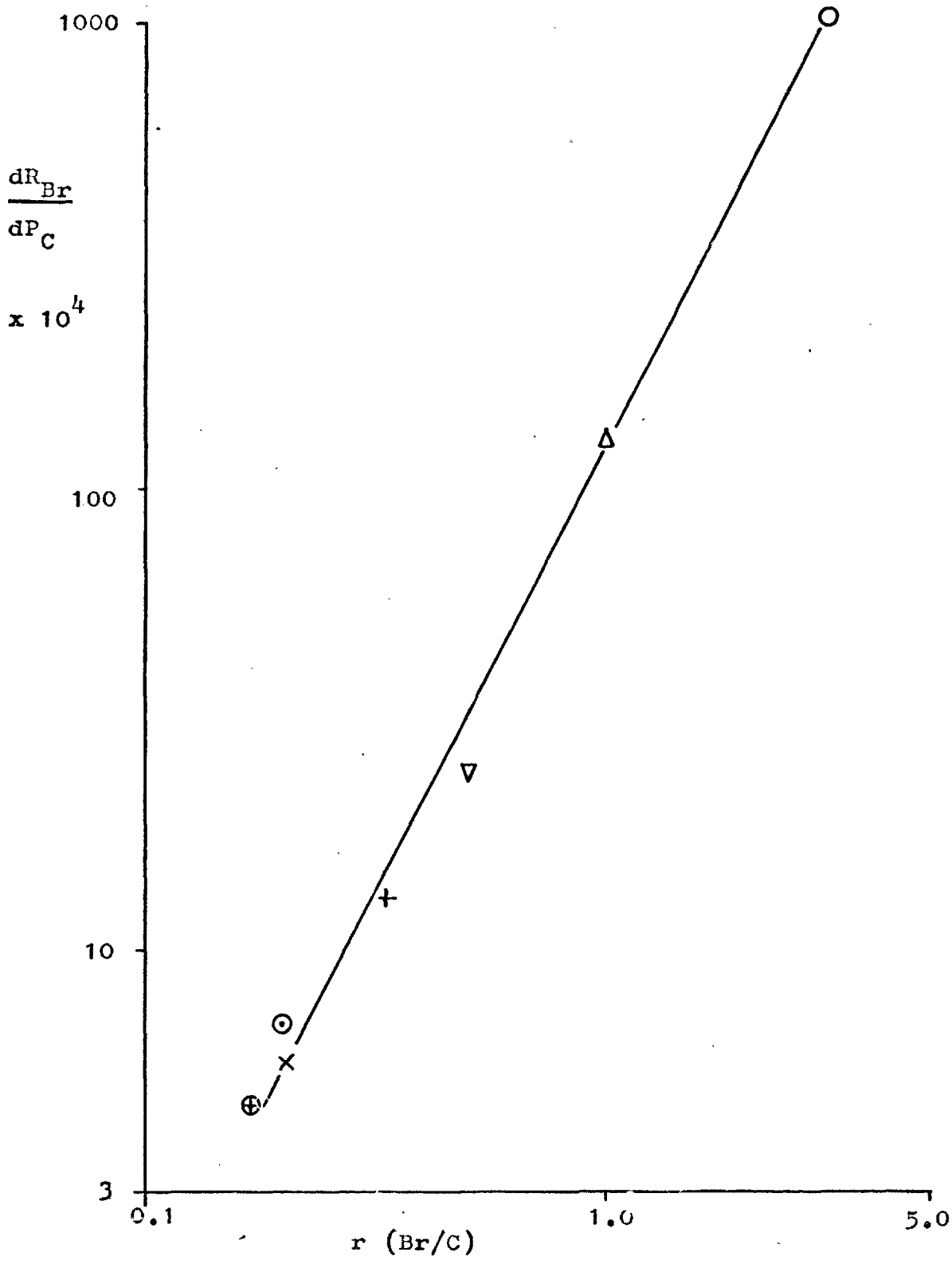
Conclusions

The present study has shown that for the limited range of sulphur, iodine, and phosphorus compounds investigated, the simple expedient of simultaneously monitoring emission from two atomic lines could be used to determine the quantitative relationship between the number of hetero-atoms and the number of carbon atoms in a compound. In each instance the measured ratio was found to be independent of carrier gas flow rate and concentration. Hence, using these atomic emissions it would be unnecessary to know the exact concentration of a compound under examination in order to determine the inter-element ratios. Nor would it be essential to obtain a good peak shape as the simultaneous responses of the two detectors at any point during the passage



VARIATION OF P_{Br}/P_C WITH P_C

Figure III.6



Symbols as for Figure III,7

LOG-LOG PLOT OF dR_{Br}/dP_C AGAINST r (Br/C)

Figure III,7

of an eluate through the plasma could be used to determine the ratio of the emissions.

The results obtained for chlorine and bromine containing compounds could be satisfactorily explained on the basis that the emitting species were diatomic (Cl_2 and Br_2). The ratios of chlorine or bromine emission to atomic carbon emission were both carrier gas flow rate and concentration dependent. A series of peak ratios for a range of concentrations of the sample under investigation would therefore be required, together with a standard sample in a similar range, in order to use these emissions for the determination of inter-element ratios.

CHAPTER IV

A NON-SELECTIVE DETECTOR USING THE MEASUREMENT OF REFLECTED MICROWAVE POWER.

Introduction

The considerable volume of work (160-169) on the use of microwave-excited plasmas as detectors in gas chromatography has been exclusively concerned with their capabilities as sources of selective spectral emission. Eluates are detected by the emission they produce when fragmented and excited in the plasma. One disadvantage of this type of system is the difficulty, even with very fast scan monochromators or using several photomultipliers and read-out systems, of detecting and determining all the species eluted from the column with only one sample injection. This may be accomplished by placing a non-destructive, non-selective detector, such as a katharometer, between the column and the plasma. However, this arrangement would increase the amount of apparatus necessary and the dead volume.

For this reason a non-selective detector which could be used simultaneously with the atmospheric pressure emissive detector described previously was developed. The detector responded to nanogram quantities of all the

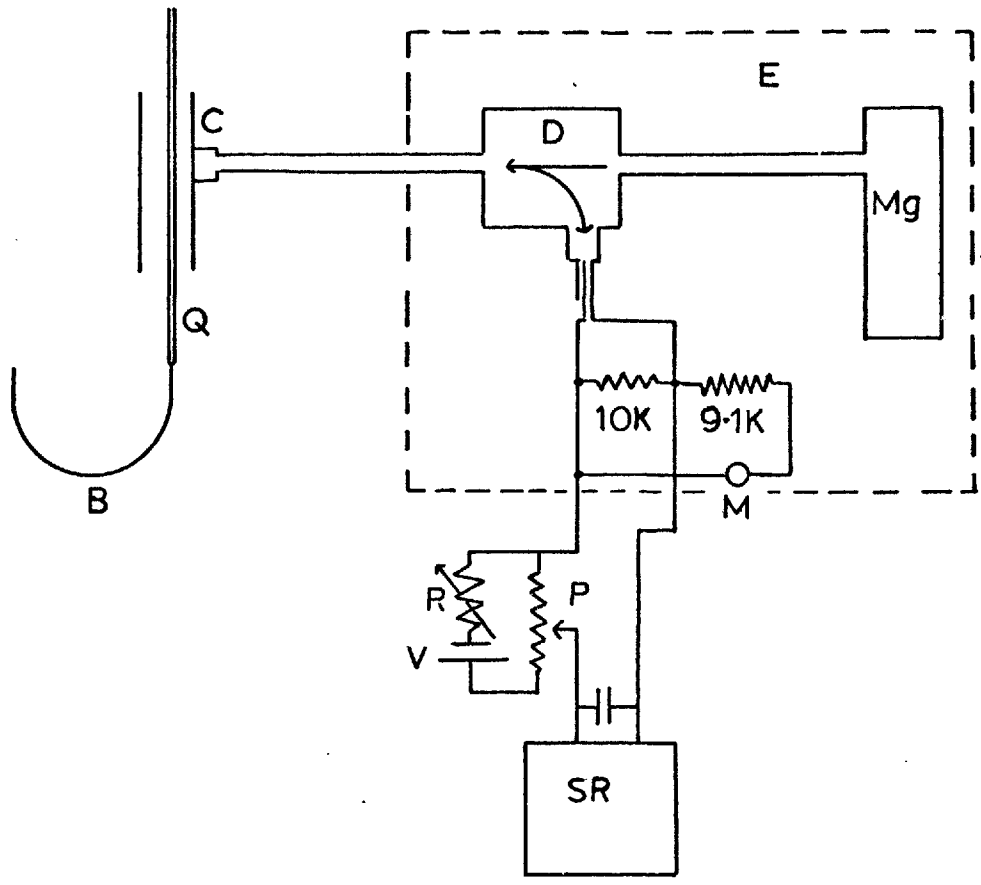
substances tested and required only a simple modification to the reflected power meter associated with the microwave power supply.

Experimental

The microwave-excited plasma system used was essentially the same as that described in Chapter I. Effluent from the gas-chromatographic column passed directly into a plasma maintained in a 1-mm i.d. quartz tube using a narrow, water-cooled, $\frac{3}{4}$-wave cavity. An emissive detector system, consisting of the Beckmann DU monochromator, EMI 9601B photomultiplier and d.c. read-out system, was used to provide a reference response.

An Evans Electroselenium (EEL) model 245 microwave generator was used as the microwave power supply. The method of detection consisted of measuring the changes in the reflected microwave power produced by a chromatographic eluate entering the plasma. The EEL 245 generator is ideally suited in this respect because it contains a built-in reflected power meter and also the magnetron power supply is current stabilised which reduces the background noise. The output of the reflected power meter was connected, via a coaxial cable and a backing-off system to a Servoscribe recorder (Figure IV,1). A damping capacitor (40 μF) was connected across the recorder terminals to decrease the short term noise on the background signal.

With the discharge operating at 90 W of microwave



B - column
Q - quartz tube
C - cavity
D - directional coupler
M - meter
P - potentiometer
R - variable resistance
V - 4.5 Volt battery
SR - servoscribe recorder
E - EEL microwave generator
Mg - magnetron valve

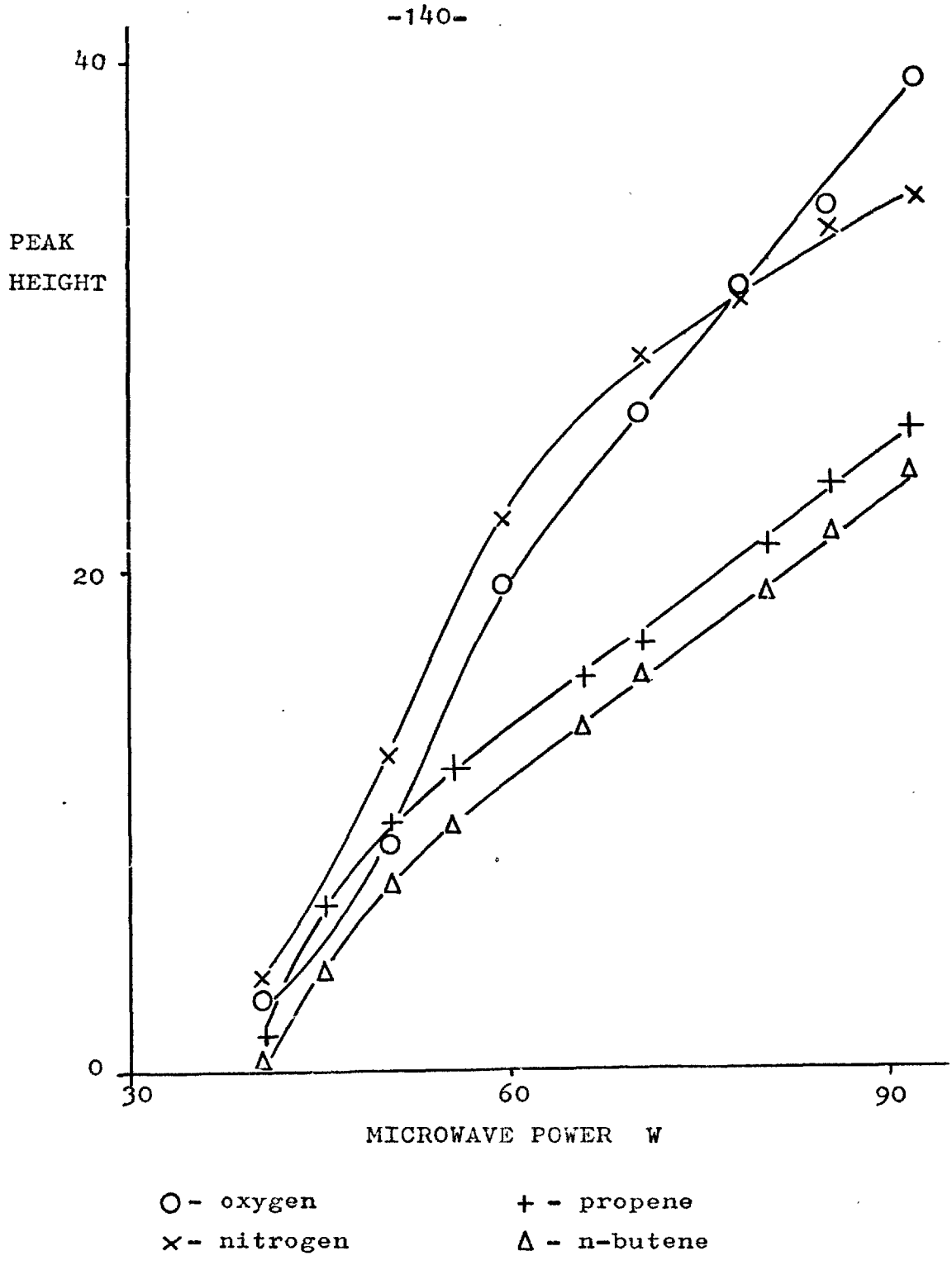
EXPERIMENTAL ARRANGEMENT

Figure IV,1

power a background signal of ca. 200 mV was produced by the reflected power meter. When this voltage was backed-off so that it could be displayed on the 10 mV range of the recorder a baseline with relatively little drift (<5 mV h^{-1}) and a low noise level was obtained. When an eluate passed through the discharge the microwave power was coupled more efficiently which decreased the reflected power and thus produced a signal peak.

The system was optimised using 5μl injections of a mixture of 2.12% propene and 1.25% n-butene in nitrogen onto Column S at 150°c. The effect of microwave power variation obtained, using an argon flow rate of 3.5 lh^{-1}, is shown in Figure IV,2, together with those for oxygen and nitrogen obtained at the same flow rate on a 3-m molecular sieve column at 25°c (Column M). The maximum power obtainable from the microwave generator was limited to 90 W. The variation in the reflected power background was also measured and found to be linear with respect to applied power. The variation of noise proved difficult to measure accurately as signal detection was drift limited which proved variable. However, no appreciable increase in noise was found at higher powers and 90 W was used throughout this work.

The effect of variations in flow rate for the same substances is shown in Figures IV,3 and 4. The effect of flow rate changes was considerable (ca. twice as great as for the emissive system as shown in Figure IV,3). However, the background drift was found to increase

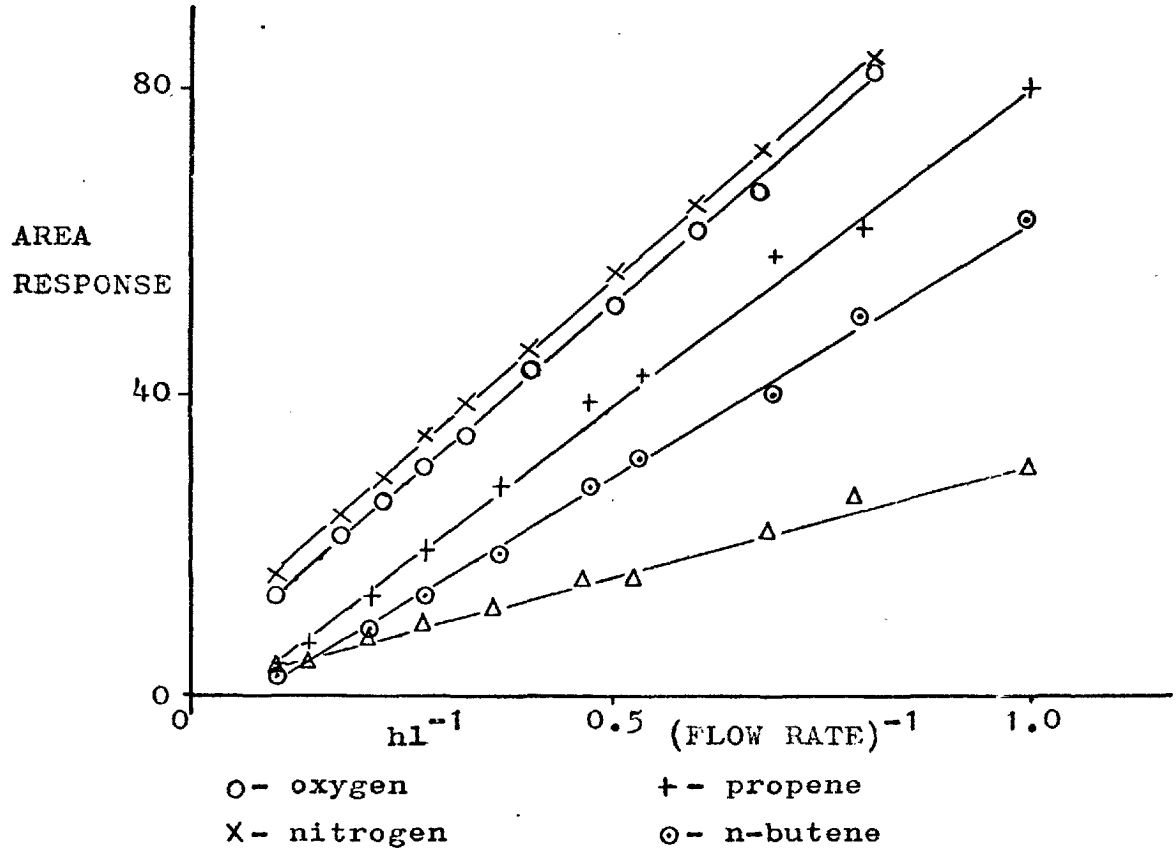


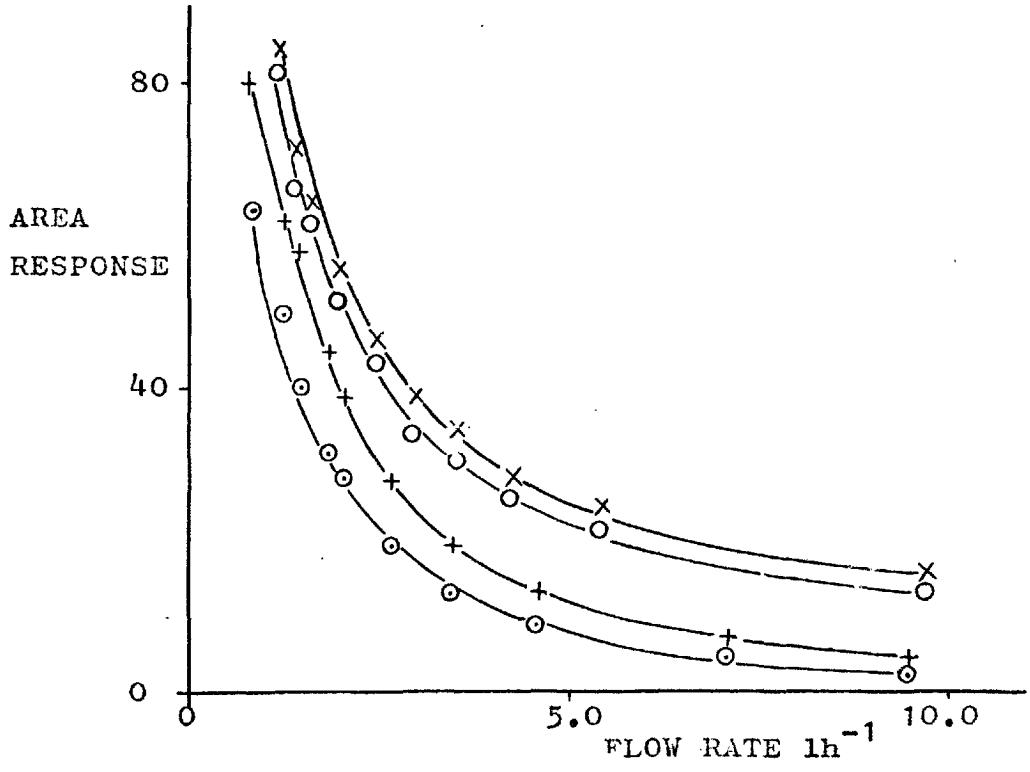
EFFECT OF MICROWAVE POWER ON DETECTOR RESPONSE

Figure IV.2

Figure IV.3

VARIATION OF DETECTOR RESPONSE WITH RECIPROCAL OF FLOW RATE





EFFECT OF FLOW RATE ON DETECTOR RESPONSE

Figure IV.4

at slower flow rates, probably as a result of increased instability in the flow rate. Hence a non-optimum, but convenient, flow rate of 3.5 lh^{-1} was used for the sensitivity studies.

The ranges of linearity for a selection of organic compounds were obtained by comparing the simultaneous responses of the reflected power detector and the reference emissive detector system set to monitor emission at 247.9 nm. The response to water was obtained in the same way, comparing it with OH emission at 308.9 nm. The conditions used are shown in Table IV,1. These comparative results were used to calculate the approximate limits of detection; the limits were determined accurately by making up solutions of appropriate concentrations, and measuring the response of the reflected power detector.

The response of the detector to a range of gases were measured directly using 5μl injections of the pure gases. For some gases, particularly nitrous oxide, oxygen and nitrogen impurities were observed and a correction was made using previously obtained sensitivities.

Results and Conclusions

The limits of detection and ranges of linearity obtained for the organic compounds and gases are shown in Tables IV,1 and 2. A comparison with the emissive detector is shown in Figure IV,5. The range of linearity

Table IV.1

DETECTOR RESPONSE TO SELECTED ORGANIC COMPOUNDS

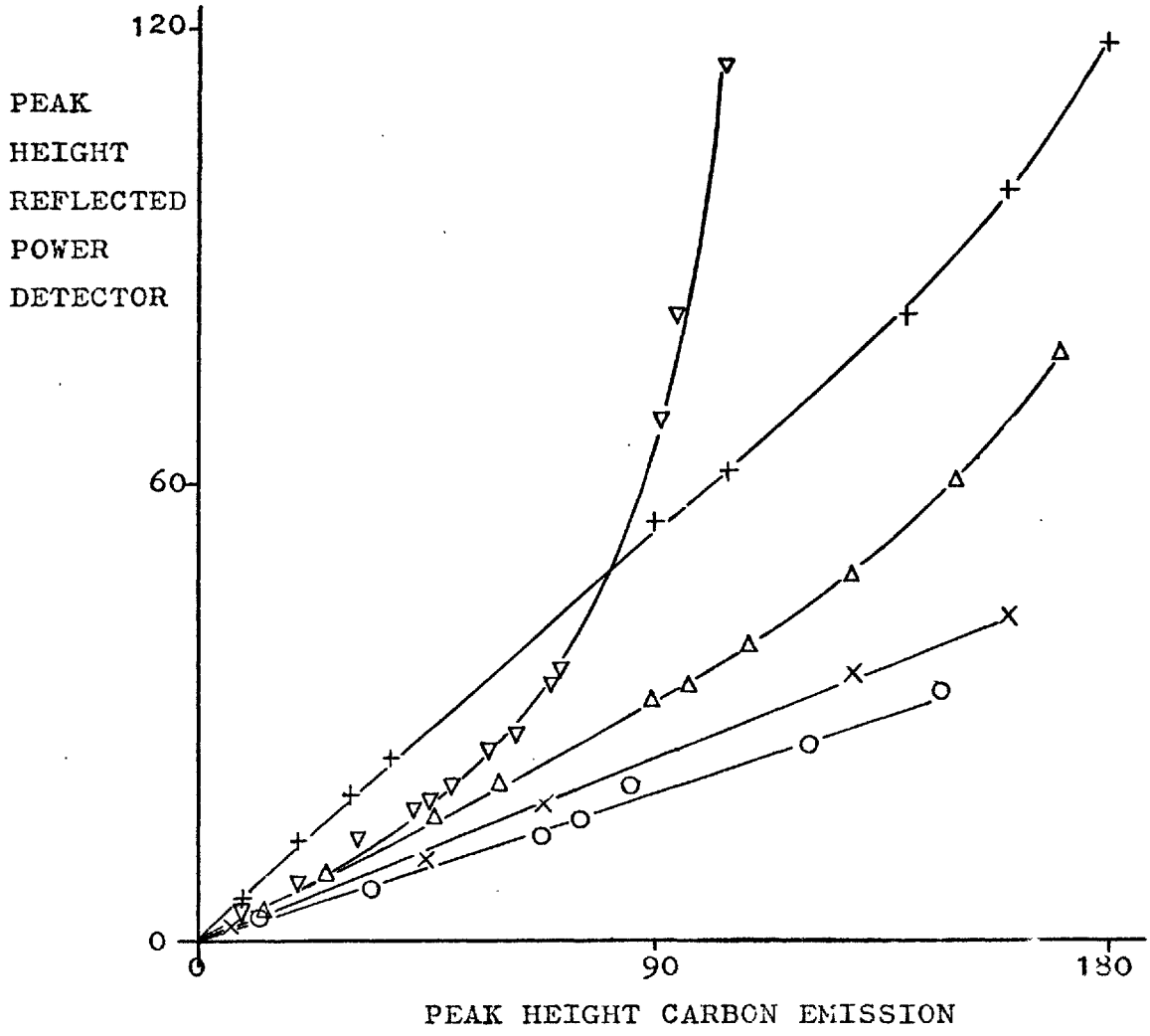
Compound	Column	Retention Time (min)	Range of Linearity	Limit of Detection ($ng\,s^{-1}$)
Acetone	S	2.96	$> 5 \times 10^2$	2.1
Diethyl ether	S	3.25	$> 5 \times 10^2$	2.8
Ethanol	S	1.92	$> 5 \times 10^2$	1.3
iso-Propanol	S	3.93	$> 5 \times 10^2$	1.3
n-Propanol	S	5.66	$> 5 \times 10^2$	1.4
Toluene	C	2.91	ca 10^3	1.4
Ethyl Iodide	C	0.92	ca 10^2	5.8
Carbon tetrachloride	C	1.25	$> 5 \times 10^2$	8.0
Chloroform	C	1.05	$> 5 \times 10^2$	5.7
n-Propyl bromide	C	0.90	$> 5 \times 10^2$	3.3
Methyl cyanide	C	0.33	$> 5 \times 10^2$	3.6
Thiophen	C	1.30	$> 5 \times 10^2$	2.3

Both columns at 150°C with an argon flow rate of 3.6 lh^{-1}.

Table IV.2

DETECTOR RESPONSE TO A RANGE OF PERMANENT GASES

Gas	Temperature (°C)	Column	Retention Time (min)	Limit of Detection (ng s^{-1})
Oxygen	25	M	1.15	3.8
Nitrogen	25	M	1.35	2.8
Helium	25	M	1.00	8.8
Hydrogen	25	M	1.03	0.3
Carbon Monoxide	50	M	2.02	3.4
Carbon Dioxide	50	S	0.73	4.2
Nitrous oxide	50	S	1.25	2.4
Methane	50	S	0.30	1.0
Ethylene	50	S	1.21	0.9
Propylene	150	S	0.52	0.9
n-Butylene	150	S	1.01	1.1



x - $C_6H_5 \cdot CH_3$

Δ - $n\text{-}C_3H_7Br$

∇ - C_2H_5I

o - CH_3CN

\+ - CCl_4

SIMULTANEOUS RESPONSES OF THE REFLECTED POWER DETECTOR AND THE EMISSIVE DETECTOR AT 247.9 nm

Figure IV.5

was greater than 500 for all the compounds investigated except ethyl iodide for which it was about 100. The upper limit of the working range was again set by plasma distortion at high concentrations. The limits of detection for all compounds and gases were quite similar, that is nanogram quantities, and the detector exhibited a particularly good response to hydrogen and to a lesser extent to hydrocarbons. No special sensitivity to N, S, O, I, Cl or Br compounds was evident. The limits of detection for organic compounds were ca. 10 to 20 times poorer than using carbon emission measurements with the emissive detector. However, the limits of detection for helium, hydrogen, oxygen and water were superior to those obtained by emission measurement both in the present work and in a previous investigation (160).

The sensitivity of this method of detection appeared to be limited by the stability of the cavity, the microwave power supply and the argon flow rate. The use of the normal, uncooled, cavities or an unstabilised power supply resulted in a marked increase (greater than 10 fold) in the noise and drift of the reflected power. Therefore, further improvements in the stability of these components would probably result in a considerable increase in sensitivity.

CHAPTER V

THE DETERMINATION OF VOLATILE METAL CHELATES USING A MICROWAVE-EXCITED EMISSIVE DETECTOR.

Introduction

The great advantages that gas chromatography has over many other separation techniques have raised considerable interest in its application to inorganic analysis. In order to use gas chromatography for the separation and analysis of metals it is desirable that the metals of interest react readily with a single reagent (or type of reagent) to give quantitative yields of metal derivatives; these derivatives must possess certain properties that meet the requirements for separation by gas chromatography. The derivatives must be volatile enough to be chromatographed in the gas phase; they must be stable at the temperatures required to maintain sufficient vapour pressure for chromatographic elution, and, finally, they should be easily formed and isolated, preferably from aqueous solution. The two main types of derivative which have been studied are the metal halides and chelates.

Metal chlorides and fluorides are among the most volatile of metal compounds and their chromatography

has been investigated in detail. Many difficulties arise due to their reactivity (210,211). They are easily hydrolyzed by atmospheric moisture and to avoid elaborate precautions during injection, systems have been devised for forming the halides in situ by reaction with fluorine (212) or chlorine trifluoride (213) prior to chromatography. The need to eliminate all traces of moisture from the carrier gas and to construct the column and detector from inert materials has limited the gas chromatography of halides to those elements which do not form other, more convenient, volatile compounds, eg. titanium (214), antimony (210), arsenic(215) and boron (216).

The gas chromatography of metal chelates has shown much greater potential than that of other metal derivatives. Lederer (217) suggested that metal acetylacetonates might prove amenable to gas chromatography but it was Biermann and Gesser (218) who described the first successful gas-chromatographic elution of the acetylacetonates of Be(III), Al(III) and Cr(III). Moshier and Sievers (219) have reviewed progress to 1965. The acetylacetonates of Cr(III), Al(III), Be(III), Cu(II), V(IV), Fe(III) and Sc(III) have been chromatographed successfully (218, 220, 221). Column temperatures between 150°c and 200°c were required for the compounds to be eluted in reasonable time periods. The other metal acetylacetonates are not sufficiently volatile to be eluted under these conditions and decompose

at higher temperatures; even in the successful cases listed above, elution is not always quantitative (219).

To extend the technique to other metals, ligands forming more volatile chelates have been tried. The two most widely used ligands are trifluoroacetylacetone ($CF_3.CO.CH_2.CO.CH_3$) and hexafluoroacetylacetone ($CF_3.CO.CH_2.CO.CF_3$). Chelates of hexafluoroacetylacetone are very volatile and readily eluted at temperatures only slightly above room temperature (220,222), but complications arise due to the formation of hydrates which may form polymeric species during chromatography (223). In addition hexafluoroacetylacetonates cannot be isolated from aqueous solution, due to hydrolysis of the ligand, and their preparation is therefore more difficult (219). Chelates of trifluoroacetylacetone are less volatile but easily formed in aqueous solution. They can be eluted at column temperatures between 80°c and 160°c and have been widely studied (220, 222, 224, 225). Marie and Sweet reported their application to the analysis of mixtures of aluminium and iron in alloys (226) and aluminium, gallium and indium in aqueous solution (227). Savory et al. (228) determined chromium in blood as chromium trifluoroacetylacetonate.

More recently the use of other ligands has been investigated. Fluoro-derivatives of dipivalylmethane ($(CH_3)_3C.CO.CH_2.CO.C(CH_3)_3$) have been used to form fairly volatile chelates with alkali metals (229). The chelates of mono-thio-β-diketones with a wide range of divalent

metals,including nickel, cobalt, zinc, palladium and platinum, are stable and volatile and have been chromatographed successfully (230, 231, 232). Amino-substituted β-diketones also show potential as chelating agents (233).

In order to provide a viable method for the analysis of metals the gas-chromatographic determination of metal chelates requires good resolution of components, minimum interferences and, in particular, sensitivities at least as high as those of other methods in common use eg. atomic absorption spectroscopy, emission spectroscopy. Hence the choice of detector is again of major importance. The principal detectors which have been used are the katharometer, flame ionization detector, electron capture detector and flame photometric detector.

The katharometer is non-selective and provides sensitivities in the range 10^{-4}-10^{-8}g (220,224). In addition, some decomposition of chelates occurs on the hot metal filaments (219). Flame ionization detectors have also been used with relatively little success. The presence of fluorine atoms and the metal atom itself in the chelate decreases the detector response and only moderate sensitivities have been obtained (221, 234).

The electron capture detector has been widely used for the determination of fluorinated chelates (222, 225) and is highly sensitive. Detection limits of 2×10^{-12}g of chromium and rhodium as the hexafluoroacetylacetonates have been reported (234). Barratt (235) detected 5×10^{-11}g of nickel as the mono-thio-trifluoroacetyl-

acetonate. The electron affinity of the chelates is a function both of the metal and any halogen atoms present; however, the detector is much more sensitive to halogenated chelates. Under comparable conditions the limit of detection for Cr(III) acetylacetonate is 2.5×10^{-10} mole, for the trifluoroacetylacetonate is 1.8×10^{-13} mole and for the hexafluoroacetylacetonate is 4.9×10^{-14} mole (222). The response is also dependent on the metal, and some slight measure of selectivity may be achieved by varying the applied potential.

Often the choice of chromatographic conditions is limited by the volatility and stability of the chelates used and, hence, complete resolution of mixtures is not always possible. Selective detection of individual metals would, therefore, be of considerable interest. It could be used both for the qualitative identification of a particular metal, and to avoid quantitative miscalculation when several metal chelates are eluted with similar retention times. Of the selective detectors used in organic analysis, the spectrometric detectors are most likely to be useful in metal chelate determination. Those detectors using pre-detector oxidation or reduction are clearly not suitable, and the alkali flame ionization detector is selective only to tin (100) and arsenic (98). Some selectivity is possible with the electron capture detector using non-halogenated chelates, however, a considerable loss of sensitivity compared with halogenated chelates is involved.

Of the spectrometric detectors described infrared and ultra-violet spectrophotometers are not sufficiently sensitive, and in addition, are unlikely to be highly selective as the molecular spectra of chelates of different metals are often similar. Flame phctometric detection of both chelates and halides has been studied by Juvet and Durbin (236,237). They viewed the emissions from an oxy-hydrogen flame using a Beckmann DU spectrophotometer. A summary of their results is shown in Table V,1. Although the sensitivity of detector response is not high, good selectivity and a range of linearity of 10^4 were obtained. In addition the detector response to chromium was unaffected by a 10-fold excess of iron eluted at the same time. A similar system was used by Juvet and Zado (238) but with less sensitive results. They also viewed the oxy-hydrogen flame non-selectively with a filter absorbing all radiation below 355 nm. This method is more sensitive but loses the advantages of selectivity.

Mass spectrometric and microwave-excited emissive detectors both proved highly sensitive in organic analysis; however, it is only very recently that mass spectrometry has been applied in the determination of chromium and beryllium chelates at the 10^{-12}g level (239) and no application of microwave-excited emission to the analysis of metal chelates has been reported. The potential usefulness of this type of emission for the determination of metals has been shown by the work of Bache

Table V.1.

Compound	Wavelength (nm)	Limit of Detection (moles)
$TiCl_4$	544.9	4×10^{-11}
$AsCl_3$	500.0	2×10^{-9}
$ZrCl_4$	564.0	2×10^{-8}
$Rh(hfa)_3^*$	369.2	1×10^{-11}
$Cr(hfa)_3^*$	425.4	1×10^{-10}
C_6H_6	431.5 (CH)	1×10^{-7}

* hfa = hexafluoroacetylacetonate.

and Lisk (240), who used emission at the 253.7 nm atomic mercury line from a low pressure helium plasma to measure the quantities of organo-mercury compounds present in fish, and by the work of Runnels and Gibson (241) and Dagnall et al.(207). These workers used microwave plasmas to excite metal emissions from compounds flash evaporated into the plasma from a platinum loop. This technique is highly sensitive but is limited by the small volume (ca. 1 μl) of solution which can be retained on the loop

and to those compounds which can be volatalised.

It was decided, therefore, to investigate the response of the atmospheric pressure emissive detector to some metal chelates. The chelating agents chosen were trifluoroacetylacetone and acetylacetone because they had been extensively used by other workers and comparison with other detectors would be possible. In addition, the ligands themselves and some acetylacetonates were available commercially. Pure metal chelates were bought or prepared, characterised, and their emission spectra in a microwave-excited plasma recorded. Solutions of the chelates in benzene were chromatographed and the major emission lines monitored. Samples of the eluates were collected and compared with the original compounds.

I Preparation of Metal Chelates

The acetylacetonates of aluminium (III), chromium (III), copper (II) and iron (III) were obtained commercially (Koch Light Laboratories, Ltd., Colnbrook, Bucks.). Acetylacetone (AA) and trifluoroacetylacetone (TFA) were also obtained from the same source and used to prepare the acetylacetonate of scandium (III), and the trifluoroacetylacetonates of aluminium (III), chromium (III), copper (II), gallium (III), iron (III), scandium (III) and vanadium (IV). TFA was found to deteriorate rapidly on exposure to air and was distilled immediately prior to use. The fraction boiling between 105°c and 107°c was collected.

1) Copper Trifluoroacetylacetonate ($Cu(tfa)_2$)

$Cu(tfa)_2$ was prepared by a method similar to that used by Berg and Truemper (243). 2.4 g $Cu(NO_3)_2.3H_2O$ were dissolved in 10 ml water and 0.5 g sodium acetate added to adjust the pH of the solution to ca. 9.0. 0.4 g TFA were dissolved in 2 ml ethanol and added to the copper solution while stirring magnetically. A blue precipitate formed immediately. The precipitate was filtered, washed with water, air dried and recrystallized from benzene. The crystals were dried in a vacuum desicator at a pressure of 1 torr for 12 hours. They were blue-violet in colour.

2) Iron Trifluoroacetylacetonate ($Fe(tfa)_3$)

The same method was used for $Fe(tfa)_3$. 0.27 g $FeCl_3.6H_2O$ and 0.5 g sodium acetate were dissolved in 10 ml water, and a solution of 0.50 g TFA in 2 ml ethanol added. A red precipitate was formed, washed with water and dried.

3) Aluminium Trifluoroacetylacetone ($Al(tfa)_3$)

The preparation of $Al(tfa)_3$ by the method used for the copper and iron chelates was less successful. On the addition of an ethanolic solution of TFA to an aqueous solution of sodium acetate and aluminium sulphate a yellow oil and crystals were obtained, which both sublimed under vacuum. Recrystallization from hexane produced a poor yield of white crystals.

The use of ammonium trifluoroacetylacetonate as an

intermediate, as suggested by Young (242), did not prove more successful. A yellow oil was again formed. A non-aqueous method was, therefore, preferred. A similar method has been applied to the preparation of $Zr(tfa)_4$ and $Hf(tfa)_4$ (220). 10 ml carbon tetrachloride were dried with phosphorus pentoxide, filtered and 0.20 g $AlCl_3$ added. On the addition of 0.7 g TFA the aluminium chloride slowly dissolved. The solution was evaporated to dryness and the product recrystallized from hexane.

4) Chromium Triflucroacetylacetonate ($Cr(tfa)_3$)

An initial attempt was made to prepare $Cr(tfa)_3$ by the method of Fay and Piper (244). A mixture of 0.4 g $Cr(NO_3)_3.9H_2O$, 0.5 g TFA, 2 g urea and 10 ml water was refluxed on a hot plate for 3 hours. A dark oil was formed from which only a poor yield of crystals of the chelate was obtained on recrystallization. Therefore, the method was modified. 0.40 g $Cr(NO_3)_3.9H_2O$ and 0.5 g urea were dissolved in 10 ml water and 0.5 g TFA in 3 ml ethanol added. The solution was stirred and 6N ammonia solution added dropwise until the precipitate formed. The violet crystals were washed, air dried and sublimed under vacuum at 100°c.

5) Gallium Trifluoroacetylacetonate ($Ga(tfa)_3$)

0.1 g gallium metal were dissolved in concentrated hydrochloric acid and the solution evaporated almost to dryness. The residue was dissolved in 10 ml water and

neutralised by dropwise addition of 6N sodium hydroxide solution. 0.5 g sodium acetate were added followed by 0.7 g TFA in 2 ml ethanol. A white precipitate formed slowly. It was washed, dried and sublimed under vacuum.

6) Vanadyl Trifluoroacetylacetonate ($VO(tfa)_2$)

A dark blue solution of vanadyl sulphate was prepared by refluxing 0.2 g V_2O_5 in 5 ml water with 0.4 ml concentrated sulphuric acid and 1 ml ethanol for 30 minutes. The solution was filtered, neutralised with sodium hydroxide and 0.3 g sodium acetate added. On the addition of a solution of 0.62 g TFA in 3 ml ethanol, a green precipitate formed which was filtered, dried and sublimed under vacuum.

7) Scandium Acetylacetonate ($Sc(acac)_3$) and Trifluoroacetylacetonate ($Sc(tfa)_3$)

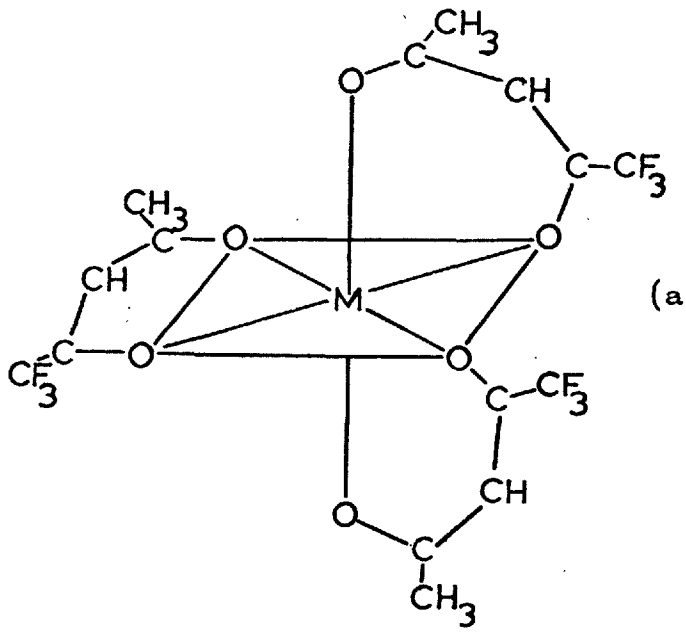
Both scandium chelates were prepared by the same method. 0.2 g Sc_2O_3 were dissolved by boiling in concentrated nitric acid, and the solution evaporated nearly to dryness. The residue was diluted with water to 10 ml. 7.5 ml of this solution were neutralised with 6N sodium hydroxide solution and 0.5 g sodium acetate added. On addition of 1 g AA in 3 ml ethanol a white precipitate formed immediately. The pH of the remaining 2.5 ml of solution was adjusted in a similar manner and 0.5 g TFA in 3 ml ethanol added. A white precipitate formed. Both

precipitates were filtered, washed and dried under vacuum.

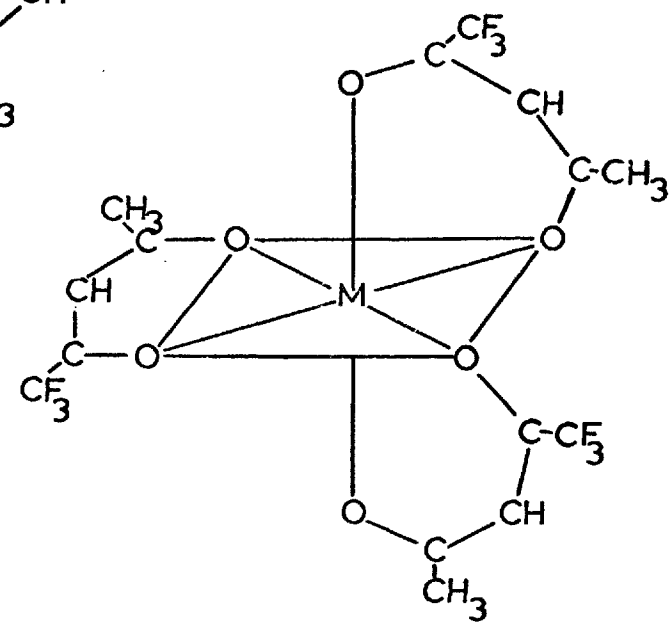
II. Properties of the Metal Chelates

Acetylacetone and its fluorocarbon analogs form metal complexes with structures of the types shown in Figure V,1 (219). With trivalent metals hexa-coordinated octahedral complexes of type 1 are formed. Only one geometrical isomeric form exists for acetylacetonates, however, for complexes with the unsymmetric ligand TFA, both cis and trans forms are possible. In the cis isomer (type 1(a)) all three trifluoromethyl groups are mutually adjacent and lie above the upper front face of the octahedron. One of the ligands is reversed in the trans isomer (type 1(b)); therefore, although its CF_3 group is still cis to one of the other CF_3 groups it is trans to the remaining group. As all the CF_3 groups are on the same side of the molecule in the cis compound this isomer would be expected to be more polar than the trans compound (219). Different melting points have been reported for the cis and trans isomers of $Cr(tfa)_3$ and $Rh(tfa)_3$ (244) and the isomers $Cr(tfa)_3$ (220), $Co(tfa)_3$ and $Rh(tfa)_3$ (245) have been separated by gas chromatography. Special columns are required to separate the isomers and under normal conditions they are eluted together. For the chelates studied so far isomerization has not caused any serious difficulties (219).

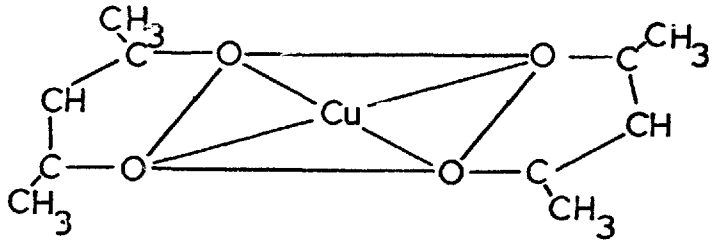
The only complexes used in the present study with



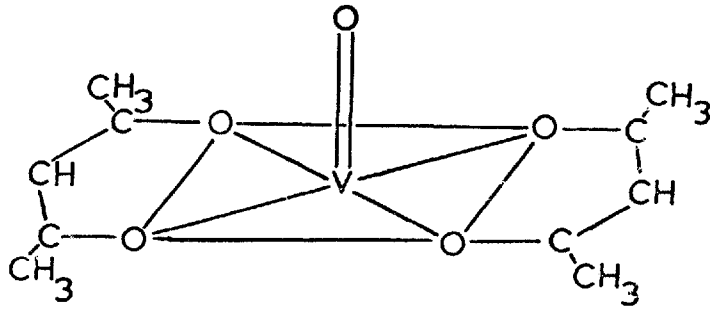
(a) trans $M(tfa)_3$



(b) cis $M(tfa)_3$



(c) $Cu(acac)_2$



(d) $VO(acac)_2$

STRUCTURES OF METAL CHELATES

Figure V.1

structures other than octahedral are those of copper (II) and vanadium (IV). The copper complex is square-planar (type 2) and the vanadyl complex is pyramidal (type 3). Although geometrical isomerism is possible for the trifluoroacetylacetonates of these metals it has not been reported.

The melting points and infrared and ultra-violet spectra of the compounds used were determined in order to confirm their identities and also so that these properties could be compared with those of the chromatographic eluates. This method has been widely used to establish that the gas-chromatographic peaks obtained are not due to decomposition products of the chelates (219).

The melting points of the chelates were measured on a Kofler block, and are shown in Table V,2, in which they are compared with the values reported in the literature. Agreement is generally satisfactory. The melting point of $Cr(tfa)_3$ was between those reported for the cis and trans isomers and the present sample may, therefore, have been a mixture of the isomers. The reason for the wide variation in values of the melting point of $Cu(tfa)_2$ is unknown.

The infrared spectra of mulls of the chelates in nujol were measured in the range 650-4000 cm^{-1} using a Perkin Elmer 157 Sodium Chloride Spectrophotometer. The results are shown in Table V,3. The assignments of the bands for the acetylacetonates are by Nakamoto (249), whereas those for the trifluoroacetylacetonates were made from the results of Nakamoto et al. (250) on a range of

Table V,2

Melting Points of Metal Chelates.

Chelate	Melting Point (°c)	Melting Point (Reference)
$Al(acac)_3$	196	198 (219)
$Al(tfa)_3$	119-120	117 (248), 121-22(trans) (244)
$Cr(acac)_3$	215	214-216 (219)
$Cr(tfa)_3$	132-135	112-114(cis) (244), 154.5-155(trans) (244)
$Cu(acac)_2$	dec.	236 dec. (219)
$Cu(tfa)_2$	180	189 (246), 201 (247)
$Ga(tfa)_3$	128	128.5-129.5(trans) (244)
$Fe(acac)_3$	179	181 (219)
$Fe(tfa)_3$	113-115	114(trans) (244)
$Sc(acac)_3$	186	187-187.5 (219)
$Sc(tfa)_3$	105-106	106-107 (248)
$VO(tfa)_2$	indefinite	indefinite (219)

Table V.3.

Principal Infrared Absorption Bands.

(a) Acetylacetonates.

(cm^{-1})

Cr	Fe	Cu	Al	Sc	Assignment
2930	2920	2910	2920	2920	$\nu(CH_3)$
2860	2870	2860	2860	2860	$\nu(CH_3)$
1570	1570	1575	1570	1575	$\nu(C\cdots C) + \nu(C\cdots O)$
1520	1520	1530	1520	1520	$\nu(C\cdots O) + \nu(C\cdots C)$
1460	1455	1460	1460	1460	$\delta(CH) + \nu(C\cdots C)$
1375	1375	1375	1375	1375	$\delta_s(CH_3)$
1275	1270	1270	1270	1275	$\nu(C-CH_3) + \nu(C\cdots C)$
1190(w)		1190	1190	1190(w)	$\delta(CH) + \nu(C-CH_3)$
1015	1015	1020	1020	1020	$\rho_r(CH_3)$
930	927	935	930	925	$\nu(C\cdots C) + \nu(C\cdots O)$
770	765	780	775	770	$\pi(CH)$
720	720	720	720	720	$\pi(CH)$

Table V.3.

(b) Trifluoroacetylacetonates.

(cm^{-1})

Cr	Fe	Cu	Al	Sc	VO	Ga	Assignment
2920	2920	2920	2900	2920	2900	2900	$\nu(CH_3)$
2860	2860	2860		2860	2860	2870	$\nu(CH_3)$
1610	1610	1612	1620	1615	1615	1620	$\nu(C\cdots C)$ + $\nu(C\cdots O)$
1530	1528	1530	1535	1530	1530	1530	$\nu(C\cdots O)$ + $\nu(C\cdots C)$
1460	1460	1460	1460	1460	1460	1465	$\delta(CH)$ + $\nu(C\cdots C)$
1365	1375	1370	1375	1365	1365	1370	$\delta_s(CH_3)$ + $\nu(CF_3)$
1294	1290	1302	1300	1295	1300	1290	$\nu(C-CH_3)$ + $\nu(C\cdots C)$
1230	1230	1230	1230	1230	1230	1230	$\nu(CF_3)$
1195	1192	1190	1195	1195	1200	1192	$\delta(CH)$ + $\nu(C-CH_3)$
1140	1140	1140	1140	1140	1135	1140	
1020	1020	1020	1010	1020	1015	1020	$\rho_r(CH_3)$
950	950	950	950	950	950	945	$\nu(C\cdots C)$ + $\nu(C\cdots O)$
863	860	866	860	860	860	860	$\nu(C-CF_3)$
800	800	800	795	800	795	800	$\pi(CH)$
780	780		780	790		780	$\pi(CH)$
730	730	738	730	730	730	730	$\nu(C-CF_3)$
720	720	720	720	720	720	720	$\pi(CH)$

1.3 -diketones and from the work of Morris et al. (251) on hexafluoroacetylacetonates. All the chelates of each ligand gave very similar spectra. Typical examples are shown in Figure V,2. An additional band at 930 cm^{-1} was observed for the vanadyl complex (a similar band was found for $VO(acac)_2$).

The ultra-violet spectra of solutions of the complexes in ethanol, obtained using a Perkin Elmer 402 Spectrophotometer, were relatively simple containing in most cases one or two broad absorption bands in the region 210-380 nm. The band maxima are listed in Table V,4 with values from the literature, where available, and typical spectra are shown in Figure V,3. Nearly all the chelates gave spectra similar to (a), just one broad absorption maximum. The exceptions were the copper and iron chelates which were similar to (b), and the chromium chelates, (c). The present results are very similar to those reported in the literature but comparisons are not possible for most of the trifluoroacetylacetonates on which very little data has been published.

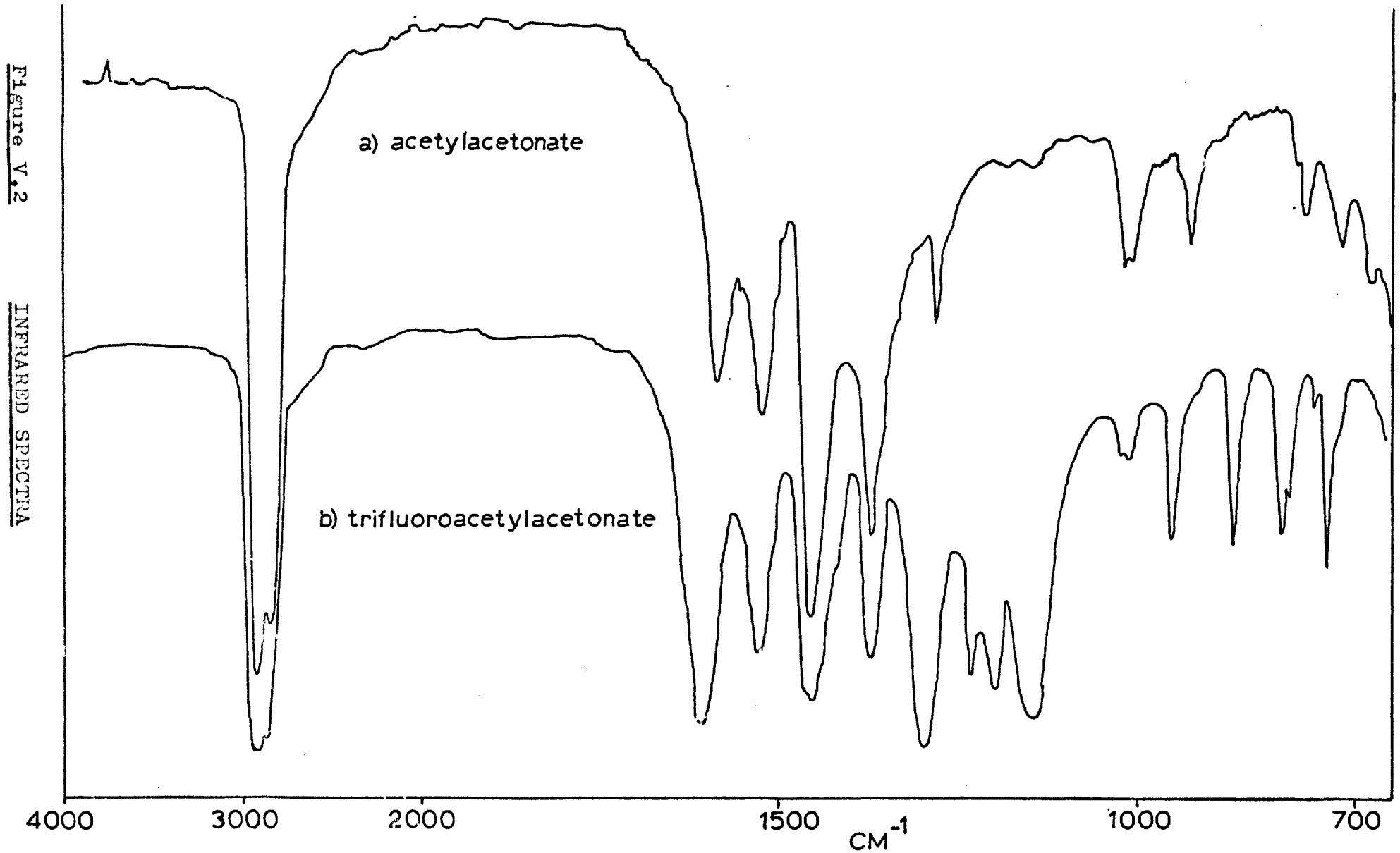


Figure V.2 INFRARED SPECTRA

Table V,4.

Ultra-violet Absorption Maxima

(nm)

Chelate	Absorption Maxima	Absorption Maxima (Reference)
$Al(acac)_3$	291	288 (253)
$Al(tfa)_3$	288	287 (252)
$Cr(acac)_3$	333,272,254,219	331,270,254 (254,255)
$Cr(tfa)_3$	340,278,263,220	cis 277,264 (244) trans 278,264 (244)
$Cu(acac)_2$	292,241	294,242 (253) 294,240 (256)
$Cu(tfa)_2$	297,237	294,240 (256)
$Ga(tfa)_3$	290	
$Fe(acac)_3$	270,234	272,235 (254,255) 271,229 (256)
$Fe(tfa)_3$	275,234	276,230 (256)
$Sc(acac)_3$	298	297 (253)
$Sc(tfa)_3$	297	
$VO(tfa)_2$	300	

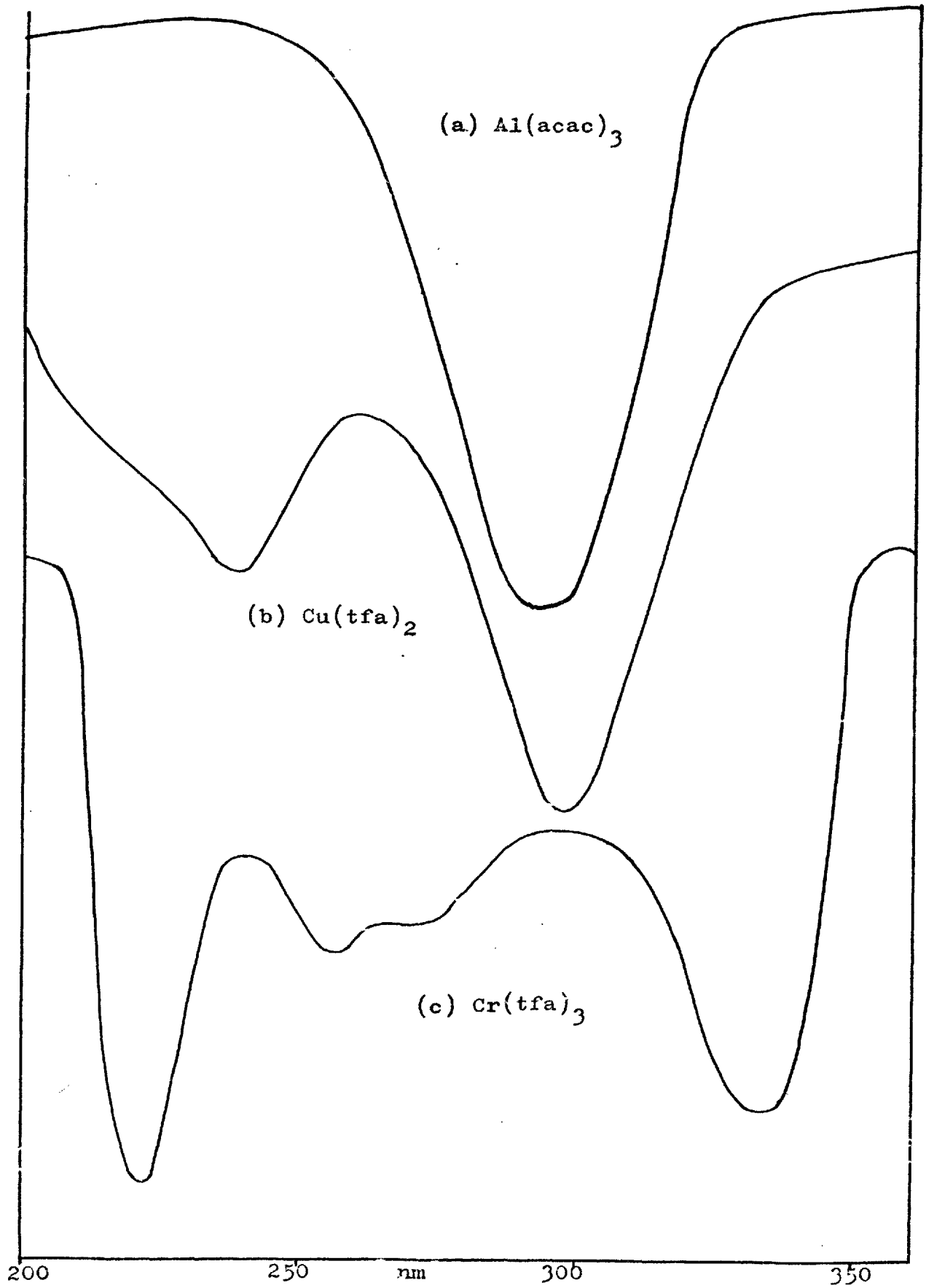


Figure V.3 ULTRA-VIOLET SPECTRA

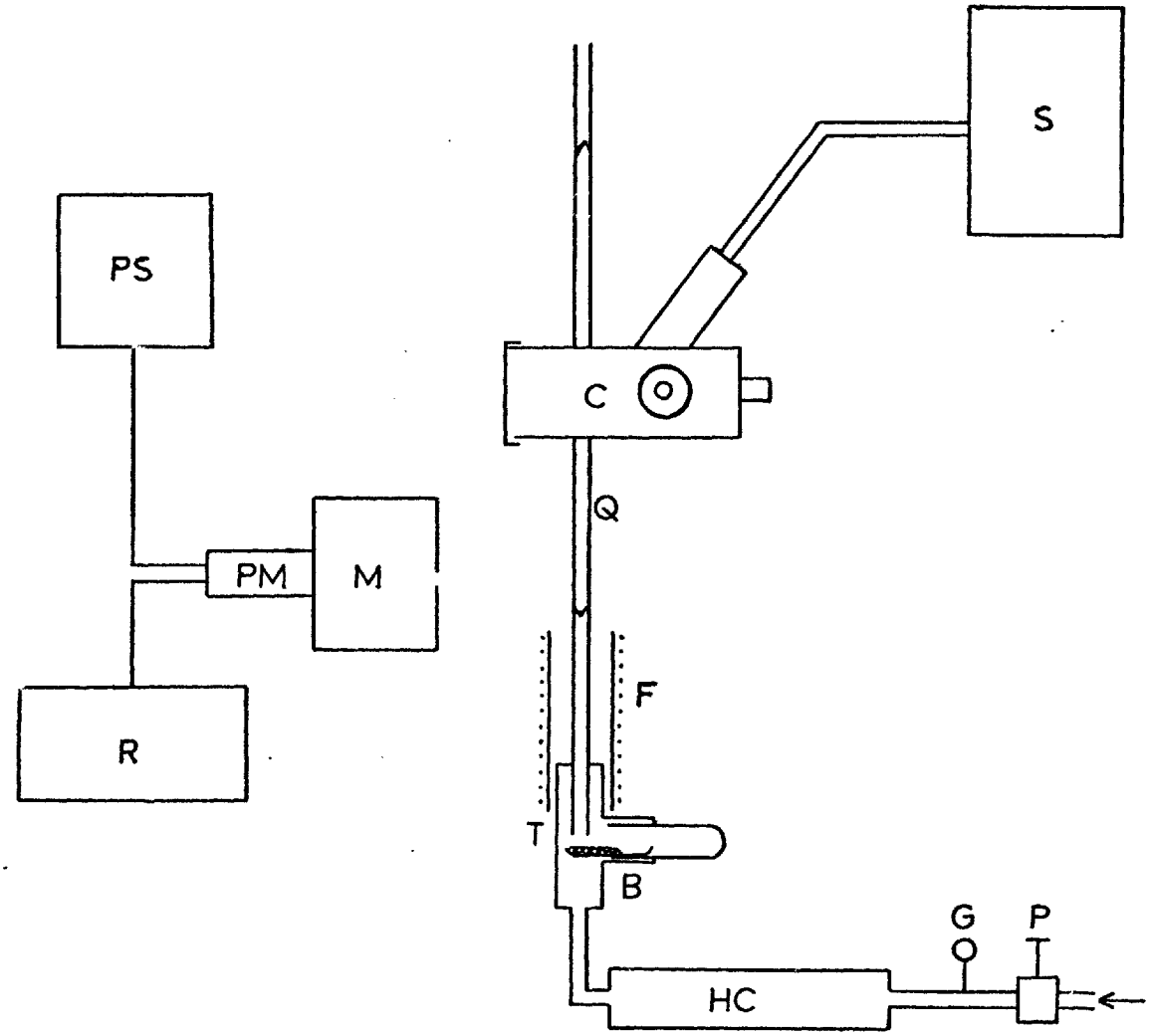
III. The Determination of the Emission Spectra of Metal Chelates in a Microwave-excited Plasma.

In the previous studies on the use of microwave-excited plasmas for the determination of metals, neither Runnels and Gibson (241) nor Dagnall et al. (207) have reported any attempt to determine the best atomic metal emissions to use. These might well be expected to be different from those of other sources, such as dc-arc, on which a comprehensive literature is available (257). In addition to the absolute line intensities, it is important that the lines used lie neither in regions of background emission (from argon, nitrogen and water) to minimize noise, nor close to emissions from carbonaceous species as these would be given by all chelates and hence reduce selectivity.

The emission spectrum of each metal chelate in the plasma was examined in order to determine the major emission lines which had the minimum of interferences from background, carbon and other metal emissions. An experimental system was set up to obtain an approximately constant, continuous level of metal chelate vapour in the argon entering the plasma. This enabled the entire spectrum to be scanned and more detailed studies to be made of the regions of interest. No attempt was made to obtain precise, quantitative data on relative peak heights as the concentration of the chelate vapour could not be maintained sufficiently constant.

Experimental

The system used is shown in Figure V,4. Initial attempts to use a similar arrangement to that described for organic compounds in Chapter I were unsuccessful due to the very low volatility of the chelates. It was found necessary to mount each chelate as close as possible to the bottom of the plasma and to heat the connecting tubing. In the arrangement used ca. 100 mg of the chelate under investigation were placed in a silica boat mounted in a brass T-piece just below the plasma. The silica tubing which contained the plasma passed into the middle of the T-piece just above the boat so that the metal chelate vapour could not easily come into contact with any hot metal surfaces. The carrier gas, argon, was preheated by passage through an empty steel column ca. 1 m in length heated by means of heating tape to ca. 200°c. A capillary restriction enabled the gas flow rate to be maintained at a rate similar to that used normally in chromatography, 3 lh^{-1}. The sample boat and silica tubing beneath the plasma were heated by means of a 120 ohm furnace, consisting of nichrome wire wound round a 17-mm diameter silica tube, 90 mm long. The wire was covered with alumina cement. The furnace and the heating tape were controlled using Variac variable transformers. The microwave system consisted of a $\frac{1}{4}$-wave Evenson-type microwave cavity and 1-mm i.d. silica tubing. A microwave power of 70 W was used throughout. The spectra were recorded with the Beckmann DU mono-



PS - power supply
R - read-out
PM - photomultiplier
M - monochromator
B - sample boat
HC - heated column
C - cavity
Q - quartz tube
S - microwave power supply
F - furnace
T - T-piece
G - pressure gauge
P - pressure controller

APPARATUS FOR THE DETERMINATION OF THE SPECTRA OF METAL CHELATES

Figure V.4

chromator and d.c. read-out system described previously.

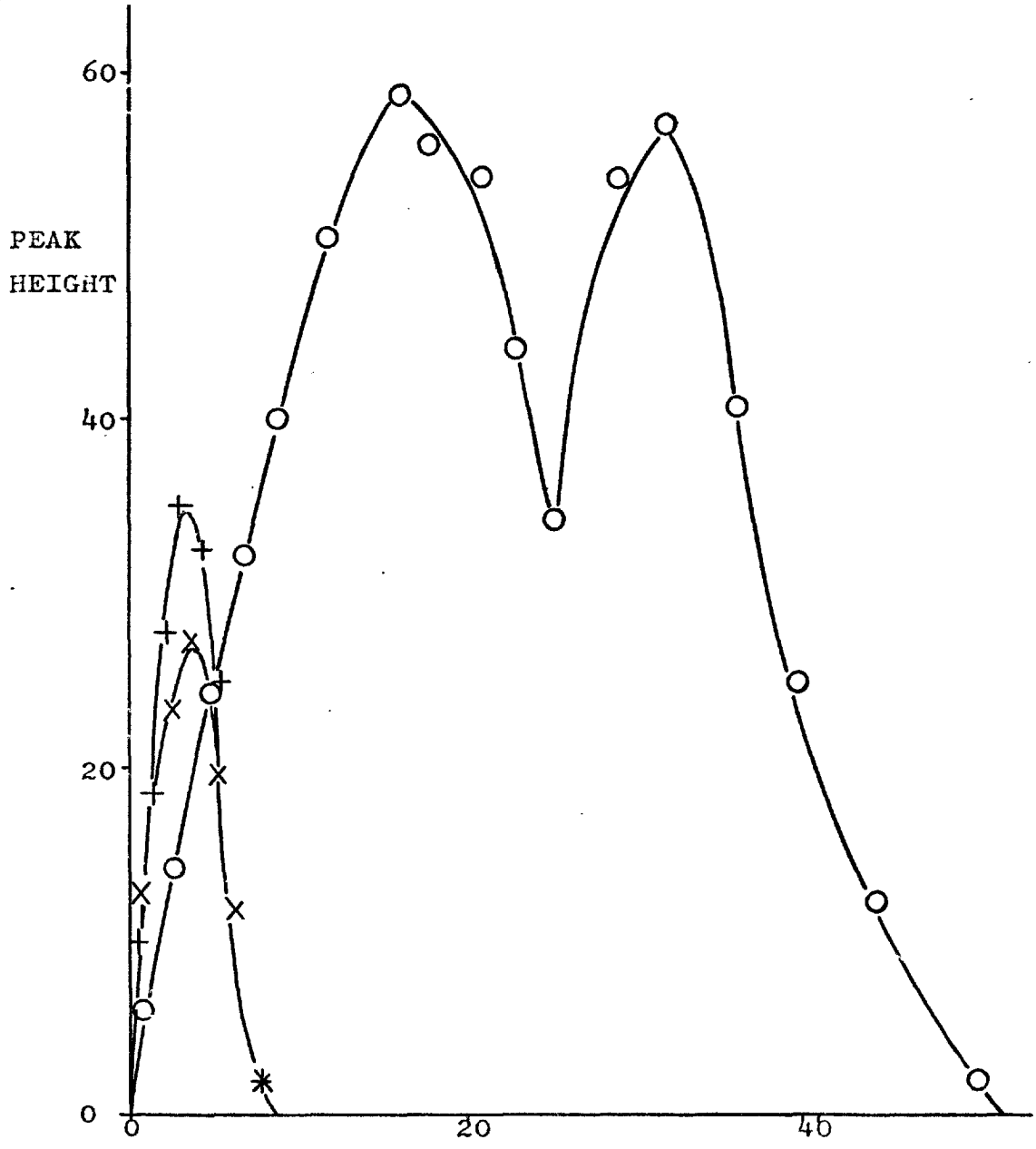
Procedure

For each set of spectral measurements the chelate in the sample boat was introduced into the T-piece, the plasma initiated, the coil of tubing heated and finally the temperature of the furnace raised slowly until carbon and metal emissions were observed. The variation of emission intensity with position in the plasma was measured in the same way as for organic compounds, ie. the vertical height of the viewing slit of the monochromator was reduced to ca. 1 mm by a horizontal slit and the cavity, and hence the plasma, moved vertically by means of a rack and pinion. With the plasma in the optimum position, the spectrum from 200 to 600 nm was scanned. When measurements for each chelate were completed the silica tubing was replaced.

Results

i. Position of Metal Emissions in the Plasma

The variation of the intensity of metal emissions with position in the plasma is shown in Figure V,5 for $Al(acac)_3$ (396.2 nm) and $Cu(acac)_2$ (327.4 nm). For comparison the variation with position of the atomic carbon emission (247.9 nm) for $Al(acac)_3$ is included. In contrast to the carbon emission, metal emissions could only be observed near the beginning of the plasma. In addition, after the passage of relatively large amounts



VARIATION OF EMISSION INTENSITY WITH POSITION IN PLASMA

Figure V.5

of a chelate into the plasma a deposit with a metallic appearance also formed near the beginning of the plasma. It was concluded that the absence of metal emissions higher in the plasma was due to the metal atoms being removed from the gas phase on collision with the walls of the silica tubing.

The concentration of metal emissions in the first 10 mm of the plasma had the advantage that some additional selectivity over carbon emissions was possible but it had more serious disadvantages. The extreme ends were the most unstable parts of a plasma and hence the variation in background emission was also greatest there. The metal deposit on the silica tubing gradually increased the background level of metal emission observed and after ca. milligramme quantities of metal chelate had passed into the plasma the deposit significantly reduced the overall intensity of light reaching the monochromator. Both these effects were minimised by the use of small samples.

ii. Emission Spectra of Metal Chelates

The results obtained for the compounds of each metal are discussed below. In all cases where two compounds of a metal were studied both spectra were found to be essentially the same (they generally differed quantitatively due to different vapour concentrations in the gas stream) and are considered together. The spectra shown in Figures V,6 to V,11 were all scanned at the same scan

speed using a slit width of 0.1 mm.

In order to confirm their identification the emissions observed were compared with those obtained from electrodeless discharge lamps of each metal under the same experimental conditions and with those listed in N.B.S. Monograph 32 (257) obtained using a 200 V d.c. arc. Due to the relatively poor resolution of the monochromator used in the present study, many atomic lines listed could not be resolved. The major individual atomic lines are shown in parenthesis after each composite emission peak observed.

1) $Al(acac)_3$ and $Al(tfa)_3$

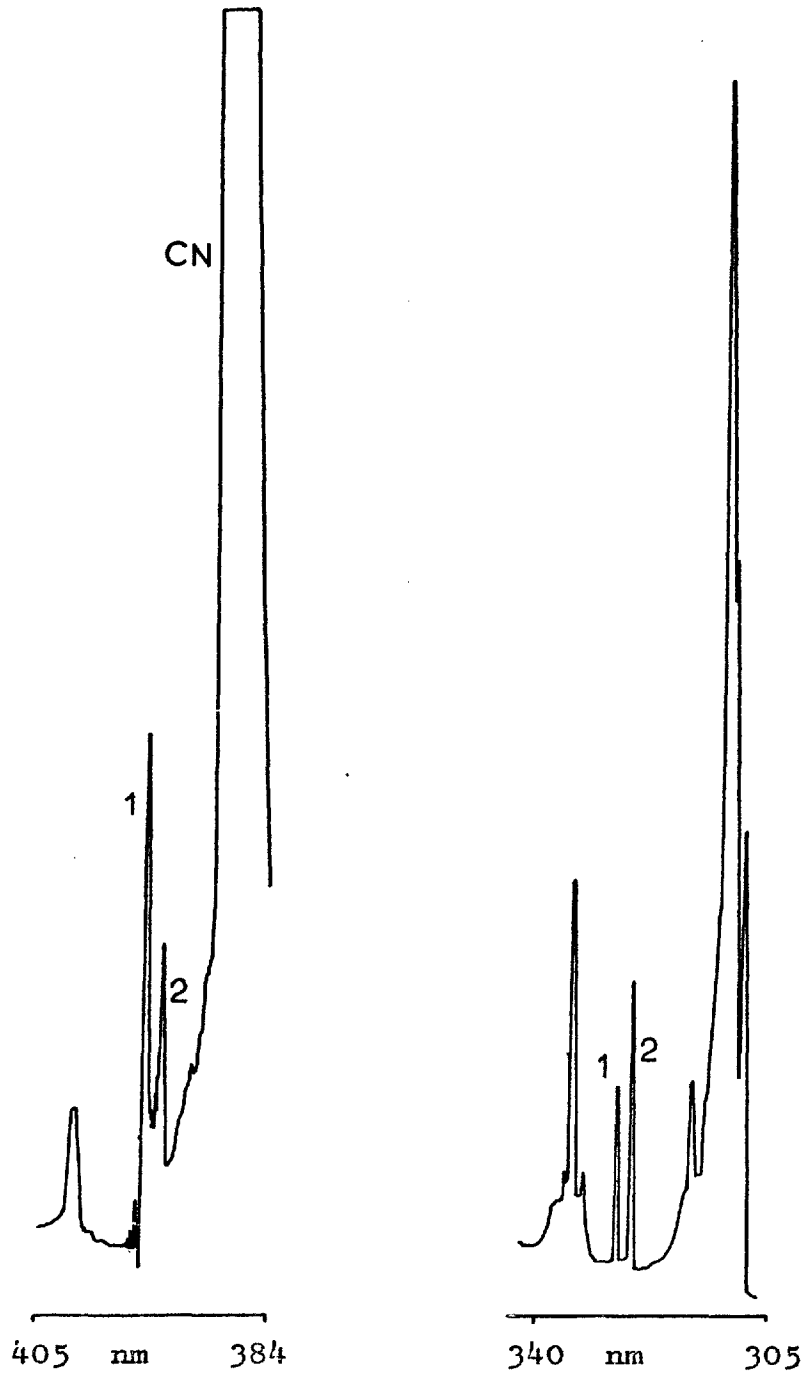
Only two atomic aluminium lines, at 396.2 nm and 394.4 nm, were observed. They are shown in Figure V,6(a). They appear on the tail of a strong CN band (band-head at 388.3 nm) and could not be completely resolved. The other two relatively strong atomic emissions obtained from a d.c. arc and an electrodeless discharge lamp are at 308.2 nm and 309.3 nm. However, if present in this system they were masked by strong OH background emission.

2) $Cr(acac)_3$ and $Cr(tfa)_3$

Atomic chromium emissions were found in the main regions shown in Figure V,7.

a. Three atomic lines at 357.8 nm, 359.3 nm and 360.5 nm. There is the possibility of some interference from a small CN band at 358.6 nm.

b. Three atomic lines at 425.4 nm, 427.5 nm and



(1) 396.2 nm
(2) 394.4 nm

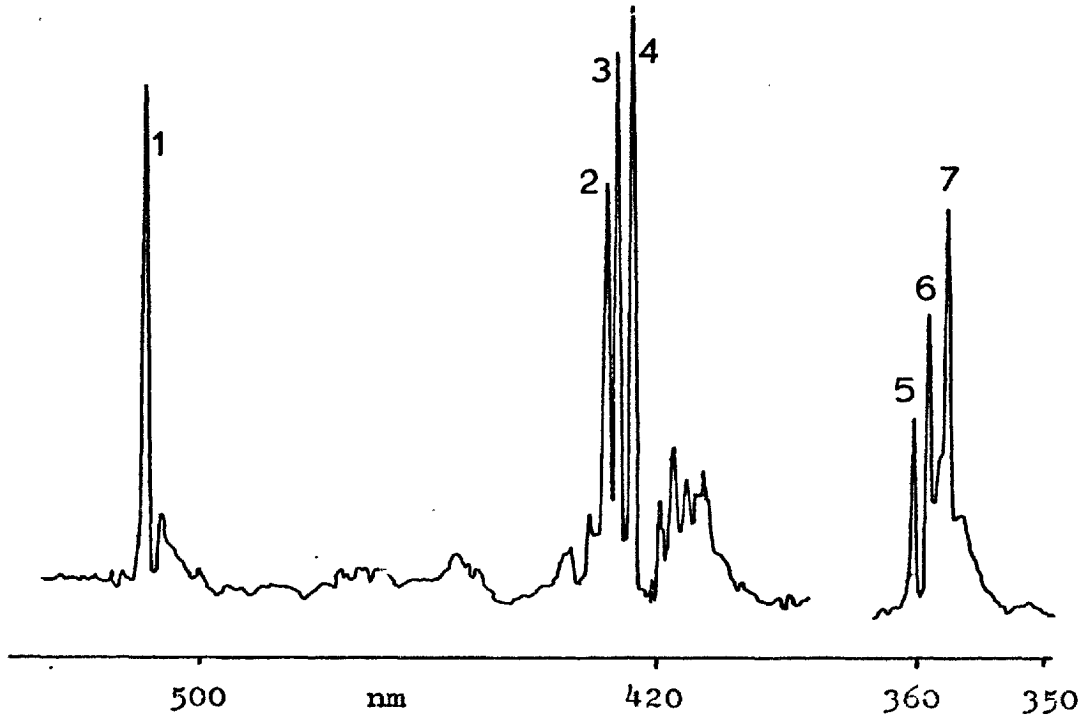
(a) $Al(tfa)_3$

(1) 327.4 nm
(2) 324.7 nm

(b) $Cu(tfa)_2$

EMISSION SPECTRA

Figure V.6



(1) 520.5 nm
(2) 428.9 nm
(3) 427.5 nm
(4) 425.4 nm
(5) 360.5 nm
(6) 359.3 nm
(7) 357.8 nm

EMISSION SPECTRUM OF $Cr(tfa)_3$

Figure V.7

428.9 nm. The small fourth peak is due to CH emission at 431.4 nm. Argon emissions at 425.1 nm and 427.2 nm are not resolved.

c. 520.5 nm (520.8 nm, 520.6 nm and 520.4 nm).

3) $Cu(acac)_2$ and $Cu(tfa)_2$

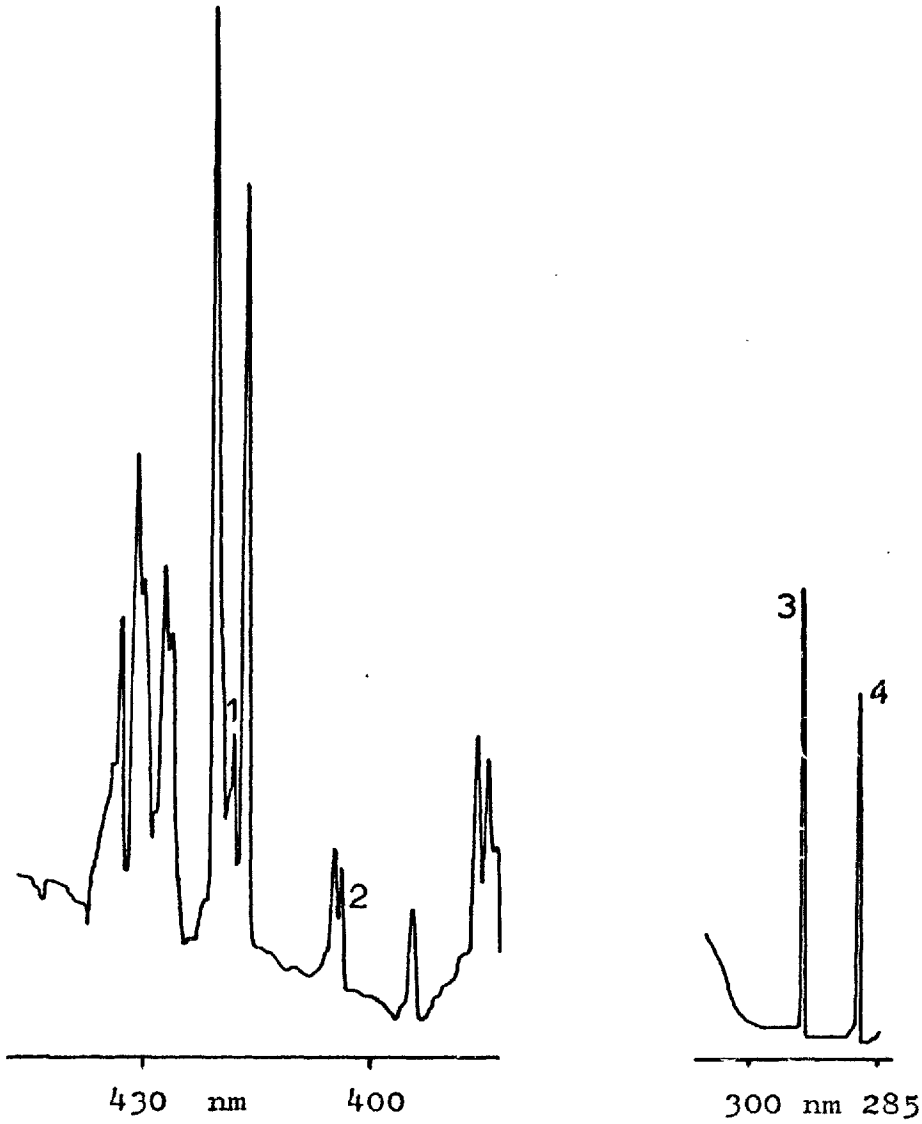
Two copper atomic lines at 324.7 nm and 327.4 nm were observed for both chelates. They are shown in Figure V,6(b), conveniently separated from the background emissions of nitrogen and water (336 nm and 308.9 nm respectively).

4) $Ga(tfa)_3$

The two gallium atomic lines observed at 287.4 nm and 294.4 nm (294.3 nm and 294.4 nm) lie in a region of very low background. The two most intense lines, at 417.2 nm and 403.3 nm overlap partially with argon lines at 416.9 nm and 404.5 nm respectively, which considerably limits their utility. The gallium emissions obtained are shown in Figure V,8.

5) $Fe(acac)_3$ and $Fe(tfa)_3$

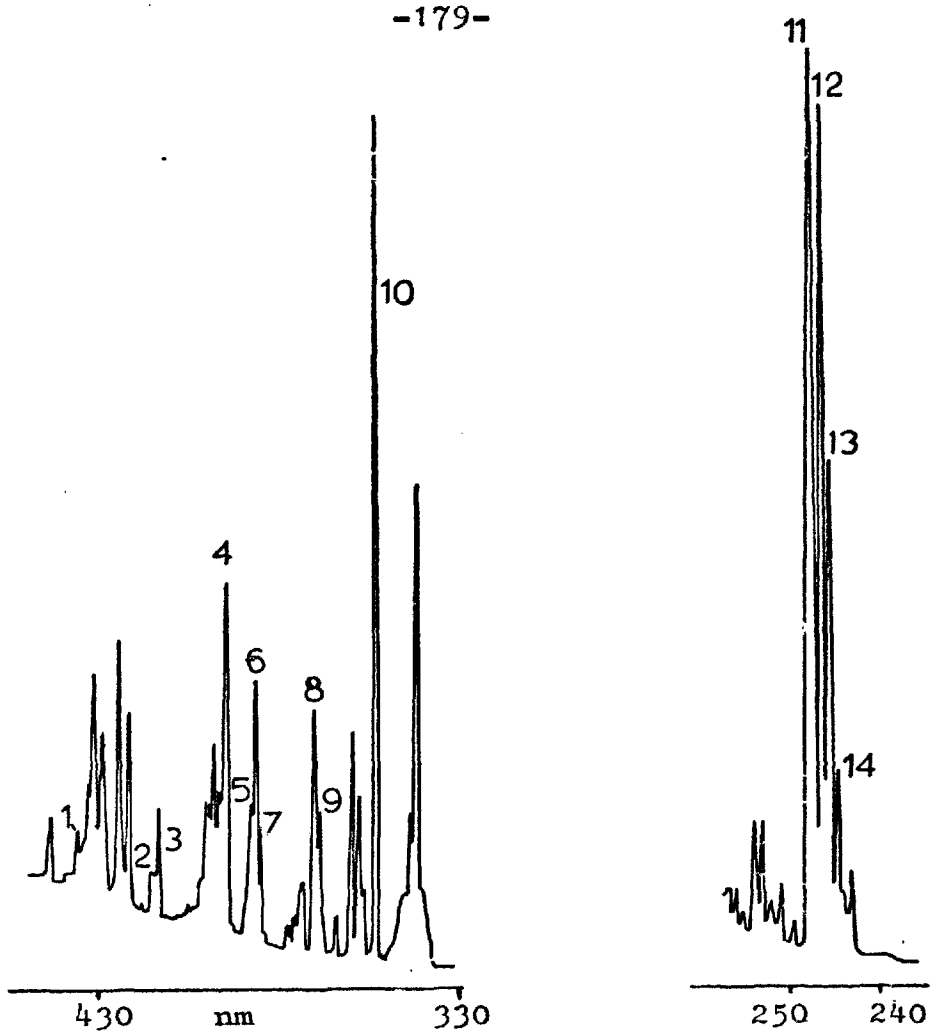
Many lines were observed in the emission spectra of both chelates. The main emissions are shown in Figure V,9. The most useful lines (ie. those with the minimum interferences) in this region appear to be those at 344.1 nm, 357.0 nm and 373.5 nm. Four strong emission peaks were observed between 247 nm and 250 nm. These are the carbon atomic line at 247.9 nm and iron atomic emissions at 248.3 nm (248.3 nm and 248.4 nm), 249.0 nm (248.8 nm, 249.0 nm and 249.1 nm) and 247.3 nm. The



(1) 417.2 nm
(2) 403.3 nm
(3) 294.4 nm
(4) 287.4 nm

EMISSION SPECTRUM OF $Ga(tfa)_3$

Figure V.8



(1) 438.4 nm
(2) 406.5 nm (406.3 nm, 407.1 nm)
(3) 404.5 nm
(4) 382.0 nm (382.0 nm, 382.5 nm, 382.7 nm)
(5) 375.0 nm (374.5 nm, 374.9 nm, 375.8 nm)
(6) 373.5 nm
(7) 372.0 nm
(8) 358.1 nm
(9) 357.0 nm
(10) 344.1 nm
(11) 249.0 nm
(12) 248.3 nm
(13) 247.9 nm
(14) 247.3 nm

EMISSION SPECTRUM OF $Fe(tfa)_3$

Figure V.9

$Fe(acac)_3$ in the sample boat was partially discoloured, possibly due to decomposition.

6) $Sc(acac)_3$ and $Sc(tfa)_3$

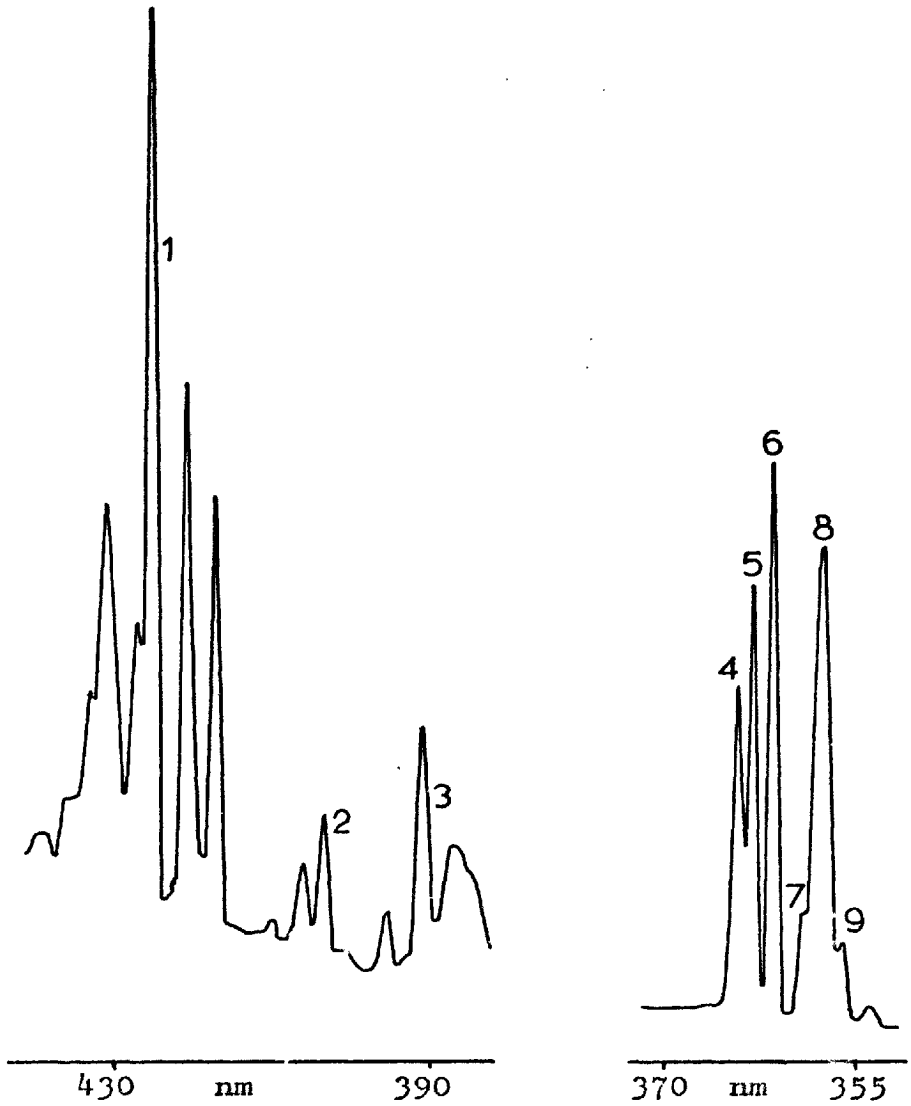
Both scandium chelates gave intense emissions at 361,4 nm, 363.1 nm, 364.4 nm (364.5 and 364.3 nm) and a broad peak at 357.5 nm (357.3 nm, 357.6 nm and 358.0 nm) with shoulders at 355.9 nm and 359.0 nm. The emissions at 391.0 nm (391.2 nm and 390.8 nm), 402.0 nm (402.0 nm and 402.4 nm) and at 424.7 nm were less useful due to overlap with emissions from other species. The emission at 391.0 nm was not completely resolved from the CN band emission and the other two emissions overlapped argon lines at 404.4 nm and 425.1 nm respectively. The spectra are shown in Figure V,10.

7) $VO(tfa)_2$

The major vanadium atomic emission observed was at 318.4 nm (318.3 nm, 318.4 nm and 318.5 nm). Weaker emissions were found at 292.4 nm (292.4 nm and 292.5 nm), 290.9 nm and 289.3 nm (289.2 nm and 289.3 nm). If present, the lines at 309.3 nm, 311.1 nm and 311.8 nm were hidden by OH emission and the lines at 437.9 nm, 438.5 nm and 438.9 nm could not be resolved from a C_2 band at 436.9 nm and argon lines at 437.1 nm and 437.9 nm. The main features of the spectrum are shown in Figure V,11.

IV. Gas Chromatography of Metal Chelates.

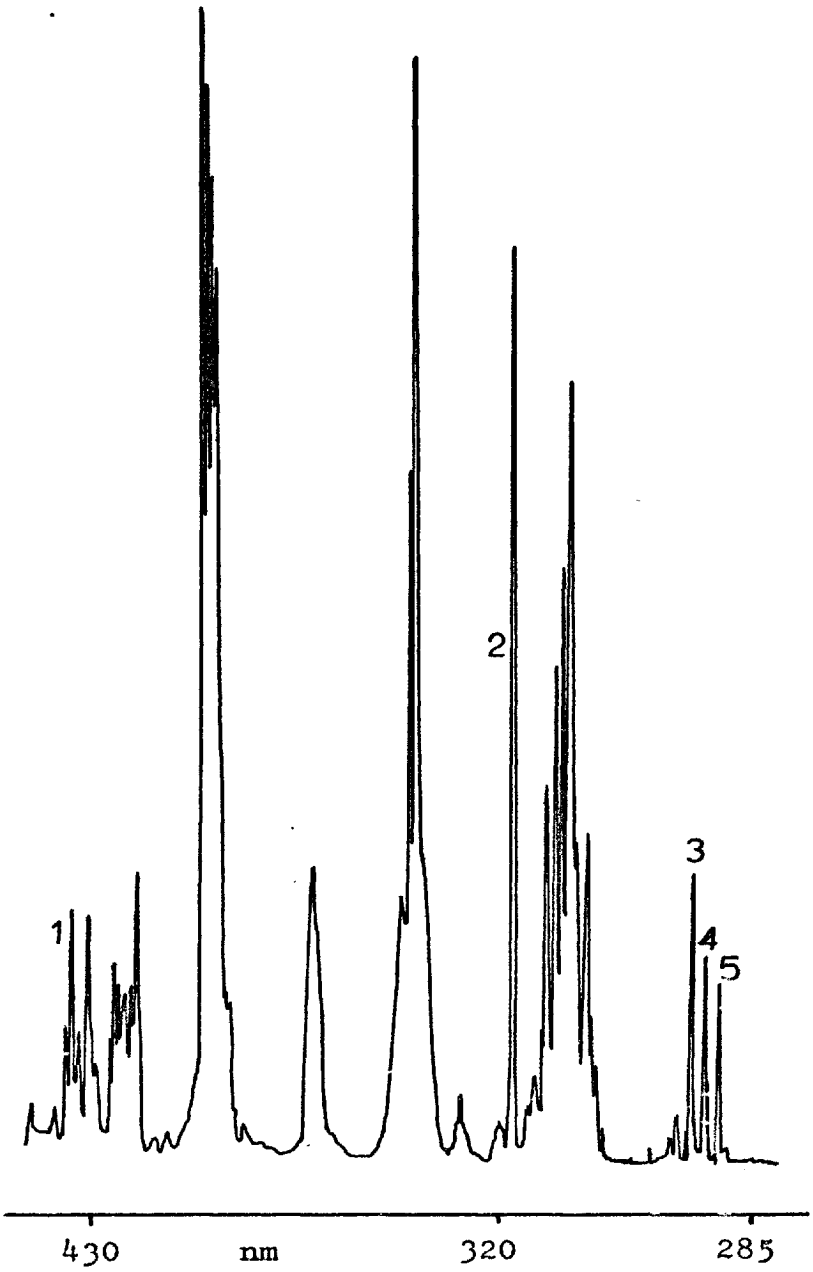
The spectra observed using the continuous system



(1) 424.7 nm
(2) 402.0 nm
(3) 391.0 nm
(4) 364.4 nm
(5) 363.1 nm
(6) 361.4 nm
(7) 359.0 nm
(8) 357.5 nm
(9) 355.9 nm

EMISSION SPECTRUM OF $Sc(tfa)_3$

Figure V.10



(1) 438.5 nm
(2) 318.4 nm
(3) 292.4 nm
(4) 290.9 nm
(5) 289.3 nm

EMISSION SPECTRUM OF $VO(tfa)_2$

Figure V.11

showed that metal emissions could be obtained from a microwave-excited plasma for all the chelates used. Therefore, a gas-chromatographic system was set up and the major emissions used to monitor the eluted chelates.

Apparatus

The detector system was similar to that used previously with some modifications. To avoid decomposition or condensation of the metal chelates the silica tubing to contain the plasma was connected directly to the column exit and the monochromator was repositioned to view the plasma just above the roof of the oven. To further reduce the risk of condensation the silica tubing between the column and the plasma was heated by means of a short coil of wire and a Variac variable transformer. This experimental arrangement required the monochromator entry slit to be ca. 100 mm from the plasma and therefore a lens was used to reduce the loss of light intensity. Its position was adjusted to give the maximum response when an argon emission line was monitored. An Evenson $\frac{1}{4}$-wave microwave cavity and 1-mm bore silica tubing were again used. The increased stability of the plasma in the narrower tubing was of particular importance when viewing the end of the plasma.

The low volatility of the metal chelates and their decomposition at high temperatures limit the range of chromatographic conditions which can be used and hence

the correct choice of column is critical. Teflon or glass columns are recommended (219) in preference to copper or steel as early work with metal columns (220) showed that occasionally the column walls either reacted with some of the chelates or catalyzed their decomposition. Generally, very inert supports coated with non-polar liquid phases have been used as the stationary phase. Solid supports made of calcined diatomaceous earth or glass beads have usually been treated by silanization or acid or alkaline washing to reduce their adsorption activity. Alternatives are powdered teflon or Kel-F (258), however they are difficult to pack and relatively poor results have been reported using them (259). The most widely used liquid phases have been silicone oils and greases, Apiezon L and M (high molecular weight hydrocarbons) and polyethylene wax.

Biermann and Gesser (218) used 0.5% Apiezon L on glass beads to separated acetylacetonates and Belcher et al. (259) obtained satisfactory separations of aluminium, chromium and iron trifluoroacetylacetonates using 10% Apiezon L on Universal B (an extremely inert support). Therefore, it was decided to try these column packings in the present studies. A 0.6 m x 4.8 mm-id. borosilicate glass column (Column1) was packed with Universal B pre-coated with 10% Apiezon L (Phase Separations Ltd., Queensferry, Flintshire) and conditioned at 200°c for 36 hours in a stream of argon. A second 0.6 m borosilicate glass column (Column2) containing 0.5% Apiezon L

on glass microbeads (0.2 mm diameter) was also prepared and conditioned in the same way. Some initial studies were carried out using Column 1 but relatively poor peak shapes were obtained for many of the chelates and therefore Column 2 was used in preference.

In order to obtain sharp peaks the chelates must be volatalised rapidly and completely on injection. This requires absorption of considerable thermal energy and therefore the injection port is normally at a temperature 25-50°c higher than that of the column. However, as a heated injection port was not available during the present studies, an alternative arrangement was used. The samples were injected directly onto a glass wool pad in the top of the column and the top of the column heated by means of the small electrical furnace described previously. The temperature of the top of the column could be maintained ca. 30°c above the oven temperature by applying a potential of 40 V across the furnace.

Experimental

The experimental parameters of the detector system were investigated using 1μ l injections of a 950 p.p.m. (W/V) solution of $Ga(tfa)_3$ in benzene. $Ga(tfa)_3$ was used because it was found to be conveniently eluted from Column 1 at 125°c after 3.1 min with a fairly good peak shape and the intense gallium atomic line at 294.4 nm lies in a region of very low background. Any variation of detector response at this wavelength could, therefore,

be associated directly with changes in the metal emission.

As expected from the studies with the continuous system metal emissions were only obtained from the first 10 mm of the plasma. The vertical position of the plasma was initially optimised by moving the cavity to give the maximum emission at 294.4 nm during the passage of an eluted band of $Ga(tfa)_3$ through the plasma. However, with the plasma in this position the variation of response with concentration curved markedly on a linear plot. In order to obtain a linear calibration curve passing through the origin it was found necessary to reposition the plasma so that emissions from the first 3 mm of the plasma could be monitored. This position was used for all measurements of chelate emissions. It has the disadvantage that an even less stable portion of the plasma was viewed but this was, somewhat, compensated by fitting a metal cap over the normally open front of the cavity. As the bottom of the plasma was well below the cavity the cap did not mask the metal emissions but reduced the light from the centre of the plasma reaching the monochromator and increased the coupling of microwave power and hence plasma stability.

The variation of the peak height at 294.4 nm with microwave power was measured by repeated injections of the $Ga(tfa)_3$ solution. For each new power setting the plasma length altered and the position of the plasma had to be reoptimised. The maximum peak height was obtained at a power of 70 W. The variation of noise with

power was found to be very small and the maximum signal to noise ratio was also at 70 W.

The variation of detector response with carrier gas flow rate was also measured by repeated injections. The area response was again found to be proportional to the reciprocal of the flow rate, and the slowest convenient flow rate was used. However, in practice, in order to reduce peak tailing a relatively fast argon flow rate of 3.3 lh^{-1} was necessary.

In summary, the optimum experimental parameters were found to be the same as those for organic compounds. A microwave power of 70 W and a carrier gas flow rate of 3.3 lh^{-1} were used throughout the metal chelate determinations.

Sensitivity and Selectivity of Metal Emissions

The signal to noise ratios for the major metal emissions observed previously were determined for solutions of each of the trifluoroacetylacetonates. In addition, the detector response at each wavelength to a 1000 p.p.m. solution of benzyl alcohol in benzene was measured in order to estimate the relative selectivities of the metal emissions over carbon compounds. Benzyl alcohol was chosen because it has convenient retention times (1.0-3.5 min) on the columns used. The molar selectivity ratio was calculated in each case as the ratio of the number of gram-atoms of carbon injected to the number of gram-atoms of the metal required to produce the same

response. Benzene was used as the solvent for all the chelates. It was eluted after only 10-20 s and the plasma was not initiated until ca. 30 s after injection.

1) $Al(tfa)_3$

Using Column 1 at 100°c $Al(tfa)_3$ gave a peak with a retention time of 4.83 min. The only major aluminium lines observable, at 394.4 nm and 396.2 nm, were not fully resolved and therefore only the more intense emission at 396.2 nm was monitored. The variations of peak height and area with concentration were linear up to 4.4×10^{-5} g and the limit of detection obtained was 3.5×10^{-10} g $Al(tfa)_3$ s^{-1}, equivalent to 1.9×10^{-11} g aluminium s^{-1}. Benzyl alcohol gave a small positive response at this wavelength, presumably due to CN emission. The selectivity ratio was 990.

2) $Cr(tfa)_3$

$Cr(tfa)_3$ had a retention time of 3.30 min on Column 1 at 130°c. Table V,5 shows the comparative results for the main chromium atomic emissions for 0.5 μl of a 995 p.p.m. solution of $Cr(tfa)_3$ in benzene. The emission at 357.8 nm was the most sensitive and sufficiently selective. The response at this wavelength was linear with detection limits of 3.3×10^{-11} g $Cr(tfa)_3$ s^{-1} and 3.6×10^{-12} g chromium s^{-1}.

Table V.5.

Wavelength (nm)	Peak Height (mV)	Noise (mV)	S : N	Selectivity
357.6	110.0	0.2	550	3930
425.4	180.0	1.5	120	6430
520.5	60.0	0.8	75	3210

3) $Cu(tfa)_2$

$Cu(tfa)_2$ gave a very poor peak shape with extensive tailing on Column 1, therefore Column 2 was used, on which $Cu(tfa)_2$ had a retention time of 2.0 min at 140°c and still gave rather a broad peak. This broadening increased at lower concentrations and the variation of response with concentration was linear only if peak areas were measured. The emission at 324.7 nm was 2.1 times more intense than that at 327.4 nm and at both wavelengths the response to benzyl alcohol was negative. The limit of detection at 324.7 nm was 4.6×10^{-11} g $Cu(tfa)_2$ s^{-1}, equivalent to 8.0×10^{-12} g copper s^{-1}, and the selectivity 2250. One problem found with $Cu(tfa)_2$ was that the deposit formed on the tubing was particularly dark and more rapidly reduced the intensity of detector response.

4) $Ga(tfa)_3$

The comparative results for the principal gallium emiss-

ions are shown in Table V,6. The line at 294.4 nm proved the most sensitive and selective. The limits of detection were 1.9×10^{-11} g $Ga(tfa)_3$ s^{-1} and 2.7×10^{-12} g gallium s^{-1} and the selectivity was 1170.

Table V,6.

Wavelength (nm)	Peak height (mV)	Noise (mV)	S : N	Selectivity
294.4	93.0	0.12	77.5	1170 *
287.4	44.0	0.12	36.7	553*
403.3	134.0	0.24	55.8	168
417.2	160.8	0.24	50.0	159

*indicates that the detector response to benzyl alcohol was negative.

5) $Fe(tfa)_3$

The results obtained at 135°c on Column 1 are shown in Table V,7. The retention time was 2.90 min.

The limits of detection at the most sensitive emission, 344.1 nm, were 1.2×10^{-10} g $Fe(tfa)_3$ s^{-1} and 1.3×10^{-11} g iron s^{-1}.

Table V.7.

Wavelength (nm)	Peak Height (mV)	Noise (mV)	S : N	Selectivity
344.1	135.0	0.4	338	1610*
357.0	15.0	0.5	30	66*
373.5	50.0	0.5	125	711*
249.0	26.5	0.3	66.7	950*

6) $Sc(tfa)_3$

Table V.8.

Wavelength (nm)	Peak height (mV)	Noise (mV)	S : N	Selectivity
357.5	296.0	0.5	592	1110
361.4	350.0	0.5	700	1620*
363.1	274.0	0.5	548	3280*
364.4	190.0	0.5	380	2830*
391.0	137.0	1.0	137	411
402.0	94.5	1.0	94.5	945*
424.7	520	1.0	520	3840

$Sc(tfa)_3$ also gave a relatively poor peak shape but the area response was linear over a wide range. The retention time at 160°c on Column 1 was 4.0 min. The characteristics of the main emission lines are shown in Table V,8. The most sensitive line, at 361.4 nm, was adequately selective and had limits of detection of 3×10^{-11} g $Sc(tfa)_3$ s^{-1} and 3.9×10^{-12} g scandium s^{-1}.

7) $VO(tfa)_2$

$VO(tfa)_2$ was eluted after 1.45 min at 160°c on Column 1. The principal emissions are compared in Table V,9. The line at 318.4 nm was the most sensitive and selective, giving limits of detection of 5.7×10^{-11} g $VO(tfa)_2$ s^{-1} and 8.5×10^{-12}g vanadium s^{-1}. Peak shapes were not good and the range of linearity was 150.

Table V,9.

Wavelength (nm)	Peak Height (mV)	Noise (mV)	S : N	Selectivity
318.4	280.0	0.2	1400	1400*
438.1	160.0	0.4	400	160*
292.4	154.0	0.4	385	490*

8) Acetylacetonates

The acetylacetonates of aluminium, chromium and

scandium were chromatographed successfully, however no peaks could be obtained for the copper and iron chelates, presumably due to the difficulty in volatalising them in the make-shift injection port used. All three acetylacetonates had good peak shapes and a linear variation of response with concentration. The chromatographic conditions used are shown in Table V,10 and the limits of detection obtained are shown in Table V,11, along with those of the trifluoroacetylacetonates.

Table V,10.

Compound	Column	Temperature (°c)	Retention Time (min)
$Al(acac)_3$	2	175	1.67
$Cr(acac)_3$	1	190	4.80
$Sc(acac)_3$	2	190	2.70

Interferences

Interference with the response of the detector to a metal chelate may be of three types :

1. Spectral emissions from other metals or carbonaceous species at the wavelength being monitored.

Table V,11.

Compound	Wavelength (nm)	Limit of Detection g metal s^{-1}	Selectivity
$Al(acac)_3$	396.2	2.0×10^{-11}	-
$Al(tfa)_3$	396.2	1.9×10^{-11}	990
$Cr(acac)_3$	357.9	2.9×10^{-12}	-
$Cr(tfa)_3$	357.9	3.6×10^{-12}	3930
$Cu(tfa)_2$	324.7	8.0×10^{-12}	2250
$Ga(tfa)_3$	294.4	2.7×10^{-12}	1170
$Fe(tfa)_3$	344.1	1.3×10^{-11}	1610
$Sc(acac)_3$	361.4	2.1×10^{-12}	-
$Sc(tfa)_3$	361.4	3.0×10^{-12}	1620
$VO(tfa)_2$	318.4	8.5×10^{-12}	1400

2. Suppression or enhancement of the detector response by another metal chelate eluted simultaneously.
3. Distortion of the plasma by a large excess of another compound.

Type 3. is common to all compounds and methods of overcoming this problem, particularly in regard to the solvent, have been discussed in Chapter I. Types 1. and 2. will be considered separately.

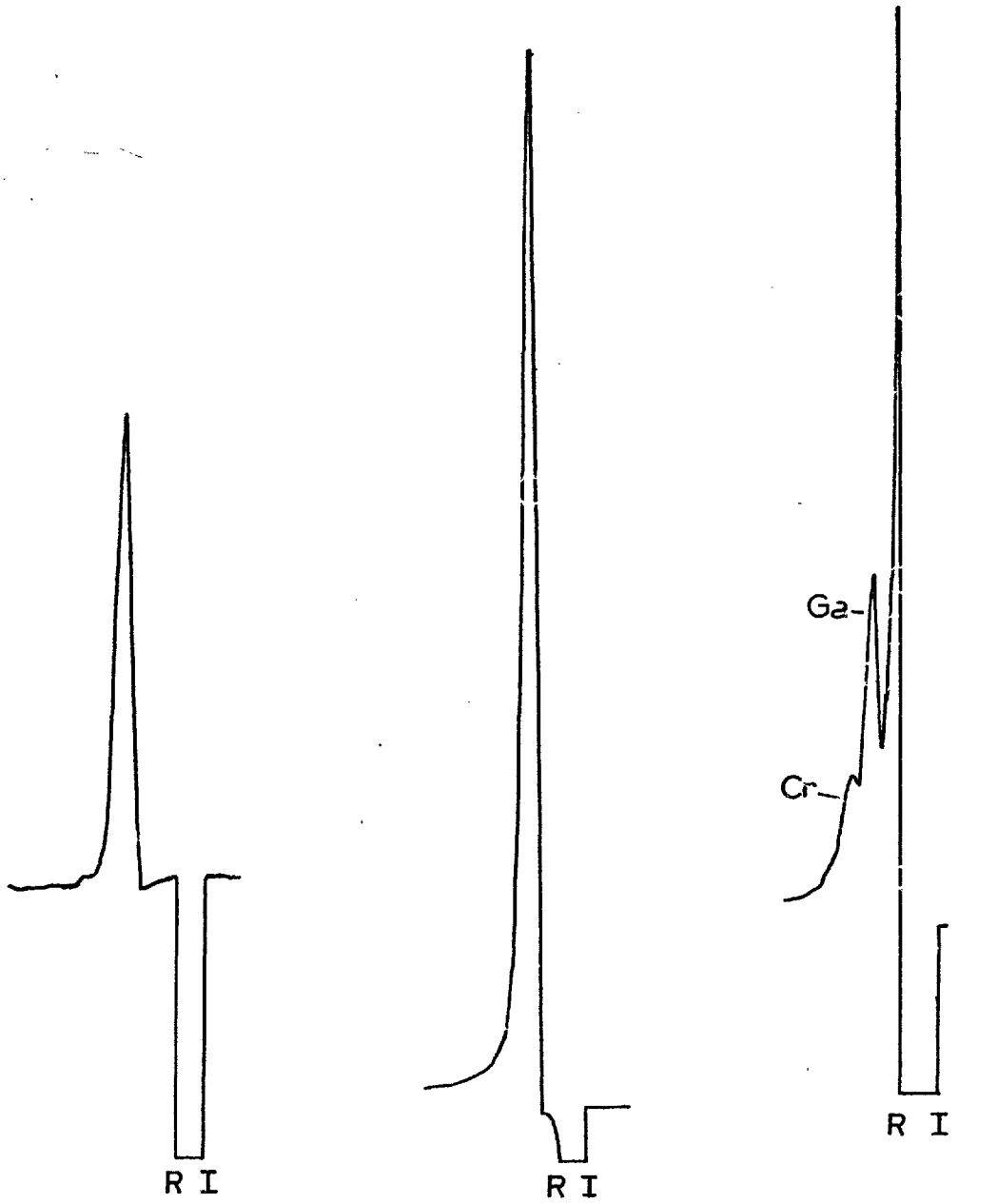
The effect of emissions from benzyl alcohol was described in the last section and was found to be generally

very small. Spectral overlap of atomic lines is less likely than with the broad molecular bands produced by carbon-containing compounds, but their greater intensity and the only moderate resolution of the monochromator makes interference from other metals a real possibility. Therefore repeated injections of 1 μl of ca. 2% solutions of each chelate in benzene were made with the monochromator set in turn to each of wavelengths listed in Table V,11. These concentrations are approximately the largest which could be injected without plasma distortion. Apart from the mutual interference of $Cr(tfa)_3$ and $Sc(tfa)_3$, the only interference observed was $VO(tfa)_2$ on $Cu(tfa)_2$. Further investigations into spectral interferences were not carried out as the selectivity could easily be increased by reducing the slit width. If a particular interference presented a problem, alternative emissions could often be used.

The second type of interference was studied by preparing mixtures of $Cr(tfa)_3$ and $Ga(tfa)_3$ in benzene and selecting gas-chromatographic conditions such that the peaks partially overlapped. Even in the presence of a 1000 fold excess of $Ga(tfa)_3$, the peak height of $Cr(tfa)_3$ did not vary by more than 2%. An example of the overlap of the peaks is shown in Figure V,12.

Characterisation of the Chromatographic Eluates

It has been standard practice (219) to collect components eluted during the gas chromatography of metal



(a) 357.8 nm (Cr)

(b) 294.4 nm (Ga)

(c) 247.9 nm (C)

R - reignition of plasma

I - injection

CHROMATOGRAMS OF A MIXTURE OF 985 p.p.m. $Ga(tfa)_3$ AND 10 p.p.m. $Cr(tfa)_3$ IN BENZENE

Figure V.12

chelates and to compare their properties with those of the original chelates, in order to establish that they are not decomposition products. This is essential when non-selective detectors are used because they can not easily distinguish between metal compounds and decomposition products eluted after similar time periods. However, with the microwave-excited emissive detector the presence of the metal emissions, particularly when two or three lines are identified, provides strong evidence of a metal compounds elution. The eluates were collected and characterised in the present study in order to confirm their identities and, in addition, to look for evidence of partial decomposition which might be shown by an impure condensate.

In order to collect sufficient of each compound 50 μl of ca. 1% solutions of each chelate in benzene were injected under the same conditions used previously. The plasma was not initiated and the silica tubing heated until the solvent was completely eluted. The tubing was cooled and the condensate collected. The melting point and infrared and ultra-violet spectra of the condensate were measured in the same way as for the chelates. The infrared spectra were not very clear owing to the small quantities of material available but the major bands could be identified. In all cases they were found to be the same as those of the pure chelates. The ultra-violet spectra were clear and showed the same absorption bands as the original chelates. The melting

points obtained are shown in Table V,12 with those of the pure chelates for comparison. The values are in close agreement.

Table V,12.

Chelate	Melting Point	
	Original (°c)	Eluate (°c)
$Al(acac)_3$	196	197
$Al(tfa)_3$	119-120	119-120
$Cr(acac)_3$	215	214-216
$Cr(tfa)_3$	132-135	152-154
$Cu(tfa)_2$	180	179
$Ga(tfa)_3$	128	128
$Fe(tfa)_3$	113-115	114-116
$Sc(acac)_3$	186	185-187
$Sc(tfa)_3$	105-106	106
$VO(tfa)_2$	indefinite	sublimed

The melting point of $Cr(tfa)_3$ is similar to that of the pure trans isomer (154.5-155) suggesting that conversion of the cis isomer to the trans form took place on the column.

Conclusions

The atmospheric pressure microwave-excited emissive detector responded to all the chelates used, both non-selectively by monitoring atomic carbon and selectively using metal emissions. The detector response was linear and highly sensitive to the metals studied with limits of detection between 2×10^{-12} gs^{-1} and 2×10^{-11} gs^{-1} (Table V,11). The limits of detection, in g metal s^{-1}, of the acetylacetonates and trifluoroacetylacetonates of the same metals were approximately equal, indicating that the detector response may well prove independent of the chelating agent used.

The sensitivity of this detector was considerably higher than other selective detectors used in metal chelate analysis, with the exception of mass spectrometry, and is comparable with that of the electron capture detector. Further, the dependence of detector response on the metal, rather than on the chelate as a whole, avoids the limitations of having a halogen atom or other electron capturing species present in order to achieve high sensitivity.

The limitations of this detector for metal analysis are similar to those for organic analysis. The principal problem is that of overloading which imposed an upper limit on the working range of the detector. In addition the formation of metal deposits required the tubing to be changed frequently when concentrated samples were used.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

The present investigation into the applications of atmospheric pressure, microwave-excited plasmas as detectors in gas chromatography has demonstrated the versatility of this type of detector. It can be used for non-selective detection by monitoring the reflected microwave power and for the selective determination of most types of organic and organometallic compounds by monitoring emissions from the plasma.

The reflected power detector provided a valuable, secondary, non-selective, detection system. Its usefulness would be increased if its sensitivity could be improved sufficiently to make it similar to that of the emissive system (ca. a factor of 5 for organic compounds). Increased stabilisation of the plasma is likely to result in higher sensitivity. Possible modifications which might lead to greater plasma stability include accurate thermostatting of the microwave cavity, cooling of the quartz tube by means of a flow of air through the cavity, more precise control of the carrier gas flow rate and a more highly stabilised microwave power supply. If the baseline drift is limited by the stability of the power

supply the possibility of comparing the reflected power from two plasmas, operating under the same conditions and powered from the same supply, also exists. In this way any drift could be compensated.

A more stable plasma would also probably result in a decrease in the background noise on the emissive detector and hence lead to an increase in sensitivity. However, more significant increases in sensitivity and selectivity with this form of the detector should result from improvements in the detection system. Of the various alternative methods of monitoring the signal produced by a monochromator and photomultiplier described in Chapter II only a.c. phase-sensitive detection offered any marked advantages over d.c. measurement. Further improvements in sensitivity could be achieved using a photomultiplier with a higher gain or an optical system which would increase the intensity of radiation from the plasma falling on the monchromator slit. The selectivity is dependent on the monochromator and slit width used. However, conditions necessary for maximum selectivity (eg. very narrow slit widths) often result in less radiation reaching the photomultiplier and, hence, in a loss of sensitivity. This was illustrated by the increase in sensitivity which resulted from the use of a solar-blind photomultiplier without a monchromator, despite the relatively low gain of this photomultiplier. The intensity of radiation reaching the photomultiplier cathode in this arrangement was much greater than that passing

through the monochromator. In view of these results the combination of narrow band-pass filters and a high gain photomultiplier might well provide the most sensitive detection system with adequate selectivity. This type of system would also have the advantage that a multi-channel arrangement with several filters and photomultipliers would be relatively easy and cheap to set up.

The detector response to a range of carbon-containing compounds when atomic carbon emission at 247.9 nm was monitored was found to be approximately independent of structure and other atoms present in the molecules and dependent only on the weight of carbon injected. If this dependence of detector response on the weight of an element present is found to hold for a wider range of compounds and for other emissions, this detector would have considerable advantages over other selective detectors. It would be able to provide a direct quantitative determination of elements present in an unknown eluate. Similarly, if the linear relationship between the ratios of atomic emissions and the inter-element ratios in a compound , which was observed for a limited number of compounds in the present study, were found to hold for a much wider range of compounds it would provide a very useful aid in the identification of unknown eluates.

The emissive detector was most sensitive to metal-containing compounds. Further research is required into the development of a technique for the formation of

chelates from very dilute aqueous solutions of metal ions, followed by their extraction and determination as gas-chromatographic eluates. Only in this way can the sensitivity of this method be compared directly with other, non-chromatographic, methods.

One form of the emissive detector which was relatively little studied during the present work was the 'open' plasma detector with the plasma maintained at the top of a quartz tube. In this arrangement the plasma was less easily extinguished but less sensitive. This form of the detector would be expected to be particularly useful for the determination of metal-containing compounds, as it would avoid the problems of metal deposits.

The sensitivity of all forms of the detector was greatest at the lowest flow rates measured, indicating that the detector might have particular applications in conjunction with capillary columns. The small dead volume of the detector would also be an advantage. However, in practice, this application has not been investigated.

It may be concluded that the present work has established the potential of the atmospheric pressure microwave-excited plasma detector in the determination and identification of gas-chromatographic eluates and indicated possible modifications which might prove useful. It remains to study the applicability of this detector to a wider range of problems and to determine what modifications are necessary to obtain optimum results in particular cases.

PUBLICATIONS.

A Simple Atmospheric Microwave-excited Emissive Detector for Gas Chromatography. Dagnall R.M., West T.S. and Whitehead P. Anal. Chim. Acta, 60, 25 (1972).

Use of the Microwave-excited Emissive Detector for Gas Chromatography for the Quantitative Measurement of Inter-element Ratios. Dagnall R.M., West T.S. and Whitehead P. In press.

A Simple Non-selective Detector for Gas Chromatography using the Measurement of Reflected Microwave Power. Dagnall R.M., Silvester M.D., West T.S. and Whitehead P. In press.

Microwave-excited Detectors for Gas Chromatography. Dagnall R.M. and Whitehead P. In press.

LITERATURE CITED.

1. Johnson H.W. and Stross F.H., Anal. Chem., 30, 1586 (1958).

2. Martin A.J.P. and Synge R.L.M., Biochem., 35, 1358 (1941).

3. Martin A.J.P. and James A.T., Analyst, 77, 915 (1952).

4. Idem, Biochem. J., 50, 679 (1952).

5. Ray P., J. Appl. Chem., 4, 21 and 82 (1954).

6. Phillips C.S.G., Disc. Farad. Soc., 7, 241 (1949).

7. Keller R.A., J. Chrom., 5, 225 (1961).

8. Tiernan T.O. and Futrell J.H., Anal. Chem., 34, 1838 (1962).

9. Anon., Gas Chromatography Terms and Relations, ASTM No. E355-68.

10. Purnell H., Gas Chromatography, Wiley, New York, London 1962, P.395.

11. Kreji M. and Dressler M., Chromatographic Reviews, 13, 1 (1970).

12. Schomburg G., Advan. Chrom., 5, 211 (1968).

13. Cremer E., J. Gas Chrom., 5, 329 (1967).

14. Martin A.J.P., Scott R.P.W. and Wilkins T., Chromatographia, 2, 85 (1969).

15. Amy J.W., Chait E.M., Baitinger W.E. and McLafferty F.W., Anal. Chem., 37, 1265 (1965).

16. Thompson A.E., J. Chrom., 6, 454 (1964).

17. Ongkiehong L., in Scott R.P.W., Editor, Gas Chromatography 1960.

18. McWilliam I.G., J. Appl. Chem., 9, 379 (1959).

19. Halasz I., Anal. Chem., 36, 1428 (1964).

20. Johnson H.W. and Stross F.H., Ibid., 31, 357 (1959).

21. Fowlis I.A. and Scott R.P.W., J. Chrom., 11, 1 (1963).

22. Williams H.P. and Winefordner J.D., J. Gas Chrom., 4, 271 (1966).

23. Swoboda P.A.T. and Burnett M.G., Anal. Chem., 34, 1162 (1962).

24. Gough T.A. and Walker E.A., Analyst, 95, 1 (1970).

25. Schmauch L.J., Anal. Chem., 31, 225 (1959).

26. Ryce S.A. and Bryce W.A., Anal. Chem., 29, 1386 (1957)

27. Keulemans A.I.M., Kwantes A. and Rijnders G.W.A., Anal. Chim. Acta, 16, 29 (1957).

28. Kieselbach R., Anal. Chem., 32, 1749 (1960).

29. Ambrose D. and Collerson R.R., J. Sci. Inst., 32, 323 (1955).

30. Hayes D.J., J. Sci. Inst. (series 2), 1, 761 (1968).

31. Chowdhury B. and Korasek F.W., J. Chrom. Sci., 8, 199 (1970).

32. Eastman R.H., J. Amer. Chem. Soc., 79, 4243 (1957).

33. Barry E.F. and Rosie D.M., J. Chrom., 63, 203 (1971).

34. Camin D.L., King R.W. and Shawhan S.D., Anal. Chem., 36, 1175 (1964).

35. Preau G. and Guichon G., J. Gas Chrom., 4, 343 (1966).

36. Claesson S., Ark. Kemi Miner. Geol., 23A, 1 (1946).

37. Martion A.J.P. and James A.T., Biochem. J., 63, 138 (1956).

38. Phillips C.S.G. and Timms P.L., J. Chrom., 5, 131 (1961).

39. Nerheim A.G., Anal. Chem., 35, 1640 (1963).

40. Martin R.L., Ibid., 32, 336 (1960).

41. Bevan S.C., Gough T.A. and Thorburn S., J. Chrom., 44, 14 (1969).

42. Guillemin C.L., Auricourt M.F., Du Crest J. and Vermont J., J. Chrom. Sci., 7, 492 (1969).

43. Bevan S.C. and Thorburn S., J. Chrom., 11, 301 (1963).

44. Bevan S.C., Gough T.A. and Thorburn S., Ibid, 42, 336 (1969).

45. Idem, Ibid, 43, 192 (1969).

46. Idem, Ibid, 44, 25 (1969).

47. Noble F.W., Abel K. and Cook P.W., Anal. Chem., 36, 1421 (1964).

48. Ryce S.A. and Bryce W.A., Can. J. Chem., 35, 1293 (1957).

49. Varadi P.F. and Ettre K., Anal. Chem., 34, 1417 (1962).

50. Boer H., in Scott R.P.W., Editor, Gas Chromatography, (1960).

51. Lovelock J.E., Shoemake G.R. and Zlatkis A., Anal. Chem., 35, 460 (1963).

52. Idem, Ibid, 36, 1410 (1964).

53. Lovelock J.E., J.Chrom., 1, 35 (1958).

54. Shahin M.M. and Lipsky S.R., Anal. Chem., 35, 1562 (1963).

55. Hill D.W. and Newell H.A., Nature, 205, 593 (1965).

56. Lovelock J.E., Ibid, 182, 1663 (1958).

57. Idem, Anal. Chem., 33, 162 (1961).

58. Berry R., Nature, 188, 579 (1960).

59. Lovelock J.E., Anal. Chem., 35, 474 (1963).

60. Idem, Nature, 189, 729 (1961).

61. Washbrooke P.F., Chemiker-Ztg., 86, 377 (1962).

62. Landowne R.A. and Lipsky S.R., Anal. Chem., 34, 726 (1962).

63. Morrison M.E. and Corcoran W.H., Ibid, 38, 255 (1967).

64. Simmonds P.G., Fenimore D.C., Pettitt B.C., Lovelock J.E. and Zlatkis A., Ibid, 39, 1428 (1967).

65. Clark S.J., Residue Rev., 5, 32 (1964).

66. Kirkland J.J. and Pease H.L., J. Agr. Food Chem., 15, 187 (1967).

67. Gaston L.K., Residue Rev., 5, 21 (1964).

68. Cook C.E., Stanley C.W. and Barney J.E. II, Anal. Chem., 35, 2354 (1964).

69. Dawson H.J., Ibid, 35, 542 (1963).

70. Lovelock J.E. and Zlatkis A., Ibid, 33, 1958 (1961).

71. Ford P.T., Ibid, 41, 393 (1969).

72. McWilliam I.G. and Dewar R.A., Nature, 181, 760 (1958).

73. Condon R.D., Scholly P.R. and Averill W., in Scott R.P.W., Editor, Gas Chromatography, 1960.

74. Thompson A.E., J. Chrom., 2, 148 (1959).

75. McWilliam I.G., Ibid, 6, 110 (1961).

76. Dewar R.A., Ibid, 6, 312 (1961).

77. Knewstubb P.F. and Sugden T.M., Nature, 181, 474 (1958).

78. Bocek P., Novak J. and Janak J., J. Chrom., 43, 431 (1969).

79. Ettre L.S. and Kabot F.J., J. Gas Chrom., 1 (10), 7 (1963).

80. Idem, J. Chrom., 11, 114 (1963).

81. Perkins G., Laramy R.E. and Lively L.D., Anal. Chem., 35, 360 (1963).

82. Maggs R.J., Column, 1 (2), 2 (1966).

83. Deans D.R., Chromatographia, 1, 187 (1963).

84. Bocek P., Novak J. and Janak J., J. Chrom., 48, 412 (1970).

85. Giuffrida L., J. Assoc. Off. Agric. Chem., 47, 293 (1964).

86. Karmen A., Anal. Chem., 36, 1416 (1964).

87. Brazhnikov V.V., Gurev M.V. and Sakodynskii V.I., Chrom. Rev., 12, 1 (1970).

88. Karmen A. and Guiffrida L., Nature, 201, 1204 (1964).

89. Karmen A., J. Chrom. Sci., 7, 541 (1969).

90. Dressler M. and Janak J., J. Chrom., 44, 40 (1969).

91. Idem, J. Chrom. Sci., 7, 451 (1969).

92. Aue W.A, Gehrke C.W., Tindle R.C., Stalling D.L. and Ruyle C.D., J. Gas Chrom., 5, 381 (1967).

93. Hartmann C.H., J. Chrom. Sci., 7, 163 (1969).

94. Cremer E., J. Gas Chrom., 5, 329 (1967).

95. Ives N.F. and Guiffrida L., J. Ass. Off. Anal. Chem., 50, 1 (1967).

96. Janak J., Svojancvsky V. and Dressler M., Collect. Czech. Chem. Commun., 33, 740 (1968).

97. Dressler M., Martinu V. and Janak J., J. Chrom., 59, 429 (1971).

98. Lakota S. and Aue W.A., Ibid, 44, 472 (1969).

99. Aue W.A., Gerhardt K.O. and Lakota S., Ibid, 63, 237 (1971).

100. Svojanovsky V., Dressler M. and Janak J., Collect. Czech. Chem. Commun., 31, 3925 (1966).

101. Karmen A., J. Gas Chrom., 3, 336 (1965).

102. Kingdon K.H. and Langmuir I., Phys. Rev., 21, 380 (1923).

103. Cremer E., Kraus T. and Bechtold E., Chem. Ing. Tech., 33, 632 (1961).

104. Larkham T. W. and Pagington J.S., J. Chrom., 28, 422 (1967).

105. McLeod H.A. and McKinley W.P., J. Ass. Off. Anal. Chem., 50, 641 (1967).

106. Devjatych G.G., Agliulov N.C. and Lucinkin V.V., Zavod. Lab., 32, 901 (1967).

107. Hartley J. and Pretorius V., Nature, 178, 1244 (1956).

108. Pitkethly R.C., Anal. Chem., 30, 1309 (1958).

109. Ryce S.A. and Bryce W.D., Nature, 179, 541 (1957).

110. Yamane M., J. Chrom., 9, 162 (1962).

111. Idem, Ibid, 11, 158 (1963).

112. Fischer E.R. and McCarthy M.Jr., Anal. Chem., 37(10), 1208 (1965).

113. Arnikar H.J., Rao T.S. and Karmarkar K.H., J. Chrom., 26, 30 (1967).

114. Idem, Ind. J. Chem., 5, 480 (1967).

115. Idem, J. Chrom., 38, 126 (1968).

116. Price J.G.W., Fenimore D.C., Simmonds P.G. and Zlatkis A., Anal. Chem., 40, 541 (1968).

117. Freeman R.W. and Wentworth W.E., Ibid, 43, 1987 (1971).

118. Lovelock J.E., Nature, 188, 401 (1960).

119. Locke D.C. and Meloan C.E., Anal. Chem., 37, 389 (1965).

120. Roesler J.F., Ibid, 36, 1900 (1964).

121. Holmes J.C. and Morrell F.A., Appl. Spectroscopy, 11, 86 (1957).

122. Littlewood A.B., Chromatographia, 1, 37 (1968).

123. Schulze P. and Kaiser K.H., Ibid, 4, 381 (1971).

124. Gohlke R.S., Anal. Chem., 34, 1332 (1962).

125. Ebert A.A., Ibid, 33, 1865 (1961).

126. Henneberg D., Ibid, 38, 495 (1966).

127. Ryhage R., Ibid, 36, 759 (1964).

128. Gryson M.A. and Wolf C.J., Ibid, 39, 1438 (1967).

129. Levy R.L., Gesser H.B., Westmore J.B., J. Chrom., 32, 740 (1968).

130. Evans S., J. Sci. Instr., 44, 676 (1967).

131. Hawes J.E., Mallaly R. and Williams V.P., J. Chrom. Sci., 7, 690 (1969).

132. Banner A.E., Elliot R.M. and Kelly W., in A. Goldup, Editor, Gas Chromatography, 1964, Institute of Petroleum, London, 1965, P. 180.

133. McMurray W.J., Greene B.N. and Lipsky S.R., Anal. Chem., 38, 1194 (1966).

134. Dorsey J.A., Hunt R.H. and O'Neal M.J., Ibid, 35, 511 (1963).

135. Leathard D.A. and Shurlock B.C., Identification Techniques in Gas Chromatography, Wiley Interscience, London, 1970.

136. Kenneth B.H., Anal. Chem., 39, 1506 (1967).

137. American Society for Testing and Materials, Committee E-14, Index of Mass Spectral Data ASTM Special Technical Publication, No.356, Philadelphia (1963) and Publication AMD11(1969).

138. Henneberg D., 4th Wilkens Gas Chrom. Symp., Great Britain, 1966.

139. Henneberg D. and Schornburg, in Van Swaay M., Editor, Gas Chromatography, 1962, Butterworth, London, 1962, P. 191.

140. Teranishi R., Buttery G.R., McFadden W.M., Mon T.R. and Wassermann J., Anal. Chem., 36, 1509 (1964).

141. Tal'roze V.L., Tantsyrev G.D. and Gorskov V.I., Zh. Anal. Khim., 20, 103 (1965).

142. McFadden W.H., Advan. Chrom., 4, 265 (1967).

143. Brody S.S. and Chaney J.E., J. Gas Chrom., 4, 42 (1966).

144. Mizany A.I., J. Chrom. Sci., 8, 251 (1970).

145. Versino B. and Rossi G., Chromatographia, 4, 331 (1971).

146. Stanley C.W. and Morrison J.I., J. Chrom., 40, 289 (1969).

147. Bowman M.C. and Beroza M., Environ. Sci. Technol., 2, 450 (1968).

148. Idem, Anal. Chem., 40, 1448 (1968).

149. Grice H.W., Yates M.L. and David D.J., J. Chrom. Sci., 8, 90 (1970).

150. Crider W.L. and Slater R.W.Jr., Anal. Chem., 41, 531 (1969).

151. Selucky M.L., Chromatographia, 4, 425 (1971).

152. Perry S.G. and Carter F.W.G., 8th International Symp. on Gas Chrom., Dublin, Sept. 1970.

153. Stevens R.K. and O'Keeffe A.E., Anal. Chem., 42, 143A (1970).

154. Aue W.A. and Moseman R.F., J. Chrom., 61, 35 (1971).

155. Novak A.V. and Malmstadt H.V., Anal. Chem., 40, 1108 (1968).

156. Bowman M.C., Beroza M. and Hill K.M., J. Chrom. Sci., 9, 162 (1971).

157. Bowman M.C. and Beroza M., Ibid, 7, 484 (1969).

158. Overfield C.V. and Winefordner J.D., Ibid, 8, 233 (1970).

159. Aue W.A. and Moseman R.F., J. Chrom., 49, 432 (1970).

160. McCormack A.J., Tong S.C. and Cooke W.D., Anal. Chem., 37, 1470 (1965).

161. Bache C.A. and Lisk D.J., Ibid, 37, 1477 (1965).

162. Idem, Ibid, 38, 183 (1966).

163. Idem, Ibid, 38, 1757 (1966).

164. Idem, Ibid, 39, 786 (1967).

165. Bache C.A., St.John L.E. and Lisk D.J., Ibid, 40, 1241 (1968).

166. Moye H.A., Ibid, 39, 1441 (1967).

167. Dagnall R.M., Pratt S.J., West T.S. and Deans D.R., Talanta, 16, 797 (1969).

168. Idem, Ibid, 17, 1009 (1970).

169. Braun W., Peterson N.C., Bass A.M. and Kurylo M.J., J. Chrom., 55, 237 (1971).

170. Kamada H. and Kokubun N., Japan Analyst, 17, 575 (1968).

171. Braman R.S. and Kynako A., Anal. Chem., 40, 95 (1968).

172. Ambrose D., Gas Chromatography, Butterworths, London, 1971.

173. Bowman M.C. and Beroza M., Anal. Chem., 40, 535 (1968).

174. Kaye W., Ibid, 34, 287 (1962).

175. Merritt J.Jr., Comendant F., Abrams S.T. and Smith V.N., Anal, Chem., 35, 1461 (1963).

176. Kaye W. and Waska F., Ibid, 36, 2380 (1964).

177. Haahti E.A. and Fales H.M., Chem. Ind. (London), 507 (1961).

178. Stime K.E., Sloane H.S. and Cavenah R.C., 17th Pittsburgh Conf. Anal. Chem. Appl. Spec., Pittsburgh Pa., Feb. 1966.

179. Coulson D.M. and Cavanagh L.A., Anal. Chem., 32, 1245 (1960).

180. Burke J. and Holswade W., J. Ass. Off. Anal. Chem., 47, 845 (1964).

181. Cavanagh L.A., Coulson D.M., McCarthy E.M., Sulas L.J. and Wilton V., Pittsburgh Conf. on Anal. Chem. Appl. Spec., Pittsburgh Pa., March 1962.

182. Klaas P.J., Anal. Chem., 33, 1851 (1961).

183. Martin R.L. and Grant J.A., Ibid, 37, 644 (1965).

184. Nelson R.C., J. Ass. Off. Agric. Chem., 47, 289 (1964).

185. Adams D.F., Jensen G.A., Steadman J.P., Koppe R.K. and Robertson T.J., Anal. Chem., 38, 1094 (1966).

186. Burchfield H.P., Rhoades J.W. and Wheeler R.J., 148th Am. Chem. Soc. Meeting, Chicago, Sept. 1964.

187. Fredericks E.M. and Harlow G.A., Anal. Chem,, 36, 263 (1964).

188. Burchfield H.P. and Wheeler R.J., J. Ass. Off. Anal. Chem., 49, 651 (1966).

189. Martin R.L., Anal. Chem., 38, 1209 (1966).

190. Hersch P.A., Ibid, 32, 1030 (1960).

191. Hillman G.E. and Lightwood J., Ibid, 38, 1430 (1966).

192. Bechtold E., Z. Anal. Chem., 221, 262 (1966).

193. Littlewood A.B. and Wiseman W.A. , in Littlewood B.A., Editor, Gas Chromatography 1966, Inst. of Petroleum (1967), P. 193.

194. Coulson D.M., J. Gas Chrom., 3, 134 (1965).

195. Idem, Advan. Chrom., 3, 197 (1966).

196. Johns T. and Braithwaite C.H.Jr., Residue Rev., 5, 45 (1964).

197. Patchett G.C., J. Chrom. Sci., 8, 155 (1970).

198. Kojiima T., Seo Y. and Nishida J., Japan Analyst, 17, 1496 (1968).

199. Janak J., Nedorost M. and Bubenikova V., Chem. Listy, 51, 890 (1957).

200. Van Duyne R.P. and Aikens D.A., Anal. Chem., 40, 254 (1968).

201. Fleet B. and Risby T.H., Talanta, 16, 839 (1969).

202. Taylor H.E., Gibson J.H. and Skogerboe R.K., Anal. Chem., 42, 876 (1970).

203. Gaydon A.G. and Pearse R.W.B., The Identification of Molecular Spectra, 3rd Edition, Chapman and Hall Ltd., London (1965).

204. Davis D. and Braun W., Applied Optics, 7, 2071 (1968).

205. Aldous K.M., Dagnall R.M., Sharp B.L. and West T.S., Anal. Chim. Acta, 54, 233 (1971).

206. Alger D., Dagnall R.M., Sharp B.L. and West T.S., Ibid, 57, 1 (1971).

207. Dagnall R.M., Sharp B.L. and West T.S., Nature (Phys. Science) 235, 65 (1972).

208. Cooke D.O., Dagnall R.M., Sharp B.L. and West T.S., Spec. Letts., 4, 91 (1971).

209. Dagnall R.M., Silvester M.D. and West T.S., Talanta, 18, 1103 (1971).

210. Juvet R.S.Jr. and Wachi F.M., Anal. Chem., 32, 290 (1960).

211. Keller R.A., J.Chrom., 5, 225 (1961).

212. Juvet R.S. and Fisher R.L., Anal. Chem., 37, 1753 (1965).

213. Dagnall R.M., Deans D.R., Fleet B. and Risby T.H., Anal. Letters, 3, 143 (1970).

214. Freiser H., Anal. Chem., 31, 1440 (1959).

215. Tadmor J., J. Gas Chrom., 2, 385 (1964).

216. Myers H.W. and Purnam R.F., Anal. Chem., 34, 664 (1962).

217. Lederer M., Nature, 176, 462 (1955).

218. Biermann W.J. and Gesser H., Anal. Chem., 32, 1525 (1960).

219. Moshier R.W. and Sievers R.E., Gas Chromatography of Metal Chelates, Pergamon Press, Oxford, 1965.

220. Sievers R.E., Ponder B.W., Morris M.L. and Moshier R.W., Inorg. Chem., 2, 693 (1963).

221. Hill R.D. and Gesser H., J. Gas Chrom., 1, 11 (1963).

222. Ross W.D., Anal. Chem., 35, 1596 (1963).

223. Morris M.L., Moshier R.W. and Sievers R.E., Inorg. Chem., 2, 411 (1963).

224. Sievers R.E., Chem. and Eng. News, 41, 41 (1963).

225. Ross W.D. and Wheeler G.Jr., Anal. Chem., 36, 266 (1964).

226. Morie G.P. and Sweet T.R., Anal. Chim. Acta, 34, 314 (1966)

227. Idem, Anal. Chem., 37, 1552 (1965).

228. Savory J., Mushak P. and Sundermann F.W.Jr., J. Chrom. Sci., 7, 674 (1969).

229. Belcher R., Dudeney A.W.L. and Stephen W.I., J. Inorg. Nucl. Chem., 31, 625 (1969).

230. Stephen W.I., Thompson I.J. and Uden P.C., Chem. Commun., 269 (1969).

231. Belcher R., Stephen W.I., Thompson I.J. and Uden P.C., J. Inorg. Nucl. Chem., 33, 1851 (1971).

232. Idem, Chem. Commun., 1019 (1970).

233. Stephen W.I., Proc. Soc. Anal. Chem., 9, 137 (1972).

234. Albert D.K., Anal. Chem., 36, 2034 (1964).

235. Barratt R.S., Proc. Soc. Anal. Chem., 9, 86 (1972).

236. Juvet R.S. and Durbin R.P., J. Gas Chrom., 1, 14 (1963).

237. Idem, Anal. Chem., 38, 565 (1966).

238. Juvet R.S. and Zado F.M., Ibid, 38. 569 (1966).

239. Wolf W.R., Taylor M.L., Hughes B.M., Tiernan T.O, and Sievers R.E., Ibid, 44, 617 (1972).

240. Bache C.A. and Lisk D.J., Ibid, 43, 951 (1971).

241. Runnels J.H. and Gilson J.H., Ibid, 39, 1398 (1967).

242. Young R.C., Inorganic Syntheses, Vol. II, 25 (1946).

243. Berg E.W. and Truemper J.T., J. Phys. Chem., 64, 487 (1960).

244. Fay R.C. and Piper T.S., J. Am. Chem. Soc., 85, 500 (1963).

245. Idem, Inorg. Chem., 3, 348 (1964).

246. Henne AL., Newman M.S., Quill L.L. and Staniforth R.A., J. Am. Chem. Soc., 69, 1819 (1947).

247. Reid J.C. and Calvin M., Ibid, 72, 2948 (1950).

248. Stanforth R.A., Dissertation, Ohio State University (1943).

249. Nakamoto K., Infrared Spectra of Inorganic and Coordination Compounds, 2nd Edition, Wiley Interscience (1970).

250. Nakamoto K., Morimoto Y. and Martell A.E., J. Phys. Chem., 66, 346 (1962).

251. Morris M.L., Moshier R.W. and Sievers R.E., Inorg. Chem., 2, 411 (1963).

252. Charles R.G., J. Inorg. Nucl. Chem., 6, 42 (1958).

253. Holm R.H. and Cotton F.A., J. Am. Chem. Soc., 80, 5658 (1958).

254. Bamum D.W., J. Inorg. Nucl. Chem., 21, 221 (1961).

255. Idem. Ibid, 22, 283 (1962).

256. Hazeldine R.N., Musgrave W.K.R., Smith F. and Turton L.M., J. Chem. Soc., 609 (1951).

257. Meggers W.F., Corliss C.H. and Scribner B.F., Tables of Spectral-line Intensities, N.B.S. Monograph 32, Part I (1961).

258. Hamlin A.G., Iveson G. and Phillips T.R., Anal. Chem., 35, 2037 (1963).

259. Belcher R., Jenkins C.R., Stephen W.I. and Uden P.C., Talanta, 17, 455 (1970).