SPECTROSCOPIC DETECTION OF VOLATILE FLUORIDES FOLLOWING GAS CHROMATOGRAPHIC SEPARATION.

by

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Abstract.

This thesis is concerned with selective detection systems in gas chromatography and with the preparation and separation of volatile fluorides.

Firstly, a reactor-injection system was designed which would form these fluorides rapidly and quantitatively in a reproducible manner.

Secondly, a spectroscopic detector was developed which is based on the emission observed in a low temperature diffusion flame. Complete spectra (280-700 nm) were obtained for all the elements under investigation and calibration curves were plotted for these elements at the wavelength of their maximum emission.

Thirdly, various separations were attempted and the eluent was examined by a katharometer and the

spectroscopic detector.

Finally, a detector selective to carbonyl compounds which was based on the polarographic reduction of the azomethine group was developed and evaluated.

Acknowledgments.

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

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Introduction.

1.Historical.

Chromatography is an analytical technique based on differences in the partition coeffieients between a static phase usually of large surface area, and a moving fluid phase. It is likely that the process has been operative in nature since earliest times, but its history as a method of analysis is only a little over sixty years. Tswett[1] was the first person whose experiments could be unequivocally regarded as chromatography. He separated the components of plant pigments by passing their solution through columns of solid adsorbents. It was the formation of these coloured solute rings that suggested the name Chromatography, (colour writing), but in view of the nature of the technique as it is applied at present it is apparent that it could be more accurately named.

The major advance, in this technique, came thirty-five years later when Martin and Synge[2] introduced the idea of paper chromatography. They went even further to suggest, in the same paper, that the liquid phase could be replaced by a gas phase. Some ten years later Martin and James[3] revived this line of approach and produced the idea of elution gas chromatography. The tremendous interest aroused by this paper is evidenced by the fact that this method has become the most widely used technique and is responsible for the ten percent of all published work in the field of analytical chemistry. Cremer and Mueller[4], Zhuklovitskii et al[5], Janak[6], Ray[7], and Patton et al[8] were responsible for the pioneering work in the field of gas-solid chromatography, while James and Martin[9], James and Phillips[10], Ray[11], and Bradford et al[12] produced the most influential papers on the gas-liquid technique. The rate at which papers are being published is still increasing, about 500 papers were published in 1958 but by 1962 this figure had leapt to a rate of 2,000 per year and in 1969 it was 3,000.

The vast majority of these papers have dealt with the feasibility of separation of particular mixtures. The rest of these papers are technique-centred and they represent about twenty-five percent of the published articles. The major areas of effort are still the evaluation of new and modified column systems. In the realm of the separation process we find two opposing developments, on the one hand we have the use of very large bore columns for preparative purposes which could possibly develop into a method of large scale manufacture of pure compounds, whilst on the other hand the use of packed capillary and open tubular columns have been shown to be advantageous for the separation of certain complex mixtures. The field still provides considerable scope for ingenuity and some of the more promising areas which are related to the subject of this thesis will now be considered in more detail.

II. Detection Systems.

With the development of the ability to separate compounds the need for the accurate determination of the composition and concentration of the eluting peaks has become more and more important. For although most aspects of gas chromatography have been extensively studied and developed, relatively little attention has been paid to methods of peak identification, in spite of the fact that without such methods analytical gas chromatography is rendered useless. This neglect is largely due to the common practice of relying entirely upon retention coincidence methods, a situation which has undoubtedly led to much qualitative error. The separation of a mixture affords three pieces of information on a particular peak, the retention volume, the peak width, and the peak height.In a few cases it is possible to achieve a qualitative and quantitative analysis on this data alone, but generally the number of ambiguities is so large that other methods of characterisation must be resorted to.

There are three major ways in which the peak may be characterised: (i) post-column trapping techniques, (ii) retention data, (iii) selective detection systems. (iv) Pre-column reactors.

II. i. Post Column Trapping Techniques.

Most designs rely upon a relatively large amount of solvent or a very low temperature to reduce the vapour pressure of an eluent to the point where it is effectively trapped. The first type of trap may suffer from the disadvantage that any subsequent treatment of the eluent is accompanied by interference from a much larger quantity of solvent. However, in certain cases such traps present no problems; for example, if the eluent is of much higher boiling point than the solvent the latter may be removed by distillation, or if an infra-red or ultra-violet spectrum may be allowed for. Nevertheless, for most purposes, the low temperature trap is the most convenient.

The rapid cooling needed to liquefy any reasonably volatile eluent usually results in the formation of a very fine mist which is swept straight through the trap. In order to retain these minute droplets, it is necessary for them to come into contact with a surface. As such droplets are frequently charged, it is possible that simple charge neutralisation processes are responsible for this behaviour. Indeed electrical precipitation is often used to improve trapping efficiences[13,14], However, it is likely that adsorption and heat transfer effects are also important. In the unpacked trap the droplets, which are formed next to the wall, stand the greatest chance of being retained. Hence, to improve trapping efficiencies it is necessary to increase the surface-to-volume ratio, as in packed columns, or to increase the number of times the droplet formation occurs, as with multiple temperature gradients. The Volman trap[15] consists of a double-walled vessel with its inner and outer walls at different temperatures and it is extremely efficient. Simple 'U' tubes cooled in liquid air and packed with materials of high surface area, such as firebrick have been used to trap the eluent with an efficiency of about 70%[16]. Other methods which involve freezing out both the carrier gas and the eluent have been described but they are even less efficient[17,18].

However, when submicrogram samples are being trapped the recovery and handling of them is critical, and wherever possible continuous monitoring of the effluent is desirable. Amy et al[19], have described an attractive technique for trapping very small samples (10^{-11} moles) prior to introduction into mass spectrometer. In this method the eluent is trapped in a short, thin-walled glass capillary filled with an adsorbant packing. These mini-columns, which enable any fraction to be trapped, are easily sealed and stored until they can be analysed.

Two trapping techniques designed especially for use with infra-red analysis have also be described. In the first of these the condensed droplets of the eluent may be directly deposited onto potassium bromide plates[20] or alternatively the condensed droplets of the eluent may be filtered on a 25µ thick cellulose membrane, with a pore size of about 0.5µ, so that the sample is ready for immediate presentation to the spectrometer[21].

II. ii. Retention Data.

The simplest method of identification of an unknown peak is to compare its retention volume with that of an authentic sample generally by the method of standard addition. This method, is extremely simple, provided the identity of the unknown sample is limited to a few possibilities.

II.ii.i. Multiple column plotting.

The use of retention data from two columns reduces the chances of incorrect assignment due to simultaneous elution particularly if stationary phases of varying polarity are employed. Perhaps it should also be mentioned that the twin-column plotting of chromatograms is useful in cases where a single peak is in fact due to two or more compounds which are not resolved. Various correlation diagrams may be used to help identify the chromatogram. For a homologous series of compounds the dependance of the log. of their retention volumes on the number of atoms in the chain is rectilinear. Also a plot of the dependance of the log. of their retention volumes, due to one column, on the log. of their retention volumes, due to another column is rectilinear. Similarly this can be extended to a third dimension by using another axis which is the log. of the retention volume, due to a third column and thus it is almost impossible for a mistake to be made in identification.

II.ii.ii. Kovats retention index.

A further method of characterising results is based on the idea of Kovats[22], which uses the retention volumes of an homologous series of n-paraffins. The retention index of any substance X is defined as:

$$I_x = 100n + 100\left[\frac{\log. Vr^x - \log. Vr^n}{\log. Vr^{n+1} - \log. Vr^n}\right]$$

where an n-paraffin retention index is $I_n = 100n$ and Vr^x, Vr^n, and Vr^{n+1} are the retention volumes of X and the n-paraffins with n and n+1 carbon atoms, chosen so that X is eluted somewhere between them.

In effect, the use of these equations is equivalent to plotting log. Vr^n against I_n ($= 100n$) and reading off the appropriate value of I which places log. Vr^x on the straight line. This method is the best approach to a universal method of expressing retention data and Kováts has collected data for a wide range of compounds employing different stationary phases.

II.iii. Selective Detection Systems.

In recent years there has been widespread interest in the development of selective detection systems for gas chromatography. These were developed so that the individual peaks could be identified and assigned conclusively. The idea of being able to assign a compound to a particular elemental or functional group is very attractive and eliminates the need for reliance on retention data.

There are two main basic types of detection systems; (i) a detector which is selective to a particular element or group of elements, and (ii) a detector which is selective to a particular functional group or series of functional groups.

II.iii.i. Elemental detectors.

These are detectors which are destructive and break the eluent into its elements before detection. There are three main types of detection systems; (i) detection systems based on flame, (ii) detection systems based on some electrical properties and (iii) detection systems based on emission excited by discharges.

II.iii.i.i. Flame detection.

The earliest type of detector to employ a flame was the flame ionisation detector. This is based on the measurement of the ionisation produced when certain molecules are burnt in a hydrogen diffusion flame. Although the extent of ionisation is related to the number of carbon atoms in the molecule[23,24], correlation is insufficiently accurate to give quantitative information about an unknown eluent with the exception of a limited range of hydrocarbons.

As it was noticed that the signals due to organosilicon compounds were negative the flame ionisation detector can be used to detect organosilicon compounds selectively if only negative peaks are considered[25]. The flame ionisation detector has also been modified so that it is only sensitive to halogen and phosphorus containing compounds[25-35]. This detector consists of a conventional detector arranged so that the flame impinges upon a wire gauze which is pretreated with an alkali metal, or alkali hydroxide, or alkali metal salt. It is found that the presence of halogen or phosphorus containing compounds enhances the rate of release of the alkali metal vapour from the heated gauze and therefore the electrical conductivity of the flame is increased. The detector is found to detect compounds in the nanogram region. Similarly the flame ionisation detector has been modified so that the detector is selective to nitrogen containing compounds[36].

Monkman and Dubois[37] described a flame photometric detection system selective to halogen containing compounds. The eluent from the column is passed into an air-methane (or coal gas) flame via a burner containing a copper element. When a halogen containing compound is introduced into the flame, characteristic radiation in the region of 520nm. is emitted. The response due to this emission is fed into a recorder and compared with the detection obtained by a non-selective detector system. This design was further modified[38] and a copper screen thimble is used in place of the copper element. The sensitivity which was obtained was 5µg. of chlorine and methods were given to enhance this detection limit. This detector is also found to respond to the cyanide group and to other groups which form cyanide in the flame.

The use of flame photometric detection systems has also been investigated[39] for the selective detection of metal chelates. The chelates studied were hexafluoroacetylacetonates of iron(iii), chromium(iii), and rhodium(iii). The eluent from the column is passed into an oxy/hydrogen flame burning on a Beckman Model 4030 atomiser burner assembly. The Beckman DU spectrophotometer is set to monitor at the following wavelengths which were found to be the optimum emission band heads: 425.4nm.for chromium, 372.0nm for iron, and 368.2nm for rhodium and preliminary estimates of the detector sensitivity were found to be as follows: chromium 2.1×10^5, iron 7.5×10^3 and rhodium 1.1×10^5 mV-ml/mg. of metal.

Kolb, Kemmen, Schlesser, and Wiedeking[40] coupled with outlet from a chromatograph to the burner of an atomic absorption spectrophotometer. This arrangement using a lead hollow cathode lamp provided a specific detector for lead. The compounds studied were lead tetraethyl and lead tetramethyl in the presence of chlorinated hydrocarbons and aromatics; no interferences were observed.

A flame photometric detector has been described which is selective to sulphur or phosphorus containing compounds[41]. The eluent (nitrogen carrier gas) from the column is mixed with oxygen (in the same proportion as in air) and then passed into a burner where it is mixed with hydrogen. Sulphur and phosphorus were found to emit radiation by a chemiluminescent mechanism and these emissions were due to the S_2 and the HPO species. These emissions have maximum band heads at 394nm for the S_2 species and 526 for the HPO species. Narrow band pass interference filters were used so that the emissions may be observed specifically. The detection system is sensitive to parts per million for sulphur and parts per thousand million for phosphorus. The response to phosphorus compounds is found to be linear over a range of at least four decades of concentration whereas the response to sulphur compounds varies exponentially in the range 1-100 parts per million. This detector suffered from no interferences even when large excesses of organic compounds containing chlorine, nitrogen, and oxygen are also involved.

Getz[42] has employed the flame photometric detector previously described[41] to determine residues of organophosphorus pesticides from various sources. It was shown that these compounds could be determined selectively in the nanogram region without the need for prior removal of large quantities of chlorinated compounds.

Juvet and Durbin continued their earlier work[39] and described a flame photometric detector which is suitable for the detection of metal halides or metal chelates[43]. The eluent from the column is passed into an oxy/hydrogen flame and the photomultiplier viewed the radiation produced in the flame after it has passed through a Beckman DU spectrophotometer. The following detection limits were obtained: titanium (iv) chloride at 544.9nm(band head) 4×10^{-11}M; arsenic(iii) chloride at 500.0nm(band head) 2×10^{-8}M; zirconium(iv) chloride at 564.0nm (band head) 2x10^{-8}M; rhodium(iii) hexafluoroacetylacetonate at 369.2nm(doublet head) 1x10^{-11}M; chromium(iii) hexafluoroacetylacetonate at 425.4nm. (triplet head) 1x10^{-10}M; and the band heads due to CH at 431.5nm. and due to C_2 at 516.5nm.gave detection limits for organic compounds of the order of 10^{-7}M. No problems of corrosion or interferences were observed.

An air/hydrogen flame photometric detector has been used[44] to study the emission due to organic compounds. By comparison of the intensity of the emission due to NH_2 at 589nm; C_2 at 516.5nm and CH at 431.5nm it is possible to detect selectively certain types of compounds.

The construction and performance of a simple, inexpensive and sensitive recording flame photometric detector has been described[45] for the determination of transitional metal halides, chelates, and organic compounds. The eluent it passed into an oxy/hydrogen flame burning on a Beckman burner and the emission is observed through A bausch and Lamb Spectronic colorimeter-spectrophotometer or a filter which transmits radiation in the region 355-625nm. The following detection limits were obtained; molybdenum(vi) fluoride selectively at 520nm $3x10^{-10}M$, non-selectively $2x10^{-11}M$; tungsten(vi) fluoride selectively at 520nm $7x10^{-10}M$, non-selectively $6x10^{-11}M$; aluminium(iii) trifluoroacetylacetonate selectively at 486nm $5x10^{-9}M$, non-selectively $2x10^{-10}M$; rhodium(iii) hexafluoroacetylacetonate selectively at 569nm $7x10^{-10}M$. non-selectively $3x10^{-10}m$; chromium(iii) hexafluoroacetylacetonate selectively at 427nm $6x10^{-10}M$, non-selectively $2x10^{-10}M$; and organic compounds at 431nm selectively $1x10^{-6}M$, non-selectively $2x10^{-8}M$. The data presented indicates that this system is unable to distinguish between tungsten and molybdenum.

A dual flame photometric detector has been described[46] capable of monitoring gas chromatographic effluents with high sensitivity and selectivity. One channel was specific to sulphur compounds and the other to phosphorus compounds. This enables both sulphur and phosphorus determinations to be performed at the same time and thus reduces the time in which complete analysis can be performed.

The modified flame ionisation detector responsive to the halogen and phosphorus compounds[26-35] has also been used where, instead of monitoring the change in electrical conductivity the emission due to sodium at 589nm. was measured. This resulted in an increase in sensitivity of the detection.

II.iii.i.ii. Detectors based on electrical properties.

Various detection systems have been described in which the eluent is titrated with coulometrically generated ions. In the majority of these determinations it is necessary to convert the eluent into a compound which may be coulometrically titrated. For the detection of nitrogen containing compounds the eluent is mixed with hydrogen and the resulting gas is passed through a nickel/magnesium oxide catalyst to convert the nitrogen containing compounds into ammonia which is then titrated with coulometrically generated hydrogen ions[48]. Similarly halogen containing compounds have been converted into halide ion which can then be titrated with electrogenerated silver ions[49-53]. However, in some cases it is not necessary to convert the eluent, for example, thiols may be titrated (to less than 1 ppm.) with coulometrically generated silver ions[54]. The Hersch cell[55] has been adapted for the measurement of oxygen from the gas chromatographic column[56] and Lucero[57] has discussed a mathematical model for the performance of membrane galvanic detectors. Littlewood and Wiseman[58] described a system in which the eluent from the chromatographic column is mixed with a stream of electrogenerated hydrogen and passed through the reactor of hydrogenation catalyst to a detector which consisted of a galvanic hydrogen cell. The output from the detector is amplified and controls the generation of the hydrogen via a servomechanism. A more recent modification of this principle utilises electrogenerated oxygen to combust the sample and an oxygen to monitor the combustion products[59].

Bechtold[60] described a detector for the selective determination of halogens and sulphur in which the eluting gas is either oxidised or reduced before it is passed into a solid state electrochemical cell. This cell consisted of;

Pt/Ag/AgI/AgS/Pt   or   Pt/Ag/AgI/Pt

As the supporting electrolyte, which was silver iodide, is completely ionised at about 180°C the cell is maintained at a temperature above 180°C. The emf of this cell is found to be proportional to the concentration of the halide or sulphide ion and the response is found to be linear over a wide concentration range. This detector is not adversely affected by high concentration of halogen or sulphur containing compounds.

II.iii.i.iii. Detectors based on discharges.

Observations of the light emitted by a species excited by a discharge, form the last major technique which is suitable for a detection system for elements in gas chromatography. The first discharge detector was developed by Sternberg and Poulson[61] and they developed two detectors based on properties of the 'Tesla' discharge. The eluent from the column passed through a capillary tube where it is subjected to a high frequency 'Tesla' source. It was found that the sensitivity of this technique increased if the pressure in the capillary tube is reduced to about 3 torr. The signal was measured either by direct measurement of the emitted light intensity or by measurement of the direct current produced between a pair of probe electrodes placed asymmetrically in the discharge. The response was found to increase with increased number of atoms in the gas. It has been suggested that this detection might have useful application for monitoring atmospheric pollutants.

The use of microwave absorption systems as detectors for gas chromatography has been demonstrated[62]. It was found that changes in relative gas composition in two transmission type cavities can be readily detected, by microwave transmission through these cavities, provided a difference in dieletric constant occurs. It was also noticed that if microwave absorption occurred the response of the instrument was enhanced. It was shown that the detector would work successfully in the detection of dichloromethane and diethyl ether.

The first detector to be developed was based on monitoring the intensity of the electronic emission spectra of the eluted organic compound in an argon carrier gas. The eluent is excited in the plasma of a 2450-MHz electrodeless discharge and detected photoelectrically in the ultra violet - visible region. The detector sensitivity was 2×10^{-16}gm. of hexane per second. A degree of selectivity was obtained by choosing the wavelength of various aromic lines and molecular bands. Thus the system is selective to halogens, phosphorus, and sulphur as well as the permanent gases. The detector is capable of extremely high sensitivity and selectivity, has a low volume, rapid response, and has a wide dynamic range. The eluent from the column is passed through a quartz capillary located in the microwave type cavity. Various spectra were plotted in order to establish the most intense lines or bands so that the intensity can be monitored.

A similar apparatus to that previously described[63] with a few minor modifications has been used[64,65], to measure the concentration of organophophorus insecticides and iodinated herbicide residues in various natural environments. The detector is set to monitor on either the atomic line for phosphorus at 253.565nm or the atomic line for iodine at 206.2nm.

It was observed that if the pressure in the discharge tube was reduced then emission intensity was enhanced. This was attributed to the increase in the mean flow path of the bombarding electrons together with a decrease in the recombination effects[66]. An overall increase in sensitivity of about an order of magnitude was observed.

A helium plasma[67], which was found to be a much more intense source, resulted in the production of many more atomic lines from organo bromine, chlorine, iodine, phosphorus, and sulphur containing compounds. The most sensitive and selective line for each element was determined and the elemental emission response was obtained. The following sensitivities were obtained for the most intense elemental lines: bromine at 478.55nm is $2\text{x}10^{-11}$ g/sec., chlorine at 479.45nm is $6\text{x } 10^{-11}$g/sec, iodine at 533.82nm is $5\text{x } 10^{-11}$g/sec., phosphorus at 545.38nm is $5\text{x } 10^{-11}$g/sec.,

Bache and Lisk[68] continued their earlier work[67] and used the system which they had developed to determine insecticides and herbicides in various agricultural samples with increased sensitivity and selectivity.

Moye[69] improved the sensitivity and selectivity of the microwave emission gas chromatographic detector by utilising argon-helium mixtures for the chromatographic carrier and microwave discharge gases. Various pesticides were detected by monitoring the appropriate lines: phosphorus at 253.57nm, chlorine at 221.00nm. and iodine at 206.20nm.

A direct current discharge in a helium carrier gas[70] had been used for the qualitative identification of materials in the vapour state eluted from gas chromatographic columns. This d.c. discharge detector is operated using a small power source with either selected interference filters or a spectrometer to yield detection limits in the range 10^{-12}. to 10^{-14}g/sec. Atomic emission for fluorine, chlorine, bromine, and iodine was obtained from halocarbons with limits of detection in the 10^{-13}g/sec.range. The influence of compound structure on the relative intensities of the emission bands due to the CN, C_2, and CH species were studied.

Dagnall, Pratt, West and Deans[71] used a microwave excited emission detector which operated at reduced pressure with the gas chromatographic separation being carried out at above atmospheric pressure. In this study organosulphur compounds were detected by monitoring the atomic line of sulphur at 190.0 or 191.5nm. or the band head due to the C=S species at around 257.6nm.

II. iii.ii. Functional group detectors.

This type of detector may be split into the following headings (i) mass spectrometry, (ii) infra-red spectrometry, (iii) ultra-violet spectrometry, and (iv) polarographic detection systems.

II. iii.ii.i. Mass spectrometry.

Mass spectrometry is well suited for qualitative analysis of the small amounts of material separated by gas chromatography. In general, any sample which has sufficient volatility for gas chromatographic analysis is volatile enough for introduction into the mass spectrometer. In gas chromatography samples may vary from 10^{-3} to 10^{-13}g depending on the method and equipment while the mass spectrometer can accept samples over the range 10^{-2} to 10^{-11}g. Clearly there are times when a direct introduction from the column into the mass spectrometer is preferred and when properly applied, the results are very satisfactory. However, generally, it is much more convenient to use a tandem G.C. - M.S.

The mass spectrometer is one of the few detectors which simultaneously provides both qualitative and quantitative information about eluent. It is the most general gas chromatographic detector in the sense that it is readily applicable to any conceivable molecule within the practical mass range. For this reason it is perhaps more useful than either infra-red or ultra-violet spectrometry and yet shares with these techniques the tremendous advantage that its spectra lends themselves to interpretation and cataloging. Thus it is not necessary to hold a vast stock of standard chemicals to cover all possible eventualities, and the results of one worker may be confidently used by another. Thus practice bypasses the notorious difficulties introduced by the irreproducibility of gas chromatographic retention data and removes much of the duplication of experimental work which is apparent in the literature.

The main requirements of G.C - M.S. are that the emergent peak is scanned in a time which is small compared with the time of emergence of the peak from the chromatograph and that the sampling system is capable of maintaining a pressure of around 10^{-5} in the ionization chamber of the spectrometer. This latter requirement may be achieved by linking only a small fraction of the eluent into the spectrometer via some means of reduction system, preferably constructed in glass to minimise memory effects[72]. The use of helium as a carrier gas, and the use of a low electron energy to prevent its ionisation ensures that a conventional gas chromatographic curve is provided by monitoring the total ionisation current and that the spectra observed will be those of the eluent alone. If gas-liquid chromatography is used then sometimes high backgrounds are obtained due to column bleed, so as a general rule the columns should be operated at the lowest temperature possible or else gas solid columns should be used instead. Scan rates of a few seconds in the mass range of 20 - 200 amu, are adequate for most gas-chromatographic detection systems, and are readily available. However, McFadden and Day[73] found that the general limitation due to the scan rate are, in general, due to the response of the auxillary equipment, (amplifiers, recorders, etc) and not due to the spectrometer itself. The detection limit of conventional low-resolution equipment is about 10^{-8} to 10^{-9}g and although a technique for increasing the effective sensitivity has been proposed by Ryhage et al [74 - 76] by concentrating the effluent and thus allowing a more concentrated sample to be used without affecting the low pressure. Two molecular separators in series are used to preferentially remove the helium. These separators rely upon the high diffusion coefficient of helium, and a design of a suitable concentration apparatus in glass has been shown to be quite simple to construct [77,78]. The detection limit of low resolution mass spectrometry is somewhat better than the flame ionisation detector with the added advantage that more information is also obtained. If a large number of mass ambiguities exist then the use of a high resolution mass spectrometer is advocated, however, this increased resolution generally results in lower sensitivity[77]. The use of computor coupling of the G.C - M.S. system has now reduced the need of expert interpretation of the mass spectrometric results, but it has increased the cost of this detector tremendously. However, the mass spectrometer has been used as a specific detector in that it is set to monitor a fixed m/e ratio [79/80]. The mass spectrometer has a few limitations for certain compounds have similar cracking patterns which can lead to mistaken identification and also it generally cannot distinguish between cis and trans isomers. However, if a gas chromatograph is used as well, these problems are easily solved since they will have different retention data.

II.iii.ii.ii. Infra-red Spectroscopy.

Since the beginning of gas chromatographic analysis infra-red spectroscopy has been used to identify the eluting compounds by a trapping procedure with subsequent analysis. It is only recently that the eluents from a chromatograph has been continuously monitored. Bartz and Ruhl[81] have been able to obtain good infra-red spectra by simultaneously scanning the ranges 2.5 - 7.0 and 6.5- 16μ in 16 seconds. The infra-red radiation is passed through a rectangular light pipe fitted to the end of the gas chromatographic column, and, by chopping the emergent beam, it is sent alternately to two spectrometers, each of which are locked on to one or the other of the ranges. Also a system of solenoid operated valves are used which enables the operator to select which peaks are scanned and to retain such peaks in the cell for further scans if necessary. After each scan the cell is purged with nitrogen and the system is capable of dealing with peaks separated by more than 32 seconds. Another system has been described which scanned the range of 2.5 - 15μ in 45 seconds, and has been used with some success in the identification of the components of cigarette smoke [82,83]. More recently, Low[86] has used computor-averaged multiple scan infra-red interferometry to obtain spectra over the region 4-40μ in 1 second with a resolution of about 20cm^{-1}.

The principal disadvantages of the system is that it requires relatively large samples to be used (10^{-3} to 10^{-4}g peak load) to obtain a good spectrum. There has not been any mention of the use of monitoring on any particular band system in order that this method of detection may be made selective, but this is probably due to its inherent low sensitivity.

II.iii.ii.iii. Ultra-violet spectroscopy.

The only mention of the use of this method of analysis in the detection of gas chromatographic eluents has been by Kaye et al[85,86]. In these communications a modified Beckman Far UV. DK-2 spectrophotometer is used in which the spectrum is scanned from 1600-2100A° in 6 seconds with a resolution of better than 1A°. Using this instrument it is possible to distinguish between various alkyl iodides containing less than six carbon atoms with a sensitivity that lies between those obtained for thermal conductivity and flame ionisation detectors. This detector has not really found great use since its application is extremely limited.

II.iii.ii.iv. Polarographic detectors.

The classical polarographic method has been almost completely ignored as a detection system in gas chromatography, despire the great potential which this technique offers for the study of physical organic problems[87], An immediately obvious application of this technique would be to follow the extent of any decomposition on the chromatographic column, i.e., by thermal or catalytic processes. From a practical point of view the use of polarography has the advantages of insensitivity to carrier gas flow-rate, pressure, and temperature. Mairanovskii and Yanatovskii[88,89] have described a polarographic detector and have applied it to the detection of carbonyl compounds. A fast linear potential sweep is used to measure the reduction potentials of the carbonyl compounds either directly after absorption in a sulphuric acid-methanol medium or indirectly after conversion to the corresponding aldimine or ketimine with ammonia. The design and evaluation of a polarographic detector system which is specific to carbonyl compounds is also described in this thesis.

II.iv.Pre-column reactors.

There are various other methods by which compounds may be identified and they are all based on pre-column reactions: (i) pyrolysis, (ii) hydrogenation, and (iii) chemical conversion.

II.iv.i. Pyrolysis.

Pyrolysis gas chromatography[90] is based on the partial pyrolysis of a compound in a flash heater prior to separation on the column. The identity and the relative peak heights of these fragments from the pyrolysis form a "fingerprint" pattern for a particular compound just as the ions produced in a mass spectrometer are characteristic of a certain molecule. It should, however, be mentioned that there is such a great scope for the designing or modification of pyrolysis units that the pyrolysis patterns change from one laboratory to another which renders compilation impossible. However, once this problem has been overcome it is certain that this technique will form the major technique in the field of analysis of organic materials especially in the case of the analysis of polymers and plastics.[91-100]

II.iv.ii. Hydrogenation.

Another method in which compounds may be analysed is based on pre-column hydrogenation. This process involves passing the sample mixed with hydrogen through a pre-column reactor which generally contains a Raney nickel catalyst which converts the sample into a mixture of hydrogenation products (mainly alkanes) which can be more conveniently analysed. This method has found quite considerable use in the analysis of compounds which would normally be difficult to separate due to low volatility. Data has been presented on the hydrogenation of acid anhydrides, halides, ketones, sulphides and various other compounds in order to discover the carbon skeleton and the point of fracture in the carbon chain.[101,102]

II.iv.iii. Chemical conversion.

This is very similar to the previous method in that its use permits the analysis of non-volatile compounds, but it also enables products which would decompose on the column to be converted chemically into more stable derivatives which can be separated. This technique has probably the greatest use in the analysis of natural products which are generally molecules of high molecular weight. Similarly, this technique can be used in cases where substances are too volatile to be separated easily and derivatives are formed in a pre-column reactor which are less volatile and thus more easily separable. Better separation of the volatile aldehydes has been obtained by separating the 2.4.dinitrophenyl hydrazone derivatives on a column containing silicon oil (SF.96) at temperatures ranging from 200-250°C [103].

III. Inorganic Separation.

While a tremendous development of gas liquid chromatography technique took place in organic chemistry after its first use by James and Martin[9] for the analysis of volatile substances, the use of this technique in inorganic chemistry developed at a much slower pace. However, the principles of gas solid chromatography were applied in inorganic chemistry as early as 1930

The work of Peters et al [104 - 107] on the separation of hydrogen sulphide, carbon dioxide, oxygen, carbon monoxide and hydrogen by the adsorption-desorption technique can be considered as the predecessor of the displacement gas chromatographic technique in inorganic chemistry. Later, the frontal and the displacement gas chromatographic techniques were used by Glueckauf et al[108] for the separation of neon isotopes. This new technique made it possible to separate and determine organic compounds which are only separable with difficulty as they exhibit almost identical chemical and physical properties. Inorganic compounds are generally more reactive then organic compounds, they are, therefore, more amenable to classical analysis, and for the same reason the application of gas chromatography is less easy to apply. In fact it may seem that there is little justification for applying gas chromatography to problems such as metal analysis, where the elements exhibit sufficient differences in chemical behaviour to allow the application of classical methods of analysis. However, gas chromatography techniques combine such important features as speed, sensitivity, selectivity, simplicity of manual operations, and adaptability to automation. It is of interest to note that the more important examples of inorganic applications of gas chromatography refer to cases where wet classical methods of analysis fail, because of the inertness or of the chemical similarity of the compounds involved.

In order to apply gas-liquid chromatography to metal separation, metal purifications, and metal analysis, a large number of metals must readily react with a single reagent to give quantitative yields of the metallic compound. This class of compound must also possess several properties of which sufficient volatility and thermal stability are paramount in importance. In the light of these requirements, there are only a few derivatives to which inorganic materials can be converted so that they may be made available for successful gas-liquid chromatographic analysis. These are the carbonyls, alkoxides, alkyls, a few metal chelates, and halides. Chelates have received considerable interest especially the acetyl-acetonates, trifluoro, and hexafluoroacetylacetonates, and an excellent review by Moshier and Sievers[109]. covers the early work in this field. In the work described in this thesis the volatile fluoride derivatives were chosen for study since this enables the technique to be applied to a wider group of elements.

Although by 1956 there was already considerable literature on organic gas chromatography [110,111] it was not until 1959 that the first experiments of inorganic separations were reported. Before then, experiments applying to gas chromatography to inorganic chemistry were limited to the separation of a few gases by gas-solid chromatography. The first published work in the field of the separation of volatile halides was by Ellis and Iveson[112], Chlorine, chlorine monofluoride, chloride trifluoride, hydrogen fluoride, and uranium hexfluoride were quantitatively analysed by gas-liquid chromatography. It was found that there were only four major materials suitable for the construction of the apparatus, namely Nickel, Monel, PTFE., and Kel-F (or Hostaflon). The column packings consisted of dispersions of up to 50% loadings of Kel-F (or Hostaflon) oil on various mesh sizes of PTFE. or Kel-F or Hostaflon solid powders. Both a katharometer and a Martin density balance proved to be satisfactory for the detection of these compounds. Nickel filaments were used in place of the normal katharometer filaments to reduce the possibility of corrosion. A sample introduction suitable for high vacuum operation was incorporated in the apparatus which enabled samples at sub-atmospheric pressure to be analysed.

Freiser[113] was the first to describe the separation of metal halides. Tin(iv) and titanium(iv) chlorides were separated on a copper column packed with n-hexadecane (31%W/W) on chromosorb at 102°C. The detector used in this experiment is not mentioned but it was noticed that the ratio of the vapour pressure of these two compounds was approximately the same as the inverse ratio of their retention times. No chemical interactions of these halides occurred with the stationary phase.

The first published one-stage reactor-injection, gas chromatographic system, suitable for metal halide analysis[114] was used to study the reaction of uranyl fluoride with chlorine trifluoride using an apparatus previously described[112]. A separation was described for the separation of volatile corrosive fluorides and their degradation products in order to develop an on-line analyser suitable for efficient plant control. Better separation[115] of chlorine monofluoride, hydrogen fluoride, chlorine, chlorine trifluoride, and uranium hexafluoride than reported earlier[112], was achieved by using a longer column.

Juvet and Wachi[116] described the use of inorganic fused salts as stationary phases. The salts used were mixtures of lead chloride and bismuth chloride, cadmin chloride and sodium chloride. These salts were mixed with firebrick (C-22) in the ratio of 70-30. On the first of these salt substrates titanium(iv) and antimony(iii) chlorides were separated at 240°C whereas the second substrate salt mixture only partially separated tin(iv) and antimony(iii) chlorides at 474°C. The choice of the fused salt is dependant upon several factors: (1) the fused salt should have a low vapour pressure at the temperature of the column, (2) the fused salt should be a solvent for volatile inorganic compounds, and (3) the fused salt should, in general, possess a common ion with that of the solute molecules. Tin(iv), titanium(iv), niobium(v), and tantalum(v) chlorides were separated on columns containing n-octadecane, squalane, silicon oil, paraffin wax, and Apiezon grease at 100°, 150°, and 200°C [117]. The separation of tin(iv) chloride on Apiezon grease at 100°C was found to be impossible. This solute did, however, separate on silicon oil but titanium(iv) chloride did not elute from the silicon oil column. The chromatograms which were obtained were poorly defined for tin(iv) and titanium(iv) chlorides on paraffin wax at 100°C as were the peaks for tin(iv), titanium(iv), niobium(v) and tantalum(v) chlorides on squalane at 200°C.

A further study of the solid supports for the separation of mixtures of chlorine trifluoride, hydrogen fluoride, and uranium hexafluoride was made[118] and the supports studied were sintered alumina, aluminium(iii) fluoride, sintered Hostaflon, Kel-f moulding powder and sintered PTFE. Only Kel-f moulding powder was found to have the necessary resistance to attack and low degree of adsorption. Various types of detector were evaluated; the flame ionisation detector was rejected as there were problems of corrosion and difficulties of high temperature, β-ray ionisation detectors were also rejected as the ionisation properties of the eluent were as yet unknown. The two detectors which were suitable for corrosive gas analysis were the katharometer with nickel filaments and the Martin gas density meter. The separation of chlorine trifluoride, hydrogen fluoride and uranium hexafluoride was achieved only in part as the peaks for chlorine trifluoride and hydrogen fluoride were only partially separated at 60°C.

It has been shown that certain volatile chlorides may be separated on more usual stationary phases and solid supports[119]. A column containing hexadecane on celite has been used to separate mixtures of hydrogen chloride, chlorine, phosgene, boron(iii) chlorine, and silicon(iv) chloride at 285°C. A thermal conductivity cell with glass coated platinum filaments was used to detect these halides.

An on-line gas chromatograph was developed[120] for analysis of plant streams containing uranium hexafluoride, chlorine trifluoride, chlorine, hydrogen fluoride and other reactive gases. To speed analysis, a split column chromatograph was developed and automated. Separation was carried out on a column comprised of Kel-F 40 oil on Kel-F 300 low density moulding powder (I:5W/W) which had been chemically conditioned with chlorine trifluoride until a single peak was obtained. The following gases were separated at 60°C;- uranium hexafluoride, bromine, chlorine monoxide, chlorine trifluoride and chlorine dioxide (partially separated) chromyl fluoride, chlorine, perchloryl fluoride, hydrogen fluoride, chlorine monofluoride, fluorine monoxide and fluorine, Hydrogen fluoride was found to give negative peaks if nitrogen is used as the carrier gas with detection by a katharometer with nickel filaments.

A rather unusual substrate has been used in the separation of silicon(iv) fluoride, carbon(iv) fluoride, nitrogen (iii) fluoride, hydrogen fluoride, sulphur(vi) fluoride, trifluorochloromethane, fluorine, trifluorobromomethane, chlorine trifluoride, chlorine, difluorodichloromethane, trifluorochloroethylene, difluorodibromomethane, and fluorodichloromethane[121]. This substrate was prepared by plasticizing halogenated polymers(Kel-F powders) with halogenated oils (halocarbon oil) to give a "monophase gell".

Nitric oxide, fluorine monoxide, nitrogen(iii) fluoride, silicon(iv) fluoride, phosphorus(v) fluoride, hydrogen chloride, carbon dioxide, nitrous oxide, and sulphur (vi) fluoride (partially separated), hydrogen sulphide, sulphuryl fluoride, sulphur(iv) fluoride, thionyl fluoride, chlorine and sulphur dioxide, were analysed on a silica gel column, which had been preheated to 900°C and coated with 30% Halocarbon oil at 30°C[122].

Tin(iv) chloride, bromide and iodide[123] were separated on columns of sil-o-cell brick coated with silicone grease (10%w/w) at 150°C and sil-o-cell brick coated with aluminium bromide (30%w/w) at 150°C, better separation was achieved with the latter column packing. Also germanium (iv) and arsenic(iii) chlorides were separated on an uncoated sil-o-cell brick column at 100°C and mercury(ii) and iron(iii) chlorides were separated on a column containing sil-o-cell brick coated with bismuth chloride (25%w/w) at 290°C. The detection system operated by using compounds labelled with β-radioactive isotopes and the eluent was examined by a liquid β-counter.

Dennison and Freund[124] used a column containing chromosorb W coated with Halocarbon 6-00 (24.5% w/w) to separate mixtures of germanium(iv), tin(iv), and arsenic(iii) chlorides at 107°C and carbon(iv), tin(iv), arsenic(iii) and titanium(iv) chlorides at 126°C. A katharometer detector was used in this study and a sampling system was described for rapid, repetitive, sampling of reactive liquids in an inert atmosphere.

The application of gas-liquid chromatography to the separation of a number of heavy metals in the form of their metal fluorides was reported[125] and the choice of liquid phase and solid support was found to be greatly limited by the reactive nature of these solutes. Molybdenum(vi) and tungsten(vi) fluorides were separated with good resolution and determined quantitatively on a column, which had been chemically conditioned with chlorine trifluoride, containing Kel-F 10 oil on a chromosorbT support (25%w/w) at 75°C and 35°C. Tantalum(v) and niobium(v) fluorides may be partially separated on a similarly chemically conditioned column containing Kel-F wax 200 on chromosorb T (25%w/w) at 210°C. It was also shown that antimony(v) fluoride could be separated above 125°C but below 180°C without decomposition, on a similar column to that used for the separation of niobium(v) and tantalum(v) fluorides.

It was also found that arsenic(iii) fluoride could be chromatographed on a column of tricresyl phosphate (30%w/w) on chromosorb P at 75°C without any reaction occurring.

In an extension of this work a reactor-injection system was developed[126] enabling metals, alloys, oxides, carbides, sulphides, and metal salts to be analysed. The samples are weighed in a nickel boat and placed in a quartz tube. These samples are then reduced to the element by heating to 1500°C in a stream of hydrogen. The reduced samples are then placed in the reactor-injection vessel on a nickel filament heater. The samples are then heated to dull-red heat and reacted with fluorine. Once the reaction is completed the products are swept onto the column,via a sampling valve, and analysed gas chromatographically. The eluent gas is monitored by a katharometer with nickel filaments. Tungsten, rhenium, osmium, and other reactive products are separated on a column containing Kel-f oil no. 10 (15%w/w) on chromosorb T at 75°C. Sulphur, selenium, tellurium, silicon, and boron(partially separated) on the same column at dry-ice-acetone temperature. Vanadium is found to be difficult to analyse, as vanadyl fluoride is formed in preference to the vanadium(v) fluoride as it is impossible to exclude oxygen from the system.

A method for determining titanium(iv) and tin(iv) oxides in various oxide mixtures has been described[127] in which the titanium(iv) and tin(iv) chlorides were prepared by reacting the oxides with an excess of carbon tetrachloride in a sealed glass ampoule at 45°C. The ampoule was then crushed by a sampling device and the resulting mixture was analysed by gas chromatography. The separation was carried out on a column, packed with Histowax (15%w/w) on a Gas Pack-F support, which had been coated with a perfluorocarbon polymer, at 77°C. A katharometer was used to determine these metals quantitatively.

Sie, Bleumer and Rijnders separated[128] the chlorides of carbon(iv), silicon(iv), phosphorus(v), sulphur(i&ii), titanium(iv), vanadium(v), gallium(iii), germanium(iv), arsenic(iii), tin(iv), and antinomy(iii&v), also phosphorus oxychloride, chromyl chloride,molydenum oxychloride, vanadyl chloride, thionyl chloride, and sulphuryl chloride. The column used contained Kel-F wax(15%w/w) on Haloport F at temperatures ranging from 75-100°C. A gas density detector is used, as the filaments are not in contact with the eluent gas. All these compounds can be determined accurately in mixtures with the exception of vanadium(iv) and antimony(v) chlorides and molybdenum oxychloride which are found to decompose. These determinations were found to be quantitative with an accuracy of around 0.6 wt%.

The effect of temperature and the degree of polymerization of the various grades of Daifloil (polytrifluoromonochloroethylene) on the HETP. of uranium(vi) fluoride with respect to fluorine was studied[129]. It was shown that Daifloils of lower degree of polymerization had a better separation factor, while a small HETP. was obtained for a high degree of polymerization. Low operation temperatures were favourable both to the separation factor and to the HETP. Also it was found that in order to obtain quantitative results several factors must be carefully controlled, namely the construction of the assembly, pretreatment of the columns by fluorine, purification of the carrier gas and also to follow a well defined pattern of operation. Tellurium (vi) and molybdenum(vi) fluorides were separated from uranium(vi) fluoride at 32° and 31°C. respectively. Katharometers with nickel filaments, both at the inlet and outlet ports of the columns were used to study the possibility of reactions occurring on the column.

A column filled with synthetic, highly purified graphite was used to separate the following mixtures[130]:
(1) aluminium(iii) and gallium(iii) chlorides at 210°C.
(2) aluminium(iii) and zirconium(iii) chlorides at 300°C.
(3) tantalum(v) and niobium(v) chlorides at 270°C,
(4) niobium(v) chloride and niobium oxychloride at 450°C,
(5) hafnium(iv) and zirconium(iv) chlorides at 295°C and
(6) aluminium(iii), hafnium(iv) and zirconium(iv) chlorides at 290°c. The design of the system permitted injection of the solid metal chlorides and both the katharometer and a gas density detector were used.

Methods have been suggested[131,132], for the determination of silicon in iron and steel and silicon and tin in non-ferrous alloys, using a gas density detection system. Weighed samples contained in a sample boat (constructed from either quartz, graphite, or sintered alumina) are introduced into a quartz tube and electrically heated to 600-900°C. Chlorine is passed over it and the volatile chlorides are collected in a dewar flask at 0-5°C. This dewar is then heated to 90-100°C and the trapped silicon(iv) or tin(iv) chlorides and other volatile chlorides are then swept onto the column with nitrogen. The separation is achieved on a column containing Kel-F wax(15%w/w) on Haloport F with the column at a temperature of 75°C for silicon determinations and at 100°C for tin determinations.

Chapter 1.

Development of a Reactor-Injection System for the Gas Chromatographic Analysis of Volatile Fluorides.

I. Introduction.

In recent years there has been increasing interest in the field of gas chromatographic analyses of inorganic compounds. The separation is usually achieved by the prior formation of derivatives with sufficient volatility to allow separation by gas chromatography. There are two main types of derivatives which have been examined and these are the halides and chelates. In this study it was decided to separate the elements in the form of the volatile fluorides. Table 1 shows the melting points and boiling points of these elemental fluorides and it also shows the elements which have been separated by

Table 1.

element.	mpt.°C	bpt. °C	chelates.
	fluorides.		
aluminium(iii)	1260	1291(s)	tfa.,hfa.,acac.
antimony(iii)*	292	376	acac.
antimony(v) *	6	149.5	
arsenic(iii)*	-8.5	63	
arsenic(v) *	-79.8	-52.8	
barium(ii)	1320	2260	acac.
beryllium(ii)	---	800(s)	tfa.,hfa.,acac.
bismuth(iii)	---	725(s)	
boron(iii) *	-127.1	-100.3	acac.
bromine(i) *	-33(d)	-20(d)	
bromine(iii)*	8.8	127.6	
bromine(v) *	-61.3	40.5	
cadmium(ii)	1049	1748	acac.
caesium(i)	682	1251	acac.
calcium(ii)	1360	2500	
carbon(iv) *	-184	-128	
cerium(ii)	1360	2500	
cerium(iii)	1460	2300	tfa.,acac.
chlorine(i) *	-154	-100.8	
chlorine(iii)*	-83	12	
chromium(ii)	1100	1200	
chromium(iii)	---	600(s&d)	tfa.,hfa.,acac.
cobalt(ii)	1150	1400	
cobalt(iii)	---	650(s&d)	t.f.a.,hfa.,acac.
copper(ii)	780(d)	---	tfa.,hfa.,acac.
dysprosium(iii)	1360	2280	acac.
erbium(iii)	1140	2200	
europium(iii)	1390	2280	tfa.,acac.
gadolium(iii)	1231(d)	---	tfa.,acac.
gallium(iii)	800(s)	1000	tfa.,acac.
germanium(iv) *	-15(p)	36.5(s)	acac.
hafnium(iv)	---	310(s)	tfa.,acac.
holmium(iii)	1143	2200	
hydrogen(i) *	-83.1	19.54	

indium(iii)	1170	1200	tfa.,acac.
iodine(v) *	9.6	89	
iodine(vii)*	5.5(p)	4.5(s)	
iron(ii)	1100(d)	---	tfa.,acac.
iron(iii)	---	1000(s)	tfa.,hfa.
lanthanium(iii)	1493(d)	---	tfa.,hfa.,acac.
lead(ii)	824	929	
lithium(i)	846	1680	acac.
lutetium(iii)	1182	2200	
magnesium(ii)	1248	2260	acac.
manganese(ii)	856	---	tfa.,hfa., acac.
mercury(ii)	645	650	acac.
molybdenum(vi)*	17.5	35	acac.
nickel(ii)	---	1000(s)	hfa.,acac.
niobium(v) *	78.9	233.3	acac
phosphorus(iii)*	-151.5	-101.8	
phosphorus(v) *	-91.6	-84.8	
potassium(i)	859.9	1503	
prasedynium(iii)	1395	---	tfa.,acac.
rhenium(vi) *	18.8	47.6	
rhodium(iii)	---	---	tfa.,hfa.,acac.
rubidium(i)	775	1410	
samarium(iii)	1306	2323	tfa.,hfa.,acac.
scandium(iii)	1515	---	tfa.,acac.
selenium(vi) *	-46.6(s)	-34.5	acac.
silicon(iv) *	-95.7(s)	-95	acac.
silver(i)	435	1159	
silver(ii)	690(d)	---	
sodium(i)	993	1704	acac.
strontium(ii)	1190	2460	acac.
sulphur(iv) *	-121	-40.4	
sulphur(vi) *	-50.8(p)	-63.8	
tantalum(v) *	96.8	229.5	acac.
tellurium(vi)*	-38.9	35.5	
terbium(iii)	1172	2280	
thalium(i)	327	655	acac.
thorium(iv)	900	---	hfa.,acac.
thulium(iii)	1159	2200	acac.
tin(ii)	219	850	
tin(iv)	705(s)	---	acac.
titanium(iii)	1100(d)	---	acac.
tungsten(vi) *	2.5	17.06	
uranium(vi) *	56.2(s)	---	tfa.,hfa.,acac.
vanadium(iii)	1406	---	acac.

vanadium(iv)	325(d)	---	
ytterbium(iii)	1157	2200	acac.
yttrium(iii)	1152	---	tfa.,hfa.,acac.
zinc(ii)	872	1500	hfa.,acac.,
zirconium(iv)	600(s)	---	tfa.,hfa.,acac.

acac.	acetylacetonate.
tfa.	tetrafluoroacetylacetonate
hfa.	hexafluoroacetylacetonate
s.	sublimes.
d.	decomposes.
p.	under pressure.
*	fluorides suitable for analysis by gas chromatography.

the formation of a volatile chelate derivative. From this table it may be seen that the following elemental fluorides have sufficient volatility to permit normal temperature gas chromatographic separation: antimony, arsenic, boron, bromine, carbon, chlorine, germanium, hydrogen, iodine, molybdenum, niobium, phosphorus, rhenium, selenium, silicon, sulphur, tantallum, tungsten, tellurium, and uranium.

Most analyses by gas chromatography aim to determine not absolute weights but relative weight proportions of the components of a sample of interest and therefore most sample injectors aim to inject a reproducible, representative sample of a mixture of interest and not an accurately known weight. It is the sample injector which remains one of the least satisfactory items of the gas chromatographic equipment; possibly for this reason, many designs for it have been produced. There are three major reasons why different sample injectors are necessary and these are dependant on the physical state of the sample ie. gas, liquid, or solid. However, in all cases there are three conditions which must be fulfilled in the introduction of the sample in order that the sample injection procedure is optimised.

1. The sample should be introduced into the column packing as a vapour in the smallest possible space and in as short a time as possible.
2. It should not upset the equilibrium conditions of the column in the process.
3. Both the quantity of the substance and the manner in which it is introduced (the prevailing conditions such as the temperature, pressure, flow-rate and energy conversion) must be reproducible with as high a degree of precision as possible.

The foundations for these three requirements for sample injectors are as follows:

1. If there is a finite time over which the substance reaches the start of the column either due to the fact that the sample is injected over a finite time or due to the fact that the injection volume is large, then the emergent peak will be broader than it theoretically should be. This may not be so important in cases where the sample is hardly retained by the column but with high retention times this becomes increasingly more important. Also the degree of separation of the eluting peaks will be adversely affected such that interpretation

of individual peaks on the chromatogram is impossible. The temperature of the injection port will also affect the geometry of the eluting peak if it takes a finite time for the sample to vaporize the peak will be broadened and therefore there should always be sufficient heat to allow evaporation and melting to take place instantly.

2. This requirement may be regarded as most closely followed if the maximum amount of sample which the column can accommodate is not exceeded. The maximum amount may be regarded practically as the amount which can be taken up in the region of a theoretical plate without disturbance of the separation process.

3. This requirement needs no justification as it follows from the other two requirements.

II. Reactor-Injection System.

II. i. Evaluation of the Juvet and Fisher System.

The handling of these corrosive and very reactive fluorides require even further precautions to be taken in order to ensure that hydrolysis or decomposition does not occur before injection onto the column. It was with this in mind and also to apply gas chromatography to the analysis of ores and alloys that Juvet and Fisher[126] designed and developed a reactor-injection system which enabled a range of elements to be converted into their fluorides by reaction with fluorine, in a precolumn reactor. Also this design will make it possible to develop a standard method of analysis as all the reaction products are in the vapour phase for as a general rule gas sampling valves are more reproducible than any other simple method of sample introduction.

In the preliminary investigation of the problem a reactor-injection assembly of the type described by Juvet and Fisher was constructed (fig.1) with the exception that fluorine was replaced by chlorine trifluoride since it was hoped that as chlorine trifluoride has a longer retention time than fluorine it would allow better separation of the very volatile fluorides.

The reaction vessel consisted of a stainless steel cylinder containing a PTFE insert. Through this insert two stainless steel rods were passed which were

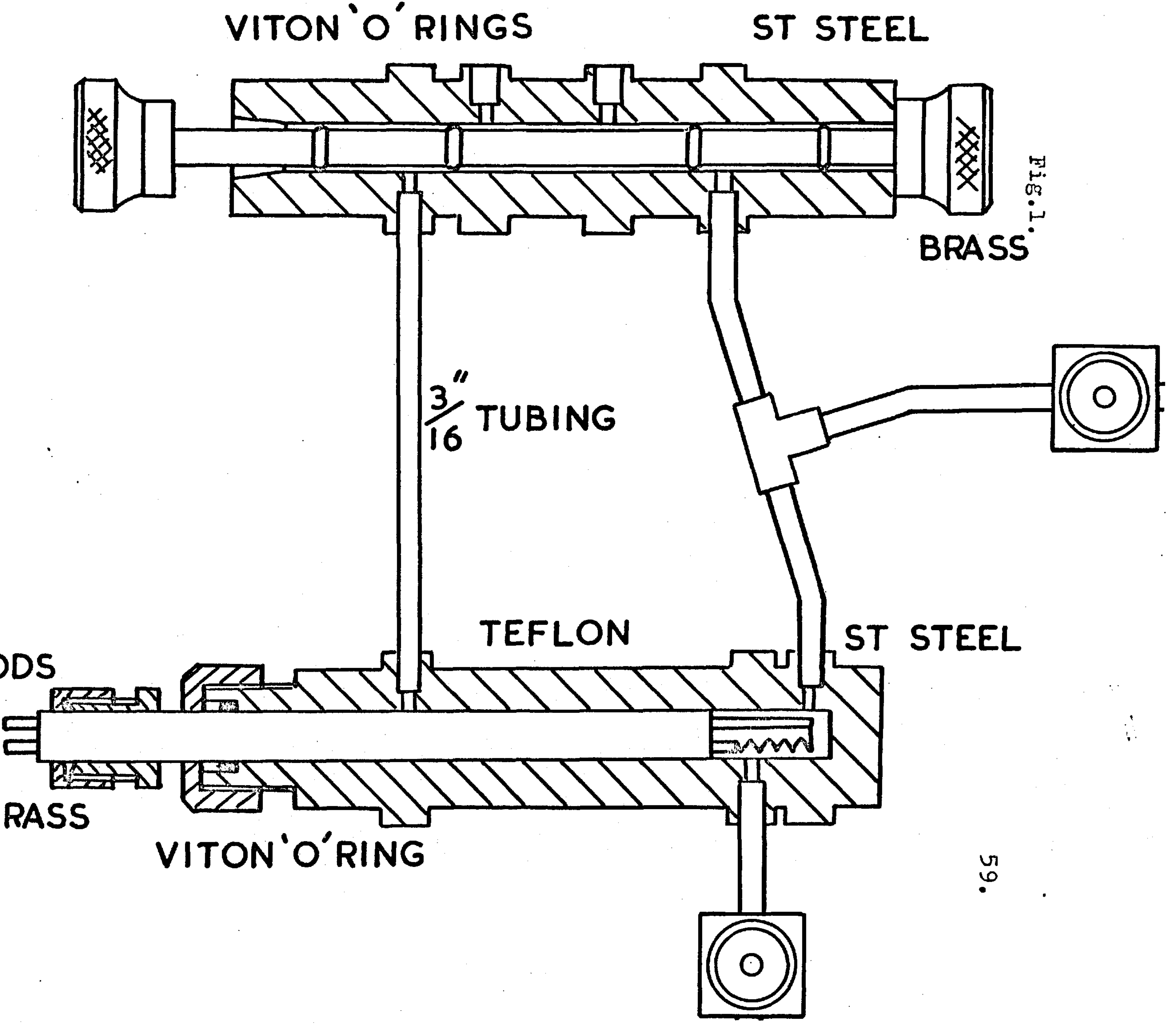

VITON 'O' RINGS
ST STEEL
BRASS
3/16" TUBING
TEFLON
ST STEEL
ST. RODS
BRASS
VITON 'O' RING

Fig.1.

electrically insulated from each other and from the body of the vessel by the PTFE.insert. A "spec" pure nickel heating filament (6" x 0.0625" x 0.005"), in the shape of a helix, was spot welded between these rods, and the reaction vessel was rendered vacuum tight by compression of Viton A 'O' rings. Three inlets were connected to the reaction vessel one of which was connected to the cylinder of chlorine trifluoride and the other two to the four-port gas sampling valve. The gas sampling valve was a two-way, "plunger type" valve which enabled either the system to be evacuated or else allowed the carrier to flow through it. The sealing on this valve was maintained by the use of four Viton A 'O' rings which were lubricated with Kel-F oil to stop the valve sticking. The outlet ports to the vacuum line and the chlorine trifluoride cylinder were controlled by stainless steel needle valves (Autoclave Engineers, Erie, P.A.)

Operation.

A weighed sample is placed in a nickel boat (pressed from 0.005" foil) on the heating filament and inserted into the reaction vessel. The reactor-injection vessel is evacuated right to the needle valve on the cylinder of the chlorine trifluoride by opening the two needle valves. Once a vacuum is achieved which is less than 1 torr. these two valves are closed and the line between the chlorine trifluoride cylinder and the needle valve on the reaction vessel is filled with chlorine trifluoride at the pressure of the cylinder. The cylinder valve is then closed and the fluorinating agent is allowed into the reaction vessel, thus it is possible to always add a reproducible quantity of chlorine trifluoride. A potential of 3 volts a.c.(supplied by a heavy duty transformer which heats the sample to dull-red heat almost instantaneously) is applied across the filament for a duration of one minute. After which time this heater is switched off and the products are swept onto the column by the carrier gas. The reactor-injection vessel is thermostated at a temperature of 80°C.

The injection vessel proposed by Juvet and Fisher was found to be unsatisfactory as it leaked severely after one or two injections. This was due to the 'O' rings being cut by the movement of the plunger over the inlet ports which caused the injection system to leak. As it was necessary to operate this valve by this movement of the plunger the 'O' rings had to be replaced very often in order that a vacuum could be maintained. Also the 'O' rings were attacked rapidly by contact with chlorine trifluoride and this made it even more difficult for the valve to hold a vacuum or withstand the pressure of the carrier gas. This design of injection system although it is popular in the U.S.A. is not really very robust and many other designs are superior.

II. ii. Modification of Juvet and Fisher Injection System.

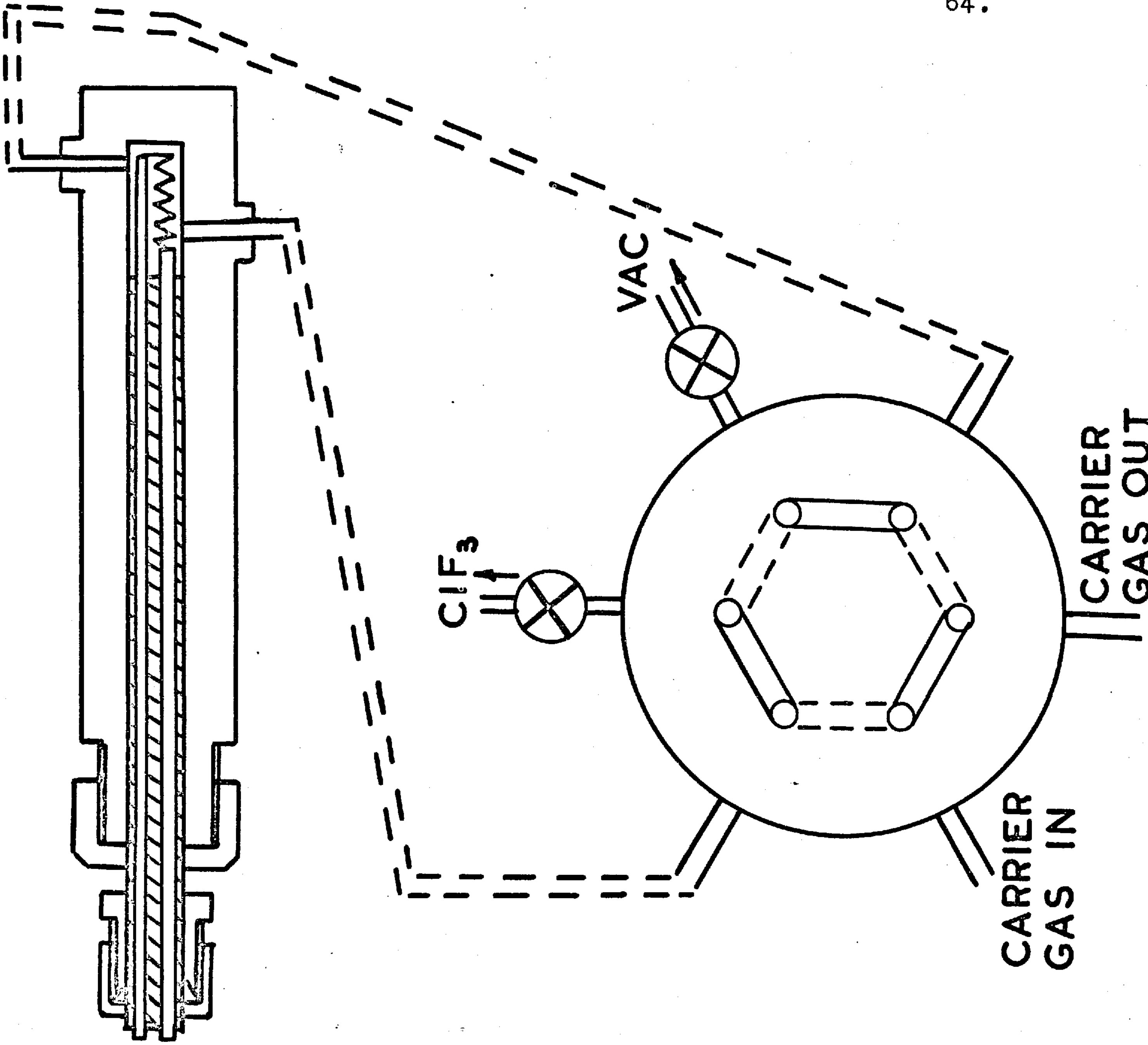
The original injection vessel was therefore replaced by a six-port two-way rotary gas sampling valve (Perkin Elmer Ltd.) which is constructed from stainless steel and PTFE. This valve has no 'O' rings in it and the moving part consists of a PTFE. disc which needs no lubrication. In normal use this valve has a constant volume sample loop which is filled with the gas under investigation. In this system developed this loop is removed and the reaction vessel is connected in place of the sample loop. The reaction vessel needed slight modification in that only two inlet tubes to the reaction vessel were required (fig.2). The operation of this system was carried out in a similar way to that previously described. No problems of leaks are observed for when this valve is in operation there are no pressure or vacuum loses.

The reaction vessel was found to suffer considerably from problems of corrosion and contamination. The filament was found to form a slightly adhesive film of the reaction products on it and since it had a large surface area considerable memory effects were concurred. Also it was noticed that the walls of the reaction vessel were coated rapidly with fluorination products whereas the PTFE. insert was not.

II.iii. Development of the Reaction Vessel.

The reactor vessel was considerably modified from the original Juvet and Fisher design to rectify the disadvantages which were observed with the reaction vessel. The body of the assembly is constructed from PTFE. as it had been noticed that PTFE. did not allow condensation to occur, and the sample is heated externally using a radio frequency generator. The body of the apparatus

Fig.2.



is a thick-walled PTFE. cylinder with a flush fitting plunger made of similar material (fig.3). The reaction vessel is made vacuum tight and pressure tight by a screw cap (also constructed from PTFE.) which compresses a Viton A 'O' ring. The reacion volume of the chamber is typically 5ml. but it may be varied easily by altering the depth of the plunger. To the plunger the sample boat is attached by a heat resisting but non-conducting inert sample boat holder. The first material used to construct this sample boat holder was silica. It was however, noticed that when arsenic was determined no arsenic (iii or v) fluoride was formed as the arsenic(iii or v) fluoride attacked the silica by an exchange mechanism which resulted in the formation of silicon(iv) fluoride and arsenic(v) oxide. This was replaced by a fine "spec." pure nickel wire and a fused alumina tube (which is not attacked by fluorides) is inserted into the plunger to stop the heat being transferred from the nickel wire to the PTFE. plunger. This was found to be satisfactory.

The sample is placed on a disposable sample boat which is pressed from "spec." pure nickel foil using a die. The shape of the boat is arranged so that most of its

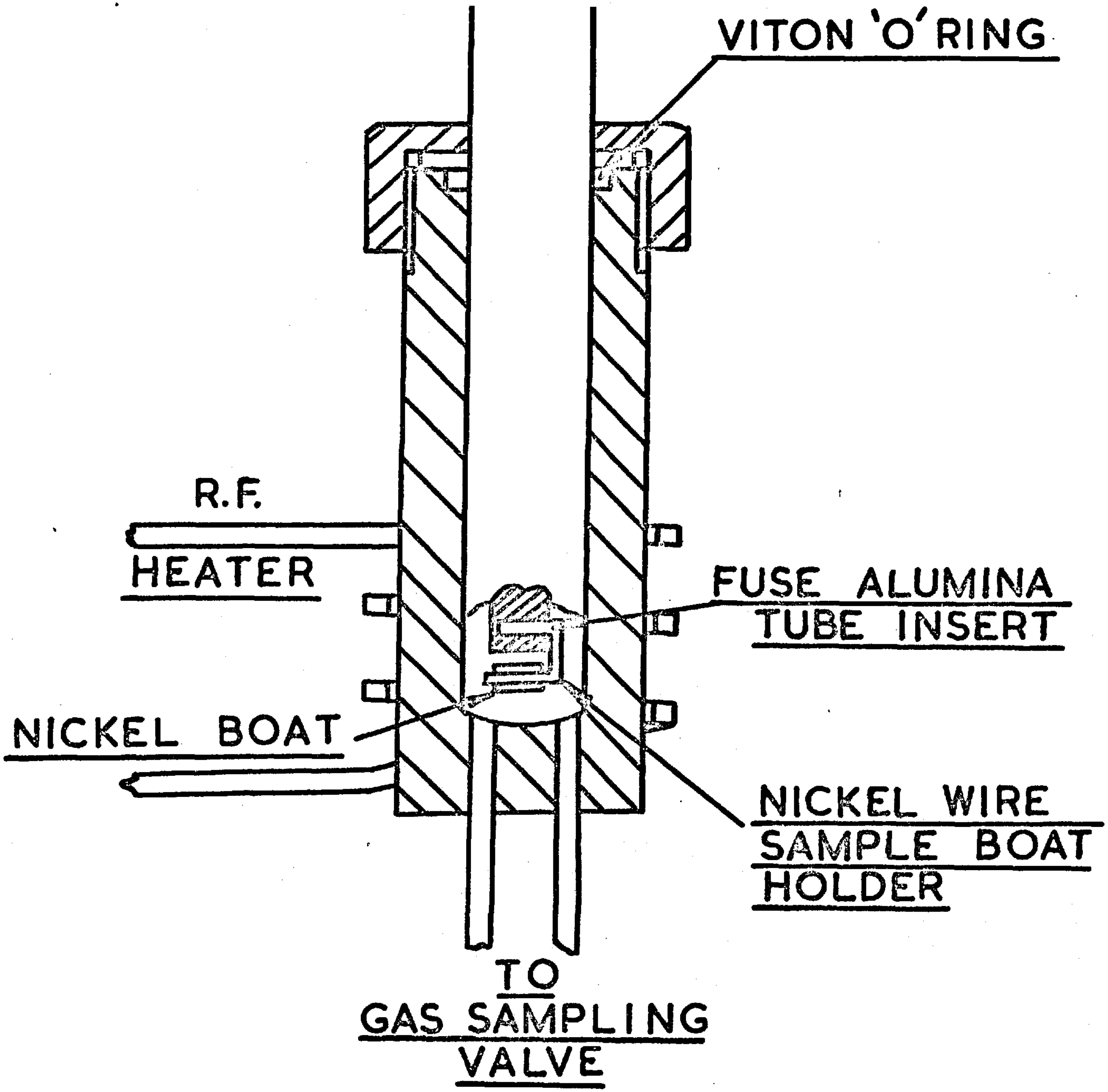

VITON 'O' RING
R.F. HEATER
FUSE ALUMINA TUBE INSERT
NICKEL BOAT
NICKEL WIRE SAMPLE BOAT HOLDER
TO GAS SAMPLING VALVE

Fig.3.

surface area is at right angles to the plane of the cylinder walls. This results in maximum coupling of the field of the radio frequency heater.

This reactor vessel is connected to the gas sampling valve (Perkin Elmer Ltd.) in place of the sample loop via two PTFE. tubes(1/8") which are situated in the base of the reaction vessel. These tubes are connected and sealed by screw fittings (constructed from PTFE.) which compress Viton A 'O' rings. This reactor-injection vessel is similarly thermostated at 80°C.

II. iv. Radio Frequency Heater.

In order to use PTFE. as a material of construction it is necessary to employ a different method of heating for the sample. It was decided that the best form of heating would be external since there would be very little risk of contamination as all the heating components would be outside the reaction vessel and therefore radio frequency heating was chosen. A radio frequency heater was designed which was a scaled-down version of a radio frequency heater already used in this department. This generator is a shunt fed Colpitts oscillator in which the tank circuit inductance forms the work coil (fig.4 and table 2.) The design and shape of the work coil were such that it fitted exactly round the body of the PTFE. reaction vessel. The frequency at which the heater operates is 550 KHz. and it was found by experimentation that in order that sufficient coupling should be attained with such a small sample boat this generator needed to supply 200 watts. Even when most of the sample boat is in the plane of the radio frequency heater the efficiency of the coupling is of the order of 10%.

II.v. Vacuum System.

As the reactor-injection system needed to be evacuated a vacuum system was designed to enable this to be performed rapidly. The use of an oil filled rotary pump to provide the vacuum made it necessary to have some form of absorber which will remove the chlorine trifluoride and other fluorinated products before they reached the vacuum pump oil. The requirements of the absorber are that it must remove the corrosive gases rapidly and that the absorber must not reduce the pumping rate of the

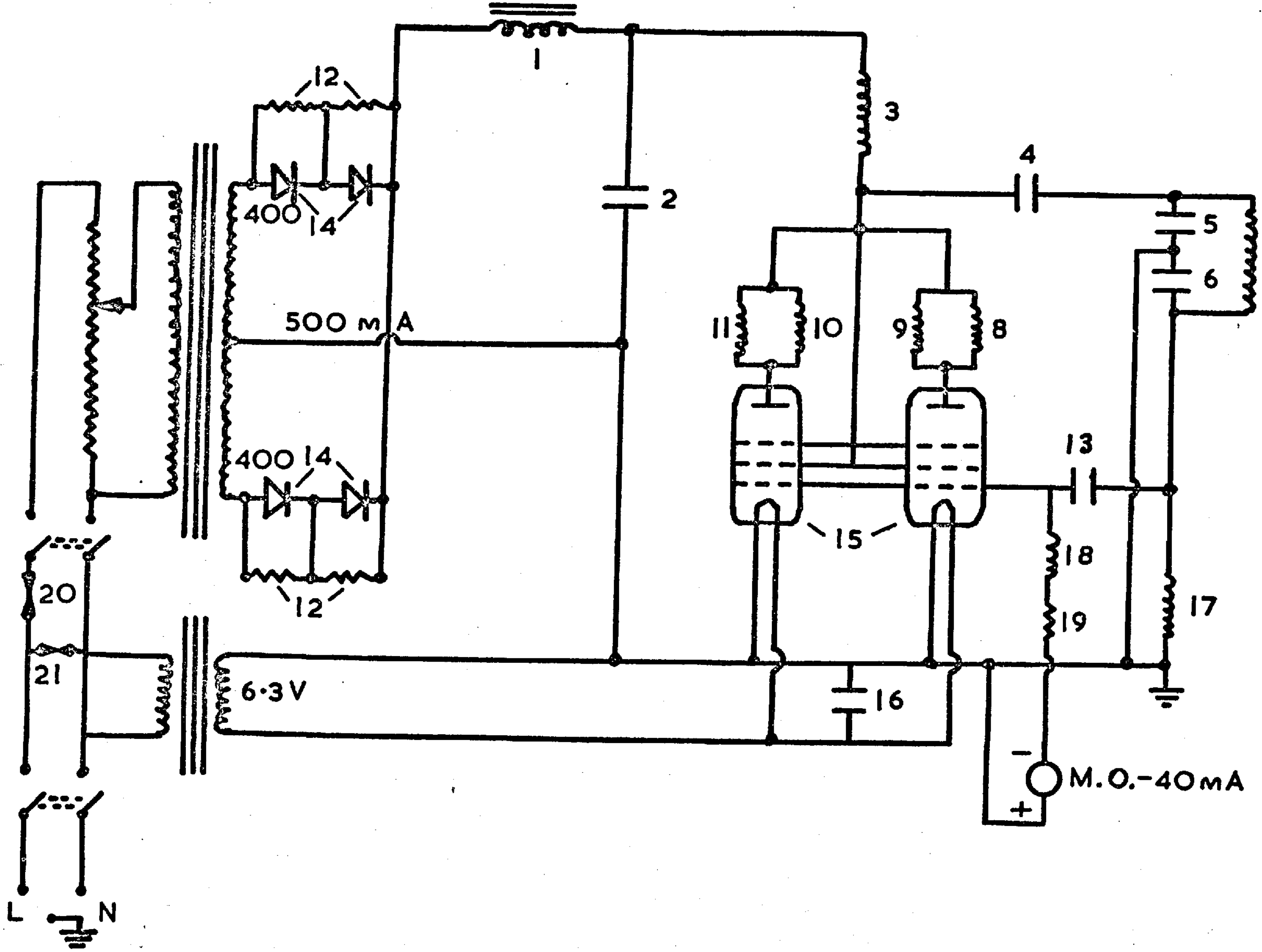

1
12
3
4
400
14
2
5
7
6
500 mA
11
10
9
8
400
14
13
15
12
20
18
17
19
21
6·3V
16
−
M.O.-40mA
+
L
N

Fig.4.

Table 2.

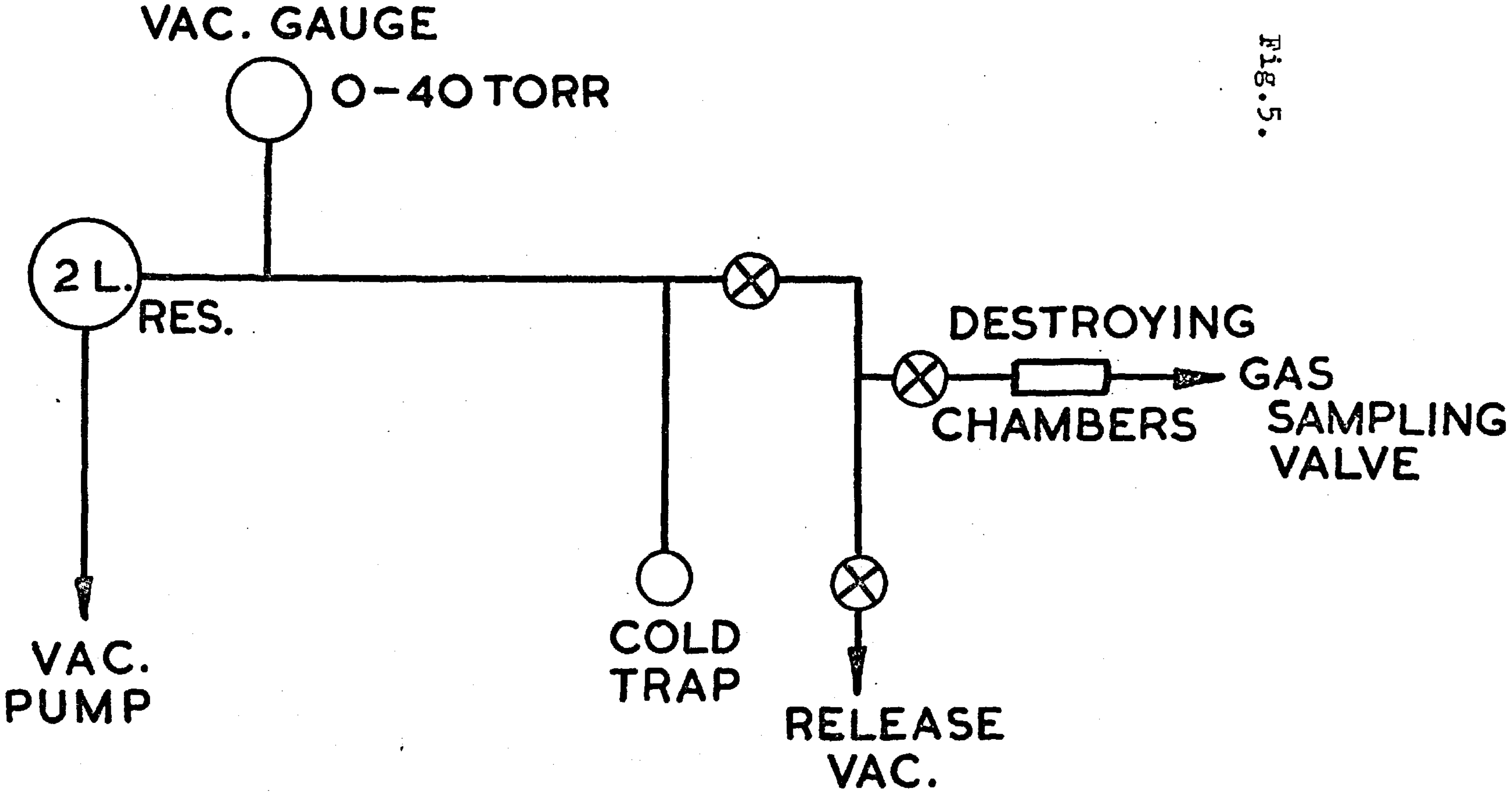
1.	Inductance	10H
2.	Capacitor	8μF
3.	R.F.Choke	500T,1"i.d.
4.	Capacitor	0.5μF
5.	Capacitor	0.02μF
6.	Capacitor	0.03μF
7.	Work Coil	18T,12swg,1.5"i.d.
8.& 10.	Resistance	15 Ω
9.& 11.	Choke	20T
12.	Resistance	470K Ω
13.	Capacitor	0.006μF
14.	Diode	REC 53
15.	Valve	Type PT 15
16.	Capacitor	0.01μF
17.& 18.	R.F.Choke	250mH
19.	Resistance	5K Ω
20.	Fuse	8amp
21.	Fuse	2amp

pump. A stainless steel column(6' x 1/4") packed with soda asbestos was tried but it was found that after a few determinations the reaction products produced a pressure gradient across the column which reduced the rate at which the reactor-injection vessel could be evacuated. A similar column was tried where soda asbestos was diluted with granular charcoal (I:I) but a similar effect resulted. Finally a scavenging chamber was designed in which a mixture of granular charcoal, molecular sieve 4A, granular sodalime and soda asbestos (1:1:1:1) was contained in a stainless steel chamber (1" o.d.). This chamber was connected to the vacuum line by stainless steel tubes (1/4" o.d.). The mixture in this absorber has to be replaced every month to ensure that it remained active. A cold trap was also used to act as a secondary trap in case the absorber failed. The vacuum is measured on a Speedivac (0-40 torr.) vacuum gauge and a schematic diagram is shown (fig.5).

Operation.

The operation of this modified reactor-injection system is similar to that described for the Juvet and Fisher

Fig. 5.


VAC. GAUGE
0-40 TORR
2 L.
RES.
VAC.
PUMP
COLD
TRAP
RELEASE
VAC.
DESTROYING
CHAMBERS
GAS
SAMPLING
VALVE

system except that the radio frequency generator is the source of heating for the sample.

Chapter 2.

Development of a Spectroscopic Detector for Fluorides.

I. Introduction.

The gas chromatographic separation and analysis of metals and non-metals via reaction or complexation with halogen molecules or ligands has received considerable interest recently. Of special concern has been the separation of volatile fluorides which, because of their corrosive character, cause special problems not only in their preparation,and separation, but also in detection.

The two main detectors, which have been used by other workers in this field to monitor these corrosive fluorides, are the katharometer and the gas-density balance.

I.i. Katharometer.

The katharometer (or thermal conductivity detector) was introduced by Shakespear[133] and it is designed to measure continuously the thermal conductivity of the column effluent. Basically a katharometer consists of a hot central area with a cold surrounding wall. Heat transfer takes place from the hot surfaces in the centre outwards, to the cooler surrounding walls via the effluent gas. This hot central area consists of a very thin, electrically heated filament of small resistance. The signal is a measure of the relative resistance of the filament in the pure carrier gas as compared with that of the filament in the effluent gas. The signal observed is proportional to the thermal conductivity of the effluent gas as the resistance is related to the temperature of the filament which in turn is dependant on the thermal conductivity of the effluent gas. The signal is measured by a Wheatstone bridge which is the most accurate method for measuring resistances, for the changes in resistance are very small. The use of a reference filament in the pure carrier gas is introduced to reduce instrumental drift and this idea has been extended to the full in that most commercially available katharometers have all four arms of the bridge in the flowing gases. This improvement not only reduces the noise level and drift but it also increases the sensitivity. The galvanometer of the bridge is usually replaced directly by a potentiometric recorder which will provide a continuous record of the out-of-balance e.m.f. of the bridge (ie. the chromatogram).

The katharometer may be used to detect most molecules since a change in thermal conductivity will be produced if any vapour reaches the filament. Thus volatile fluorides may be detected even though they are extremely corrosive. The material of construction must be chosen carefully to ensure that the katharometer is not corroded, and the filaments must be constructed from either pure nickel or else the usual platinum-nickel or platinum-iridium alloy filaments should be coated with PTFE. The use of these filaments generally results in a reduction in sensitivity of the katharometer. As a general rule only helium or hydrogen should be used as the carrier gas as they have high thermal conductivities which will give greater sensitivity. Also there is a disadvantage in using gases with low thermal conductivities in that there is a possibility of both positive and negative peaks being obtained. This is caused by the effluent gas having either higher or lower thermal conductivity than the reference gas. When volatile fluorides are being monitored this becomes very important for hydrogen fluoride and other fluorides have greater thermal conductivities than nitrogen which leads to negative signals. The major advantage of this detector is that it has a wide linear signal to concentration relationship.

I.ii. Gas-Density Balance.

Martin and James[134] developed a detector which provided a continuous monitor of the density of the effluent gas so that only vapours with densities which differ from that of the carrier gas are recorded.

The gas-density balance is designed so that the reference gas and the gas under investigation flow through four channels. These channels are linked in a similar manner to that of a Wheatstone bridge. If differences in densities occurs in the two gas streams they are compensated for by a cross stream flow of gas. This cross stream of heated gas passes over a thermocouple, which measures a change in temperature. The thermocouple converts this change of temperature into a voltage variation which is amplified by a d.c. amplifier and displayed on a potentiometric recorder. This detector is thus very sensitive to small changes in density which makes it necessary to keep the detector block at a constant temperature since slight changes in temperature will affect the density.

The sensitivity of this detector will increase if the thermocouples are constructed from very thin wires as this will ensure that the small changes in temperature are not conducted along the thermocouple filament. The choice of the optimum carrier gas, for this detector, is exactly opposite to that for the katharometer. A carrier gas of low thermal conductivity is required as these gases are more sensitive than gases with high thermal conductivity. This is probably due to the fact that gases with high thermal conductivities reduce the temperature gradient along the thermocouple. The gas-density detector may be readily used to monitor corrosive fluorides providing consideration is paid to the choice of materials of construction.

This detector has a principal advantage in that, within its range of linearity, its response is proportional to the change in density and this in turn is proportional to the difference between the molecular weight of the vapour and the molecular weight of the carrier gas.

II. Development of a Spectroscopic Detector.

The application of flames to excite the emission spectra of molecules or atoms lends itself as a method by which detector selectivity can be achieved following gas chromatographic separation as well as providing a detector which functions well in the presence of corrosive materials. Juvet and Durbin[39,43] have proposed the use of a turbulent oxy/hydrogen flame burning on a total consumption burner for the selective detection, via molecular emission, of chromium, iron, and rhodium hexafluoroacetylacetonates, and titanium, arsenic and zirconium chlorides. Zado and Juvet[45] in a similar study used a filter photometric system to view the flame non-selectively and a monochromator photometric system to view the flame selectively to determine molybdenum, and tungsten fluorides, tin chloride, and aluminium, chromium, and rhodium fluoroacetylacetonates. No details were given of the spectra observed, however, except for the optimum wavelength of measurement for each element. Furthermore, it is probable that the range of elements which can be detected using this type of flame is somewhat limited because its high temperature would tend to produce mainly atomic species.

A nitrogen/hydrogen diffusion flame supported on a burner into which aqueous solutions can be nebulised has been used in our laboratories for molecular emission studies of sulphur[135], phosphorus[136], tin[137], and the halogens (except fluorine)[138]. It was found that this type of flame provided an efficient reaction cell for the production of many excited (chemiluminescent) species which are either not observed, or their emission intensity is only very weak, in most other flames.

II.i. Development of the Burner Assembly.

The burner assembly is designed so that the effluent gas from the gas chromatographic column is passed into the centre of the flame before it is mixed with the flame gases. A design of burner similar to those previously used in our laboratories for atomic spectroscopic purposes[139] was chosen.

An emission burner assembly of similar design to that manufactured by Pye-Unicam Ltd. was constructed from stainless steel (10 mm circular burner) but without the side inlet from the nebuliser. Two gas inlets were constructed in the base of the burner stem enabling the gases to be premixed in the cylindrical stem. The burner head is constructed from stainless steel and connected to the stainless steel cylindrical stem via a screw thread.

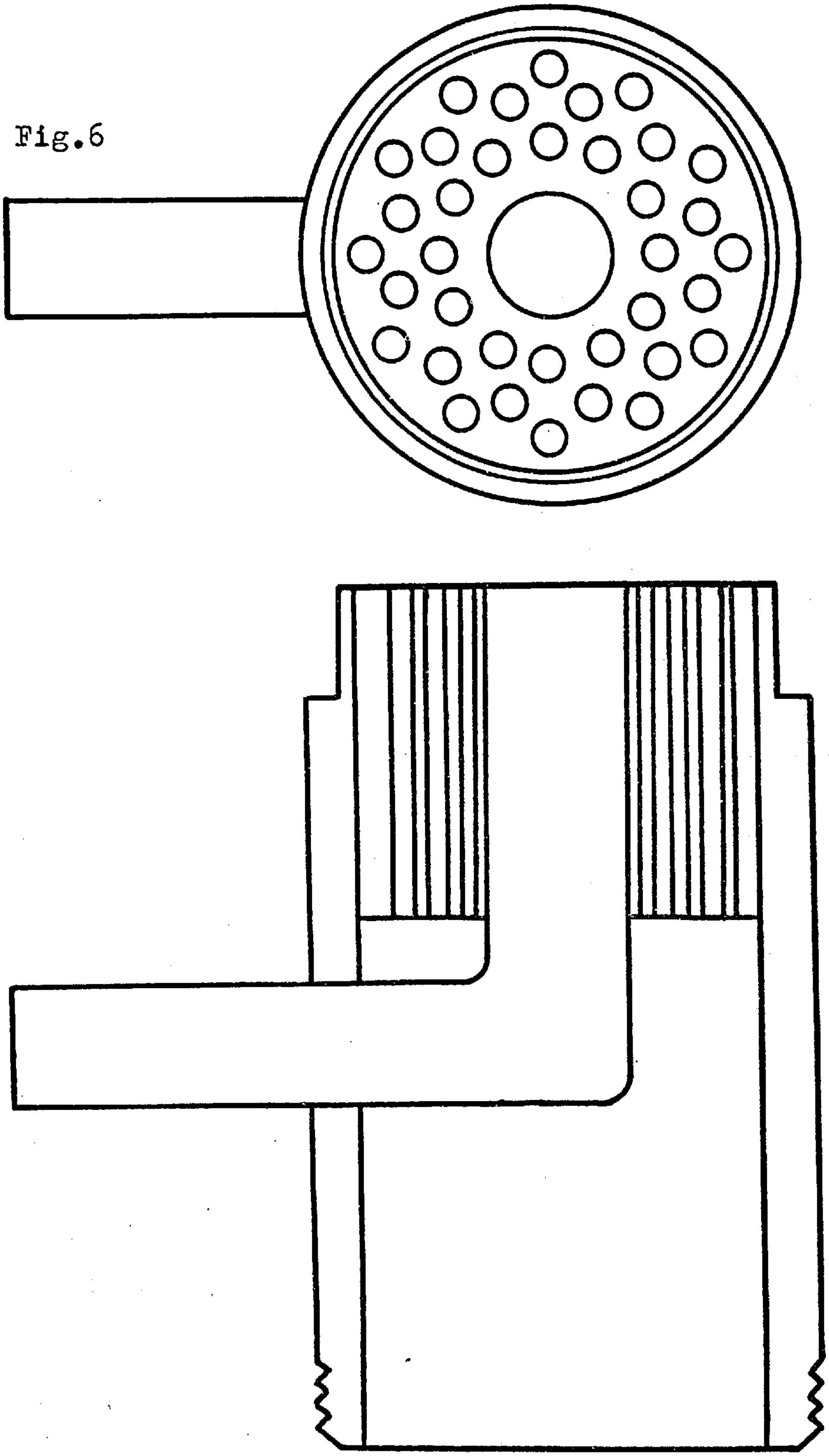
The gases are burnt on the burner head on hypodermic stainless steel tubing (0.69 mm o.d., Accles and Pollock) cut into 2 cm. lengths. These capillaries are packed round a stainless steel capillary (1.27 mm), which is situated in the centre of the burner head, through which the effluent gases from the gas chromatographic column passes. These tubes are smeared with high temperature resistant epoxy resin (Araldite type Ay105 with hardener HY953F, Ciba Ltd.) and the resin left to harden. Thirty-six capillaries are used to prepare the head and the epoxy resin is allowed to fill the interstitial gaps in order that the gases only flowed inside the capillaries. To prevent overheating of the capillaries which results in the destruction of the epoxy resin about 6 mm. of the capillary tubing is left projecting above the level of the burner body. Once the resin has hardened the tops of the capillaries are ground level by a horizontal grinding machine.

The design of the burner head is shown (fig.6.). The gas flows to the burner are controlled and measured with rotameters.

II.ii. Development of an Optical and Read-Out System.

A Beckman DU.u.v. and visible spectrophotometer is used in this study which is modified so that it can view the flame. The photocell, the source and cuvette holder are replaced by an eleven-stage photomultiplier (E.M.I.9601B) and the burner assembly. A light-tight housing is constructed from brass to hold the photomultiplier and

Fig.6



the entrance to the monochromator is extended to the burner head by a brass rectangular tube. Also a wavelength drive motor is fitted to the monochromator, via a gear wheel system, to facilitate the plotting of spectra.

The photomultiplier is powered by an E.H.T. stabilised power supply and the signal which is produced is displayed directly on a 0-10 mv f.s.d. chart recorder.

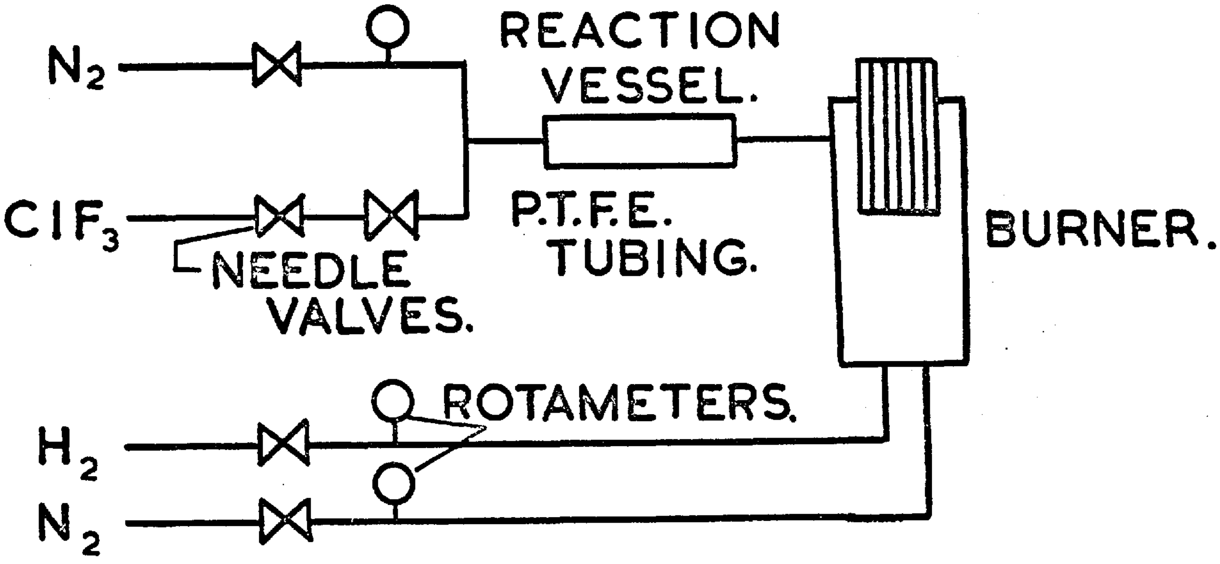
II.iii. Development of a Continuous Reaction System.

A system is designed to form the volatile fluorides continuously. This is to establish whether emission occurs in a low temperature hydrogen diffusion flame and if it does at which wavelength. Most of the fluorides studied are formed at ambient temperatures. Therefore, if chlorine trifluoride is passed over the element under investigation at a slow rate, it is possible to produce a steady, slow rate of production of the volatile fluorides. It was, however, decided to dilute the chlorine trifluoride with an inert diluent gas (nitrogen) to ensure that the rate of reaction may be controlled. In view of the reactivity of chlorine trifluoride it is difficult to measure the flow-rate with any degree of accuracy. In consequence the flow-rate of the chlorine trifluoride is adjusted to the minimum value required to give spontaneous and controlled reaction. This critical control of the flow-rate of the chlorine trifluoride is performed by using two stainless steel needle valves (Autoclave Engineers Ltd., Erie, Pennsylvania U.S.A.) in series. In order to follow the rate of production of the fluorides, visually, the reaction cell is made from transparent silica tubing (8 mm. i.d.). This tube is not attacked at room temperature by chlorine trifluoride. The element under investigation is placed inside this tube and the reaction products, pass, via a PTFE. tube (3.125 mm. o.d.), into the inlet capillary in the burner head , via a stainless steel coupling (Swagelok Ltd.). The nitrogen flow-rate is controlled and measured with a rotameter and a schematic diagram of this apparatus is shown (fig.7).

III. Emission Spectra and their Interpretation.

The E.H.T. supply is set to provide 1150 volts and the dark current and background radiation are backed-off on the chart recorder. About 0.5 g. of the element to be

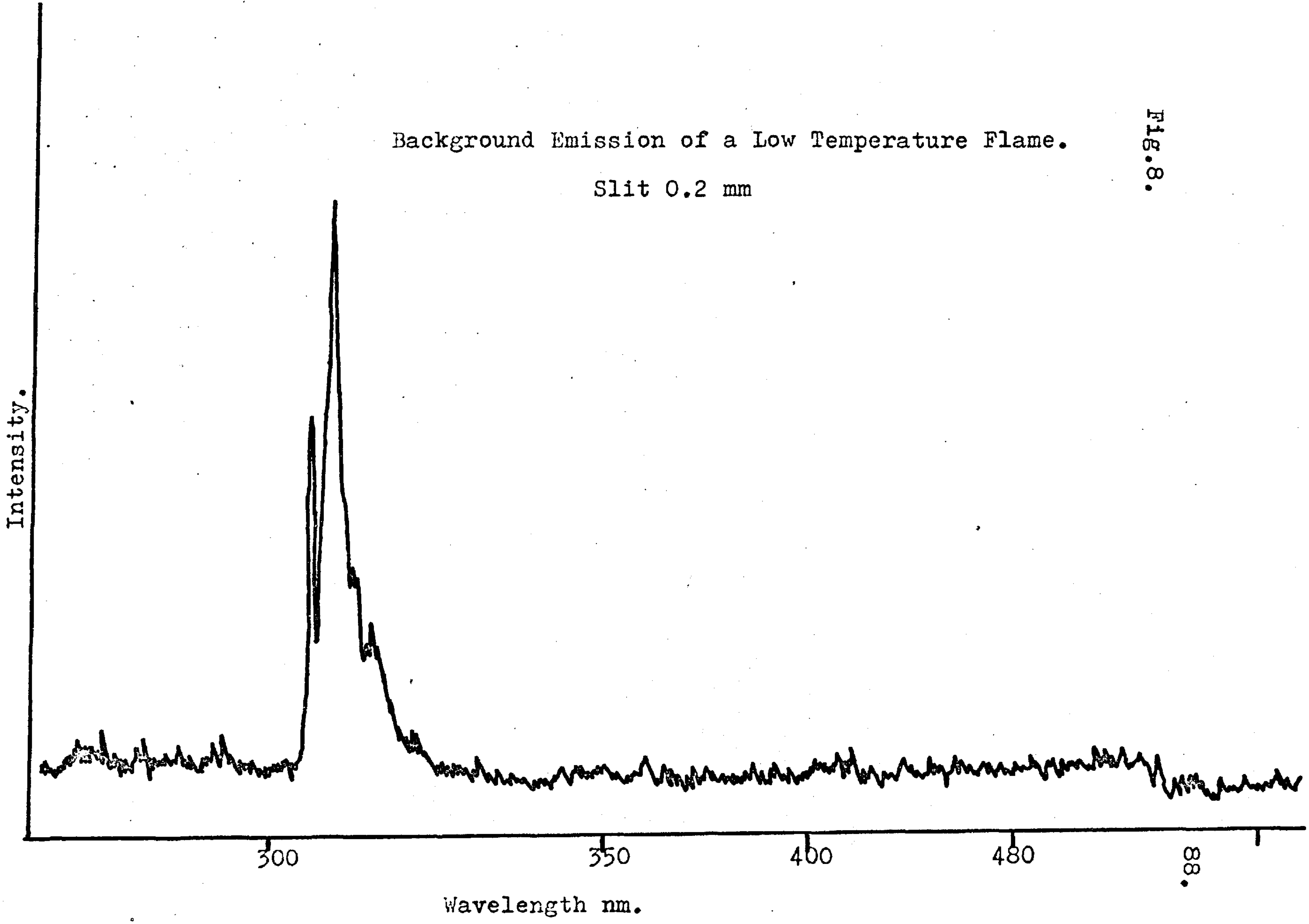
Fig.7.


N_2
REACTION VESSEL.
ClF_3
P.T.F.E. TUBING.
NEEDLE VALVES.
BURNER.
ROTAMETERS.
H_2
N_2

studied is placed inside the silica reaction tube, and the nitrogen diluent gas is adjusted to a flow-rate of 100 ml./min. The flow-rate of the chlorine trifluoride is adjusted to a minimum value. The volatile fluorides thus produced pass directly into the low-temperature hydrogen diffusion flame (nitrogen and hydrogen flow-rate of 4.7 and 2.6 litres/min. respectively) and a spectrum is recorded from 280-700 nm. The slit width of the monochromator is adjusted so that the resulting spectrum justs fits the chart paper. The elements studied included antimony, arsenic, boron, carbon, germanium, iodine, molybdenum, phosphorus, rhenium, selenium, silicon, sulphur, tellurium, tungsten, and uranium. Uranium is the only element investigated which did not give rise to either a line or banded spectrum.

III.i. Flame Background.

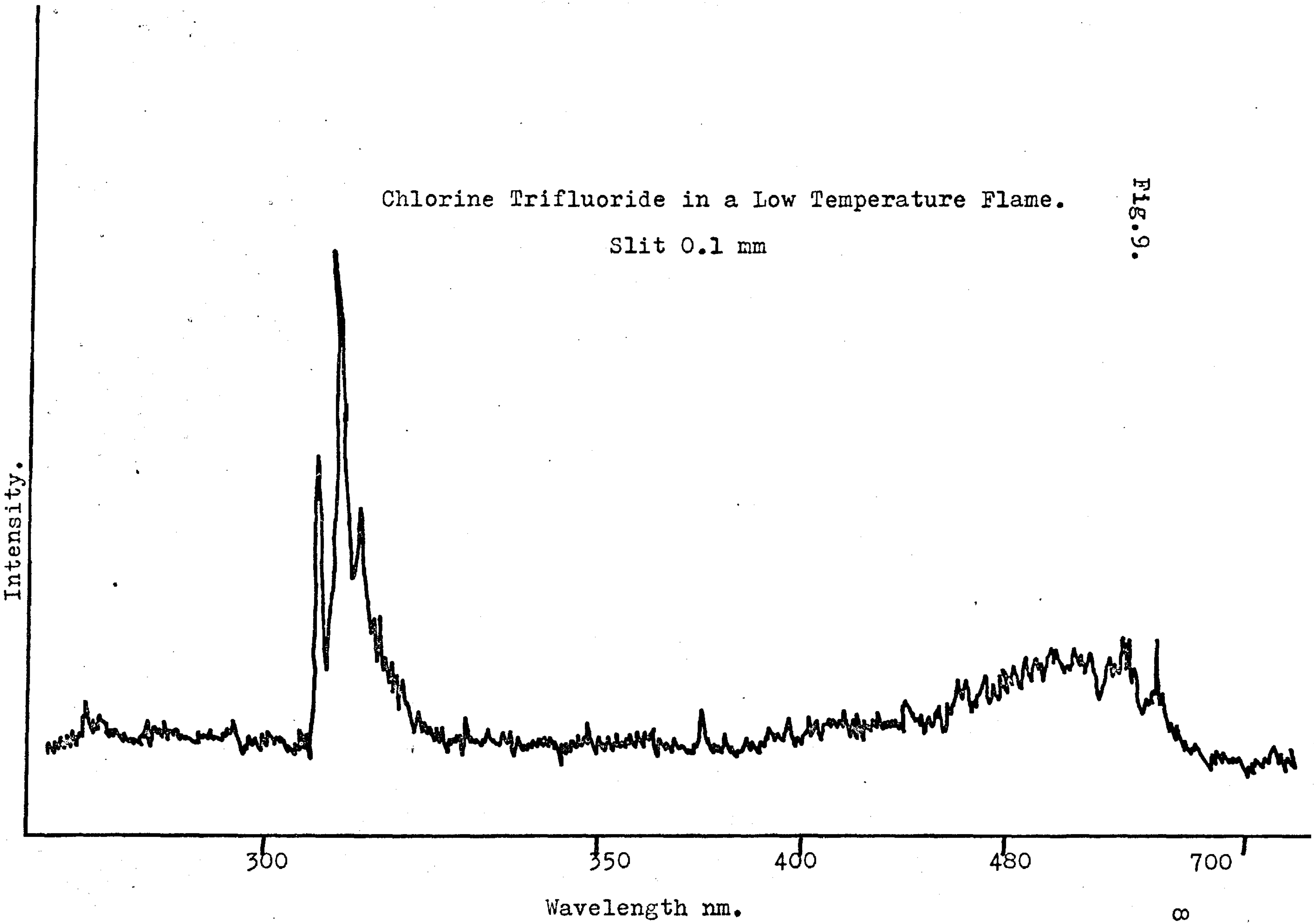
The only emission observed (fig.8) is a weak OH band head at ca. 301 nm. In the presence of chlorine trifluoride (fig.9) the OH background increases slightly. No other lines or bands are observed under the above operating conditions in the diffusion flame.



Background Emission of a Low Temperature Flame.

Slit 0.2 mm

Fig.8.



Chlorine Trifluoride in a Low Temperature Flame.

Slit 0.1 mm

Fig.9.

III.ii. Antimony.

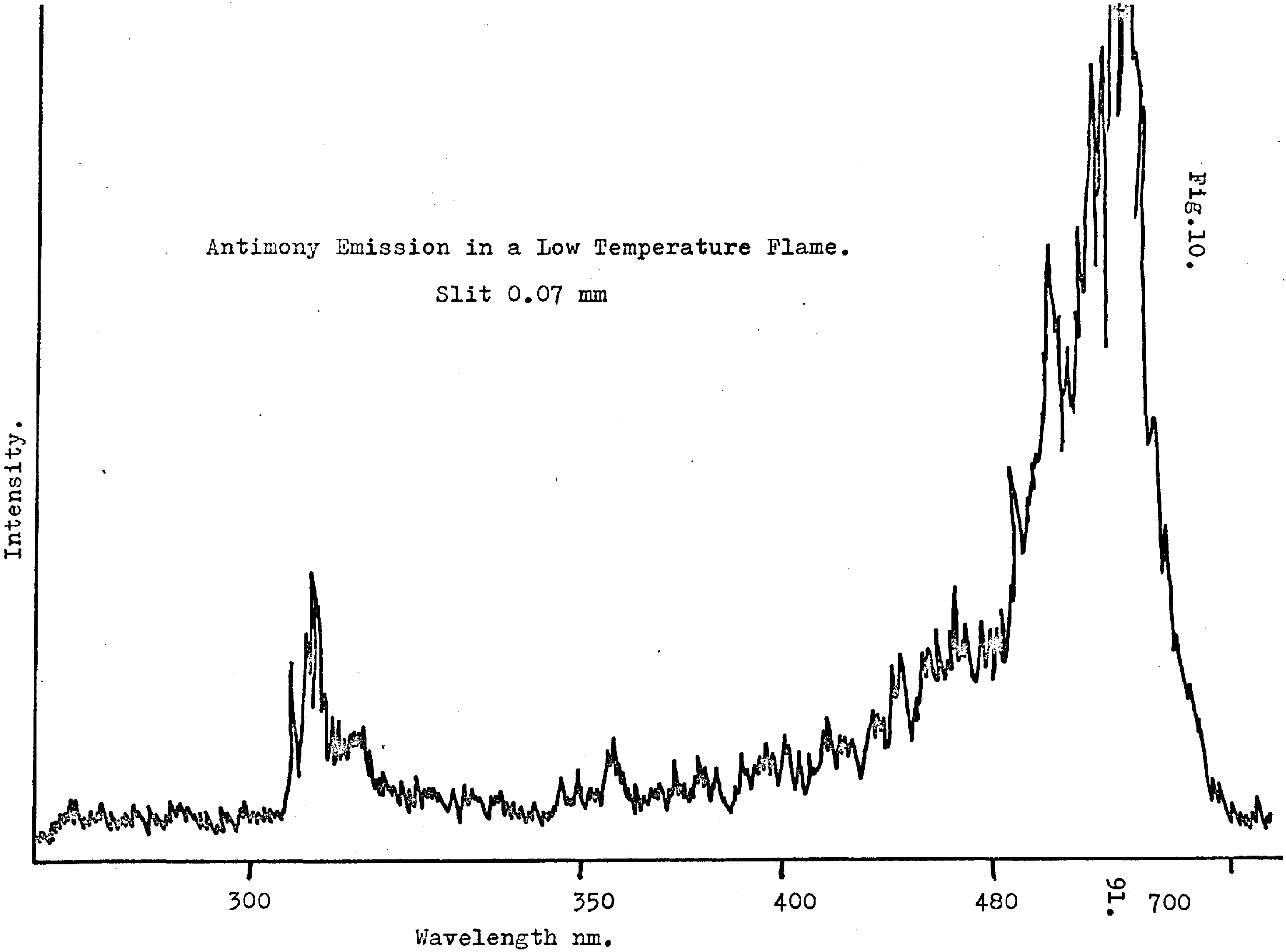
Antimony is found to emit a broad continuum over the range 440-700 nm with a maximum at ca. 580 nm (fig.10). The only continuum reported in the literature[140,141,142] either using arcs in air or a discharge tube is found to occur over the range 450-680 nm and is attributed to the SbO species. A comparison of these spectra suggests that the continuum given in the low temperature flame is also due to the SbO species.

III.iii. Arsenic.

Arsenic gives a broad continuum over the range 360-600 nm (fig.11) with pronounced maxima as follows:

Wavelength (nm)	Relative Intensity
410	8
460	10
515	8
580	10

The species responsible for this emission is not known, although arsenic is reported to emit a continuum in an air/hydrogen flame[143] but no wavelengths are mentioned.

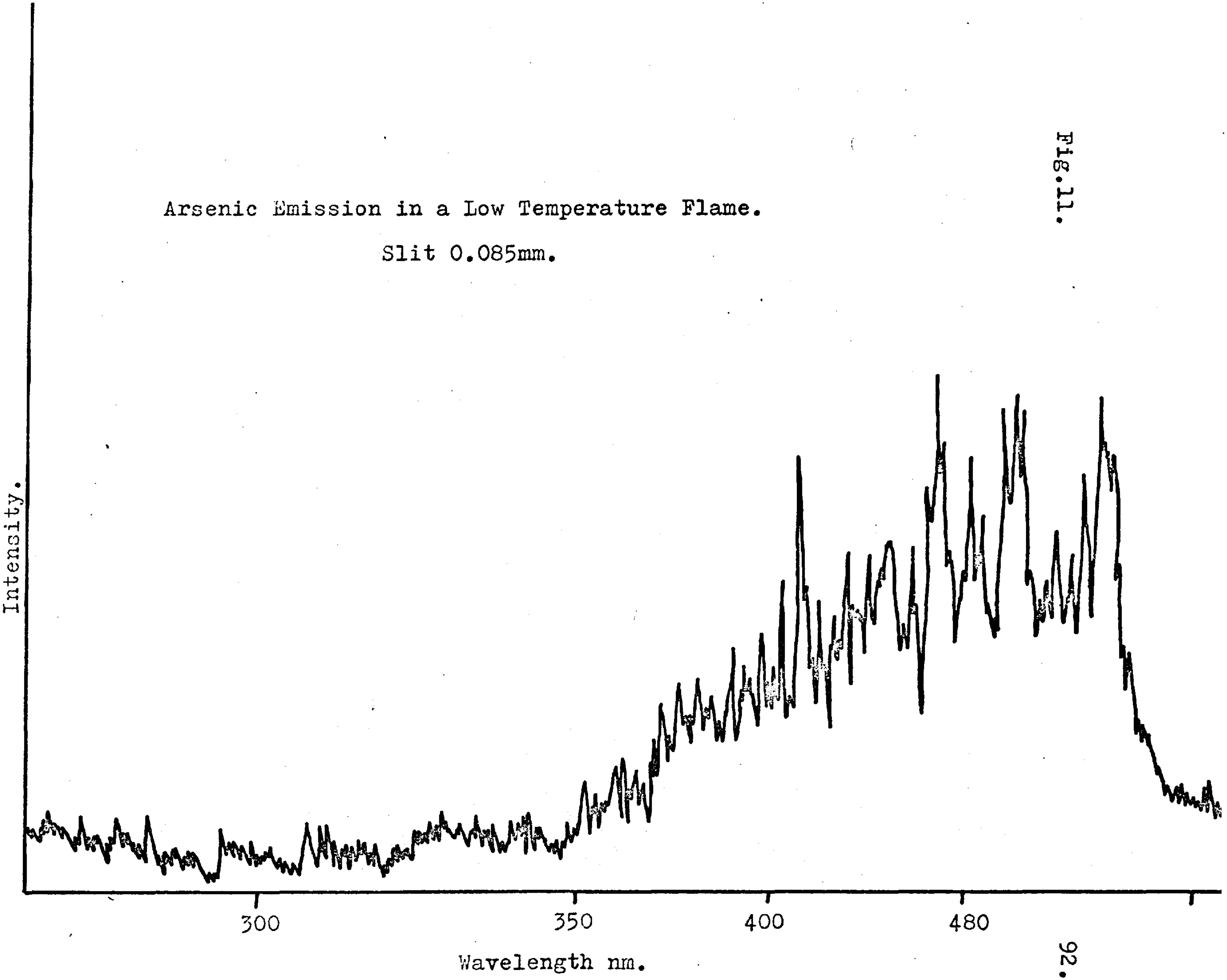


Antimony Emission in a Low Temperature Flame.

Slit 0.07 mm

Fig.10.

Fig.11.



Arsenic Emission in a Low Temperature Flame.

Slit 0.085mm.

III.iv. Boron.

Boron is found to give a banded emission (fig.12) with principal band heads at the following wavelengths:

Wavelength (nm)	Relative Intensity	Wavelength[144]*
471	1	471
492	5	493
548	10	545
580	10	580
602	5	602

* Boron, as the BO_2 species, in an oxy/hydrogen flame.

It appears to be conclusive that the emission in the hydrogen diffusion flame is also due to the BO_2 species.

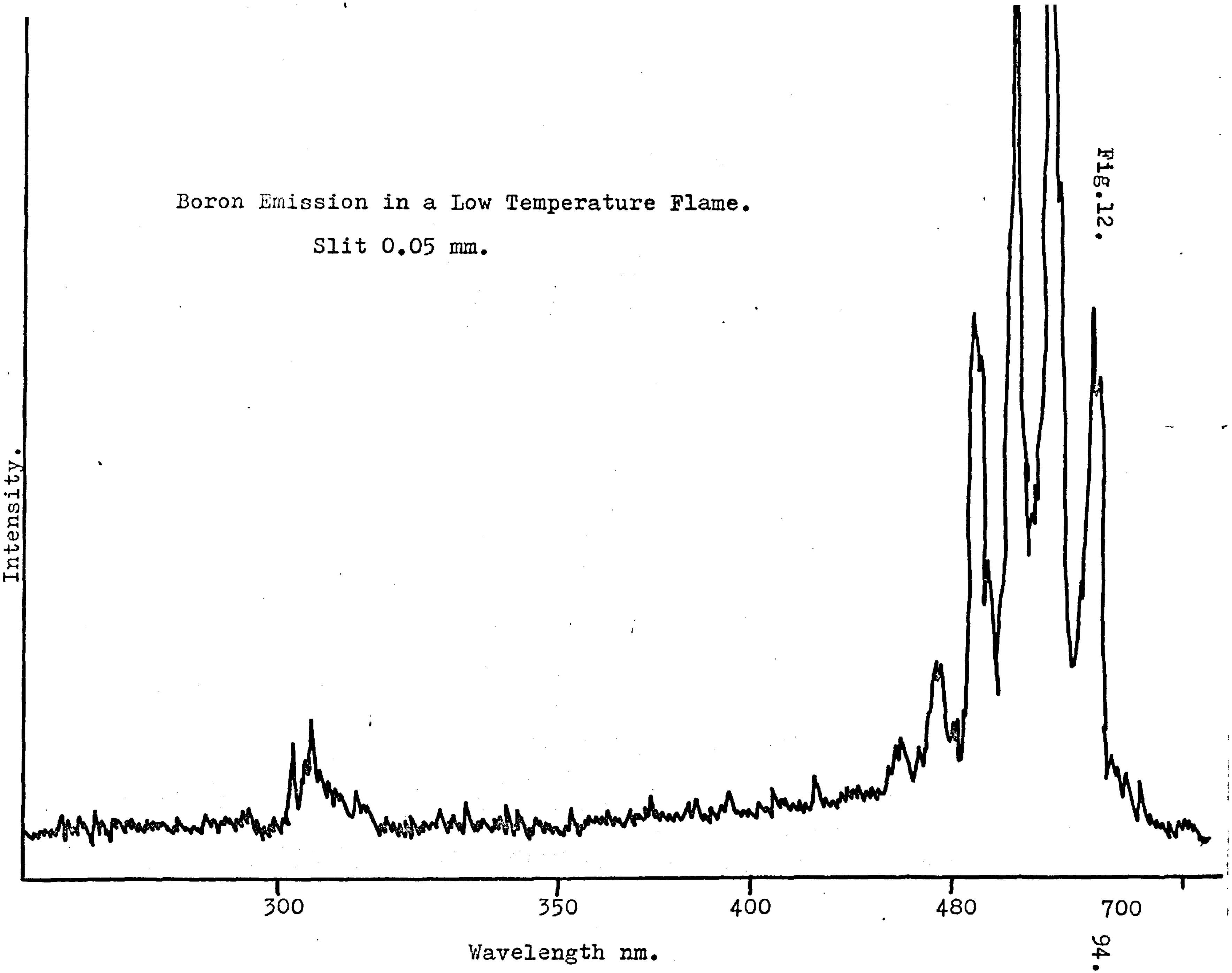
III.v. Carbon.

Carbon emits a broad continuum over the region 420-700 nm (fig.13) with a maximum at 560 nm. Emission from carbon in a discharge tube is well documented[145] and a comparison of the spectra is indicative of the presence of the CO molecule in the above study.

III.vi. Germanium.

Germanium shows a broad continuum over the region 350-

Fig.12.

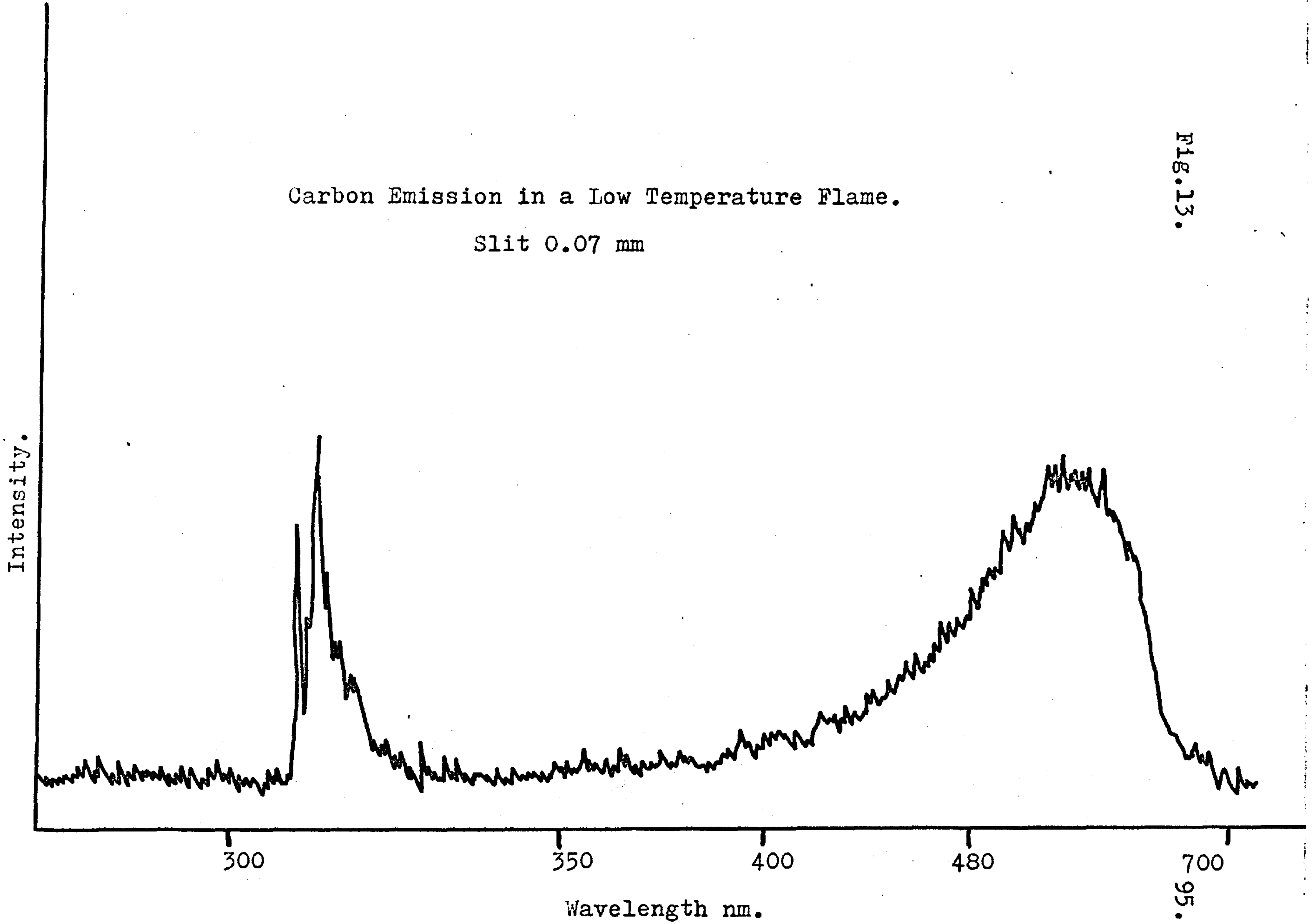

Boron Emission in a Low Temperature Flame.

Slit 0.05 mm.

Fig.13.

Carbon Emission in a Low Temperature Flame.

Slit 0.07 mm



700 nm (fig.14) with a maximum at 458 nm. Two continua attributed to germanium species have been reported[146,147] but neither correspond well with that observed in this study; (the first occurs over the region 270-480 nm and is due to the GeF species obtained in a discharge tube, and the second occurs over the region 250-300 nm and is due to the GeO species.).

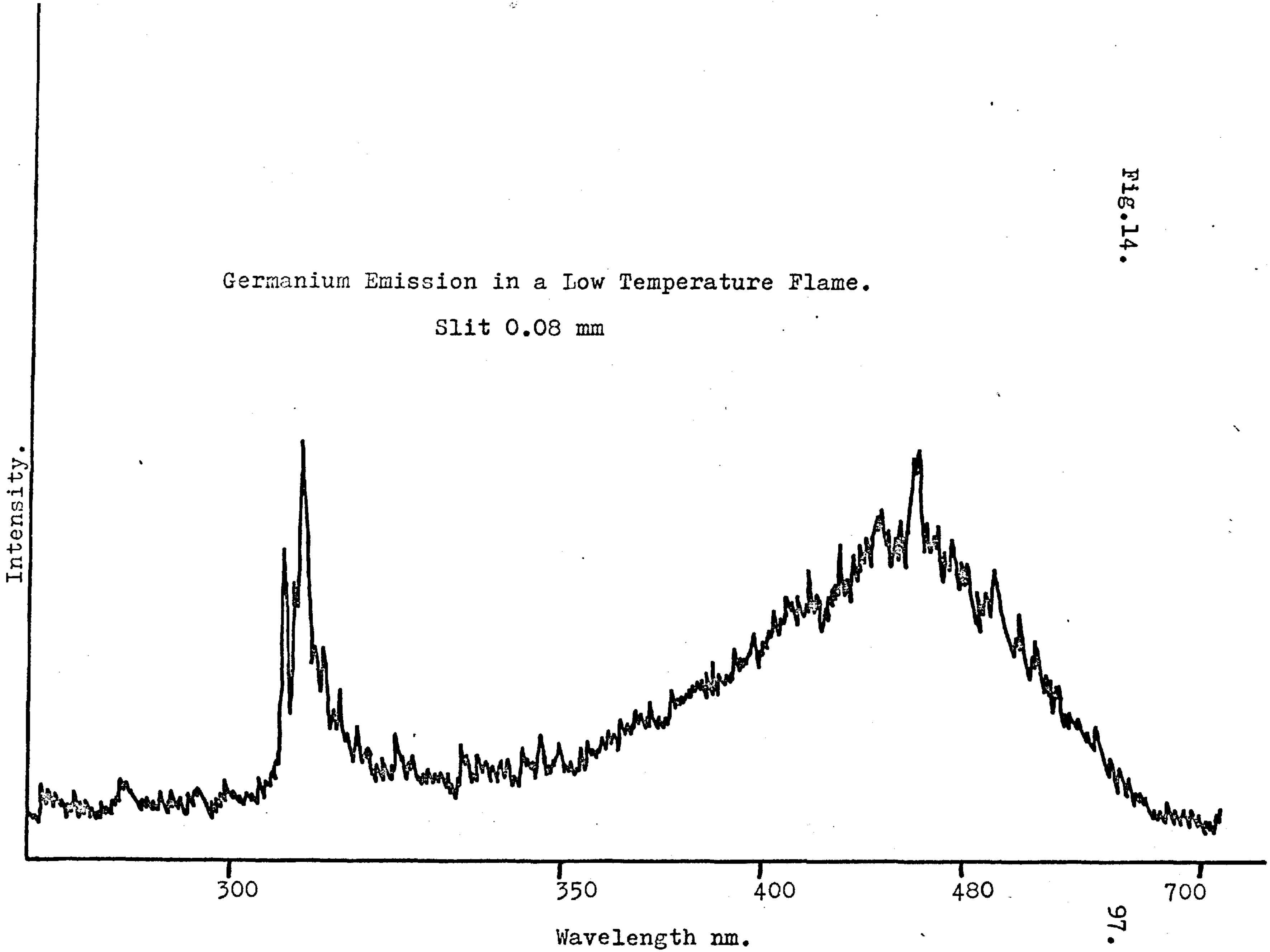
III.vii. Iodine.

Iodine emits a broad continuum over the region 490-700 nm with a maximum at 616 nm (fig.15). This resembles the continuum given in a flame produced by the reaction between iodine and fluorine (due to the IF species)[148] and also the continuum given by the IO species in an oxy/hydrogen flame[149]. It is probable that the spectrum emitted in the diffusion flame is a result of the presence of both these species.

III.viii. Molybdenum.

The broad continuum given over the region 490-700 nm with maxima at 580 and 622 nm (fig.16) is apparently due

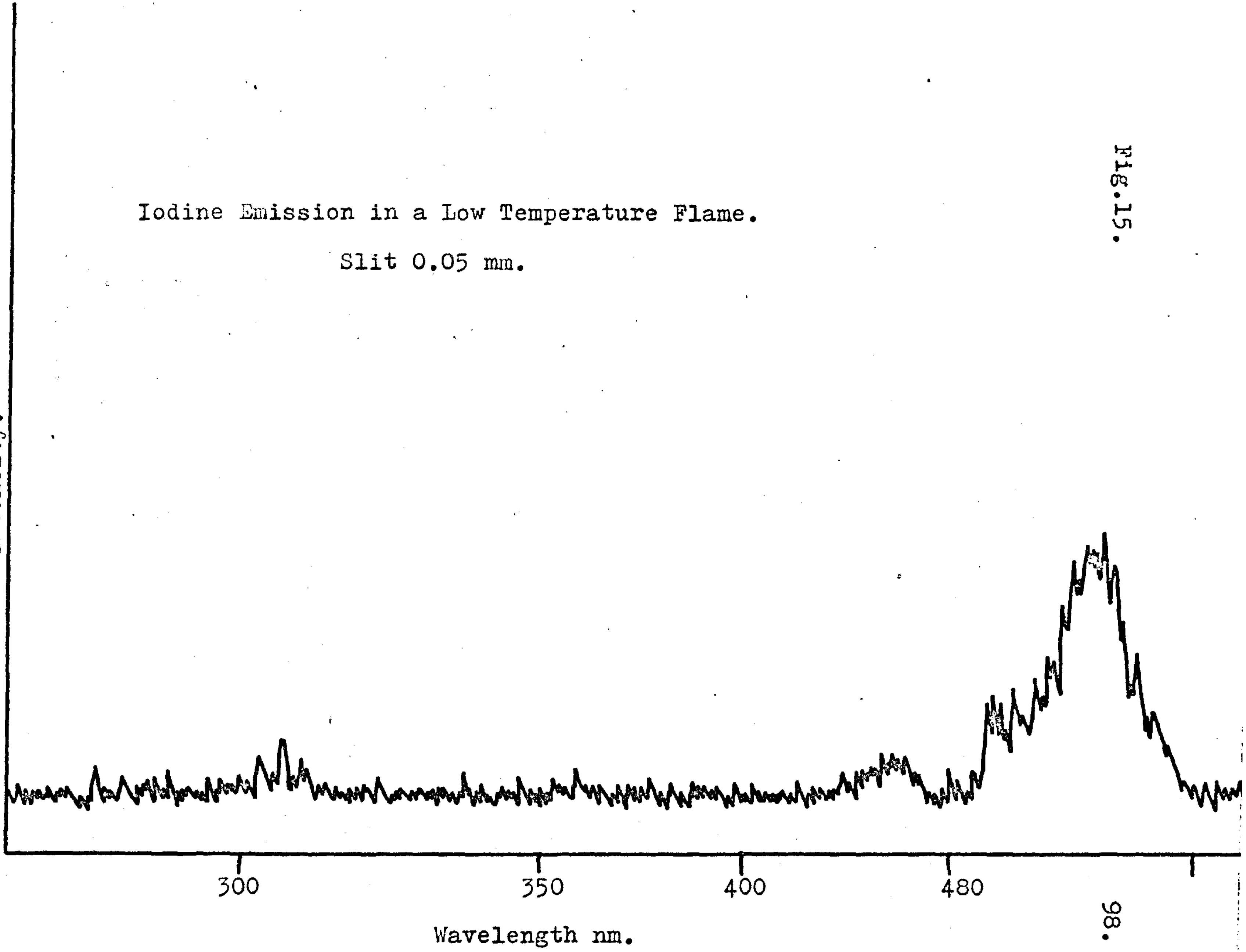
Fig.14.



Germanium Emission in a Low Temperature Flame.

Slit 0.08 mm

Fig.15.


Iodine Emission in a Low Temperature Flame.
Slit 0.05 mm.
Intensity.
300
350
400
480
Wavelength nm.

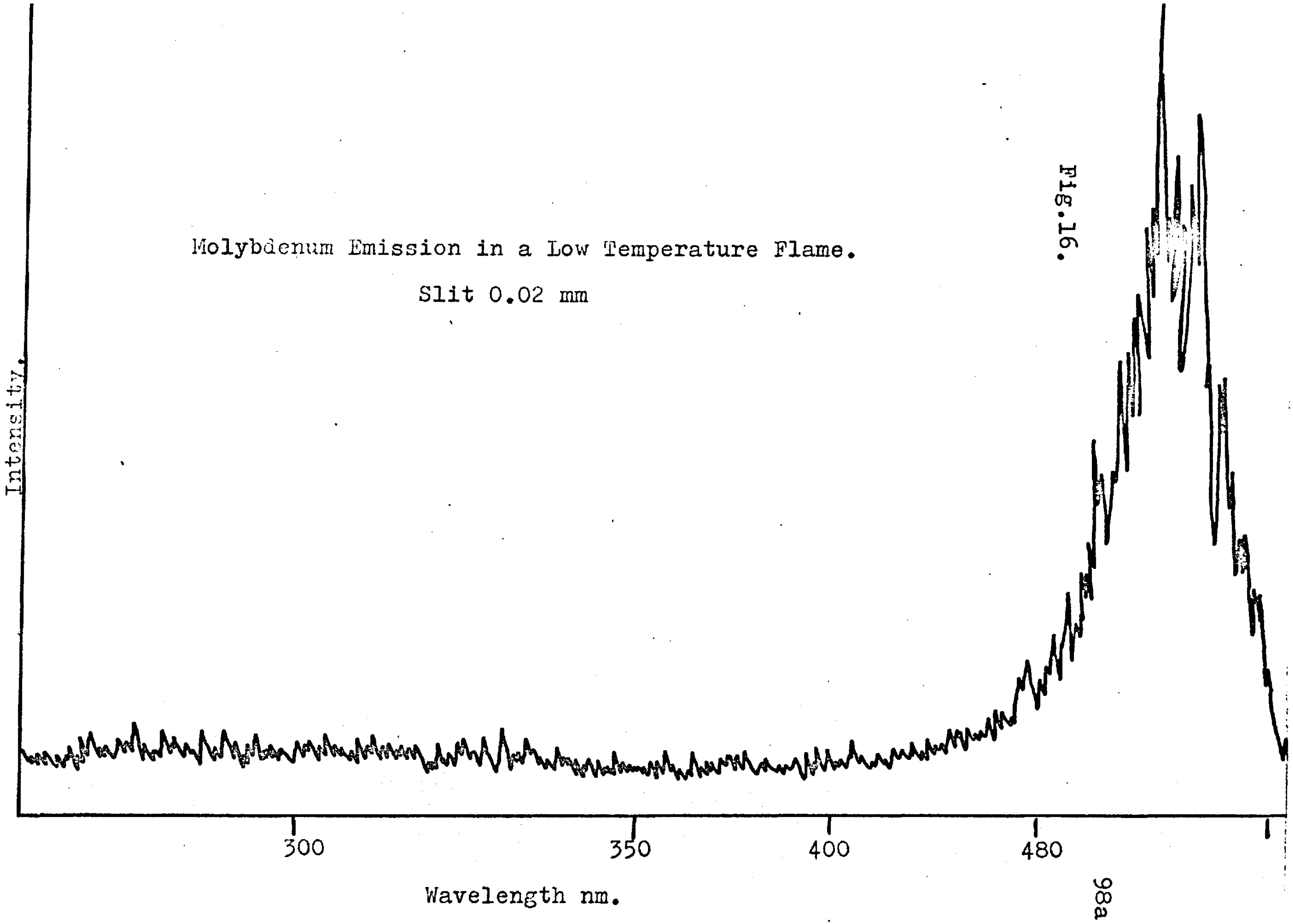


Fig.16.

Molybdenum Emission in a Low Temperature Flame.

Slit 0.02 mm

to excited MoO molecules. It resembles closely the spectrum given by the MoO species formed in an arc continuum over the region 480-660 nm with maxima at 522 and 630[150]. The observed emission spectrum also corresponds with that given by the MoO species in a separated nitrous oxide acetylene flame (band heads at 599.1, 601.0, 611.0, 612.2, 613.4, 614.7, 623.0, and 624.6 nm)[151].

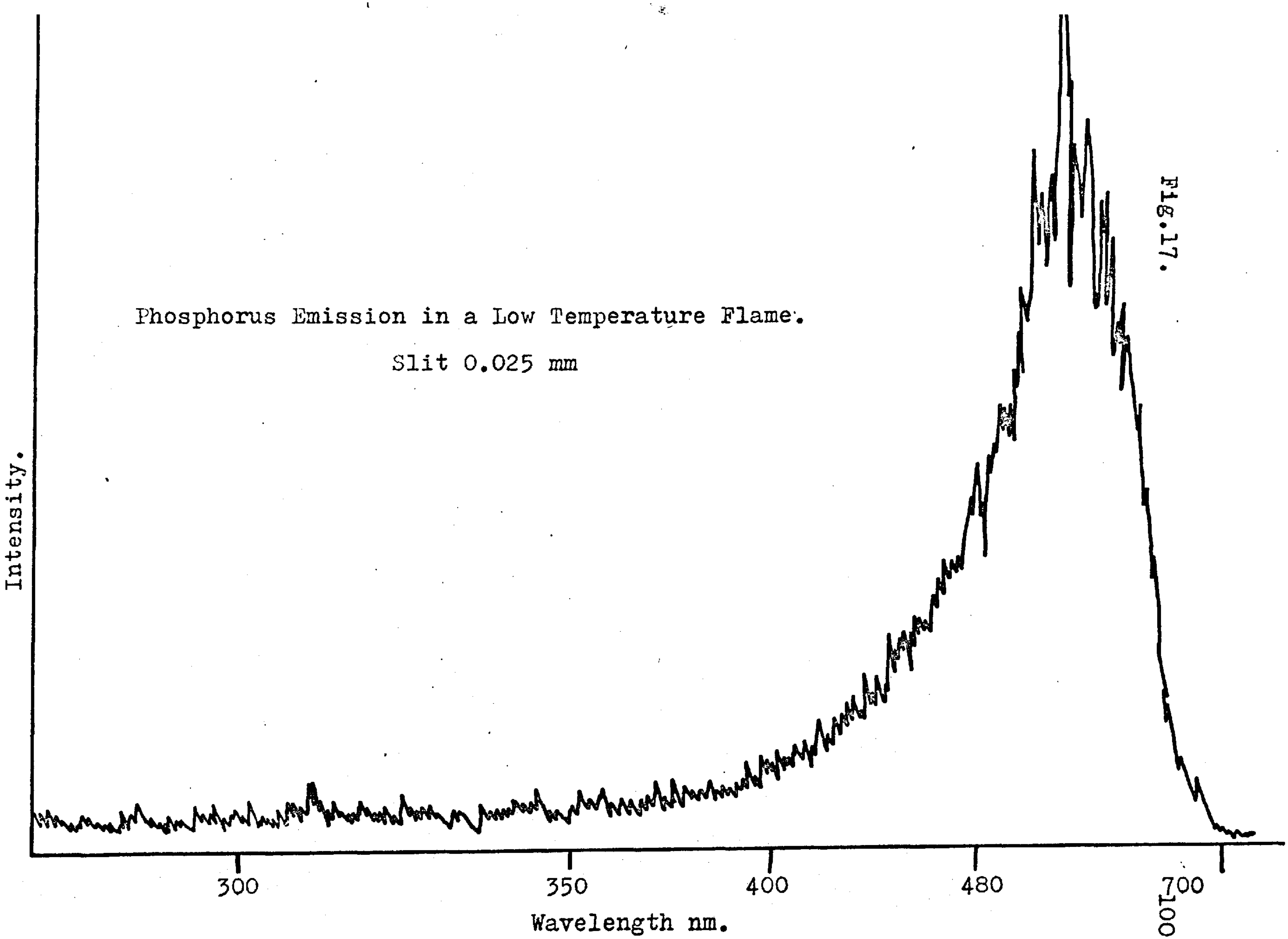
III.ix. Phosphorus.

Phosphorus is found to emit a broad continuum over the region 420-700 nm with a maximum at 528 nm (fig.17). This corresponds well with the continuum reported in a similar hydrogen diffusion flame due to the H-P-O species[136].

III.x. Rhenium.

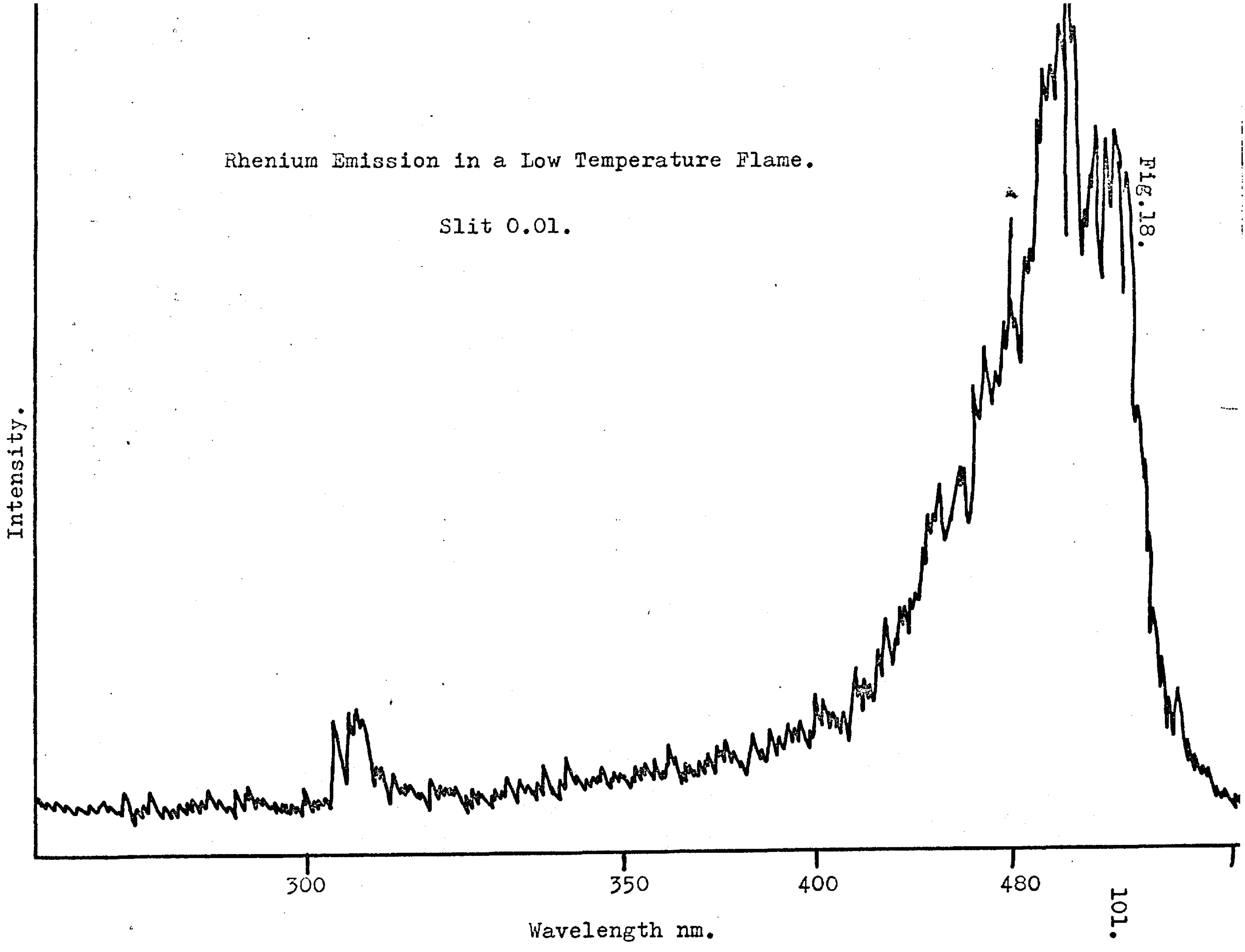
Rhenium is found to emit a broad continuum over the region 400-700 nm (fig.18) with a maximum at 525 nm. To the authors' knowledge no such molecular emission spectrum has been reported previously for rhenium.

Fig.17.



Phosphorus Emission in a Low Temperature Flame.

Slit 0.025 mm



Rhenium Emission in a Low Temperature Flame.

Slit 0.01.

Fig.18.

III.xi. Selenium.

Selenium gives a banded emission (fig.19) with principal band heads at the following wavelengths:

Wavelength (nm)	Relative intensity	Wavelength[152]* (nm)	Relative[152]* intensity	Wavelength[153,154]** (nm)
338	5	338.5	6	338.32
348	6	348.85	9	348.35
358	7	358.85	9	354.54
370	9	370.03	9	370.64
381	10	381.56	10	381.53
394	10	394.29	10	392.91
436	10	-	-	434.00
452	10	-	-	455.00

* principal band heads due to excited SeO species produced in a hydrogen discharge tube.

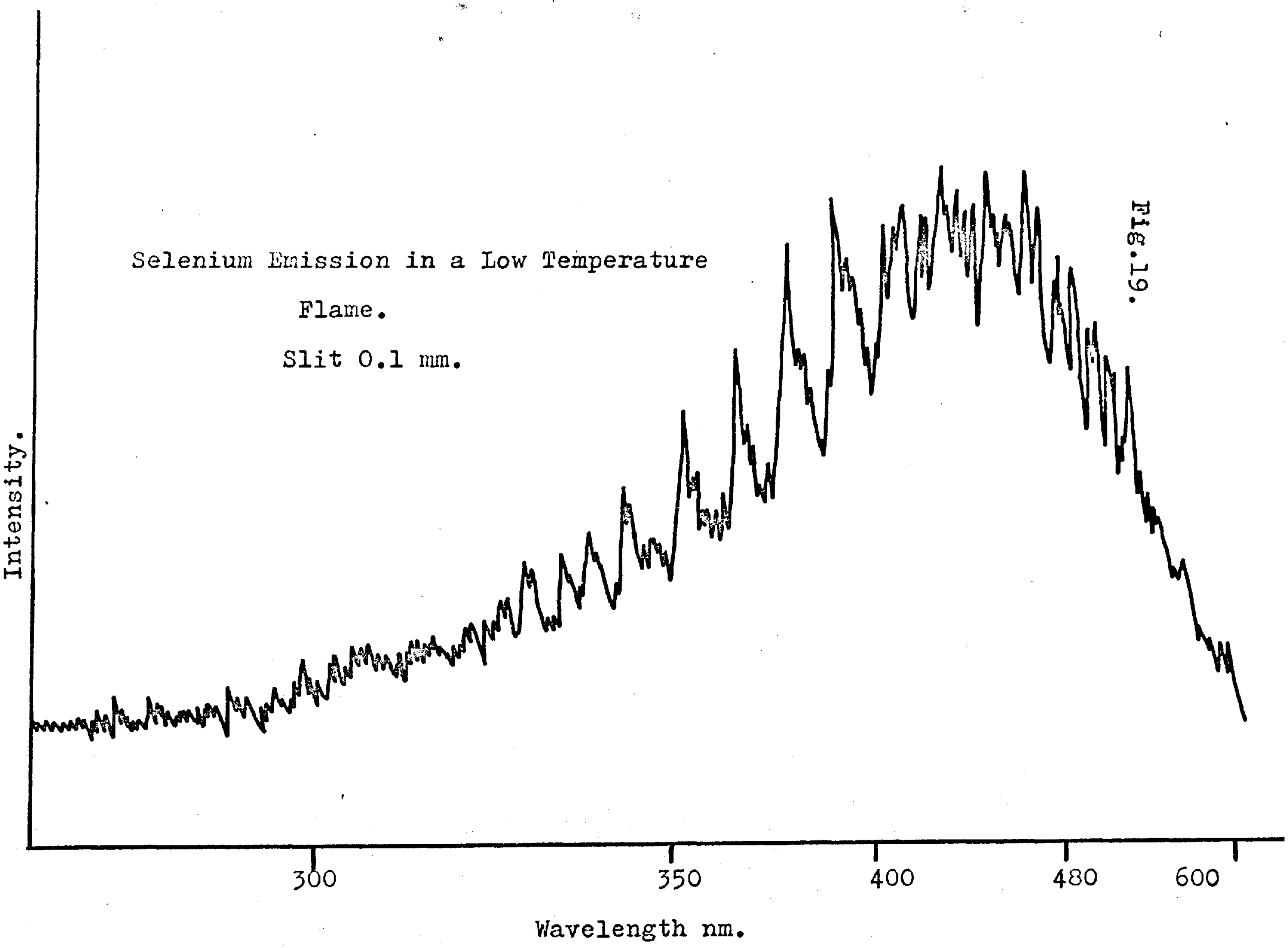
** principal band heads due to the Se$_2$ species.

The observed spectrum appears to be due to the presence of both the SeO and Se$_2$ species.

III.xii. Silicon.

Silicon emits a banded emission (fig.20) with principal band heads at the following wavelengths:

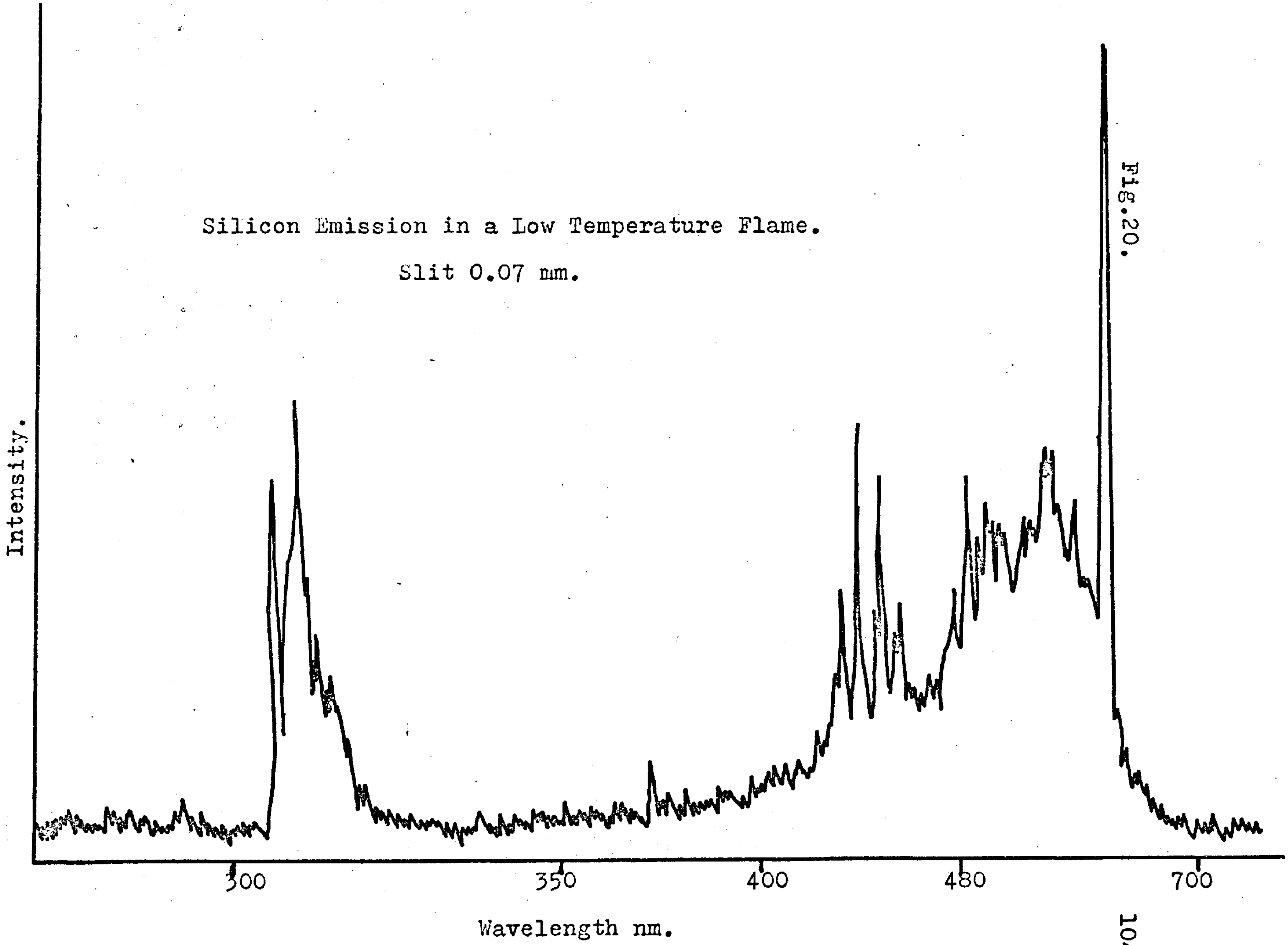
* principal band heads from the SiF species in discharge tubes. At least part of the spectrum can be attributed to



Selenium Emission in a Low Temperature Flame.

Slit 0.1 mm.

Fig.19.



Silicon Emission in a Low Temperature Flame.

Slit 0.07 nm.

Fig.20.

the SiF species.

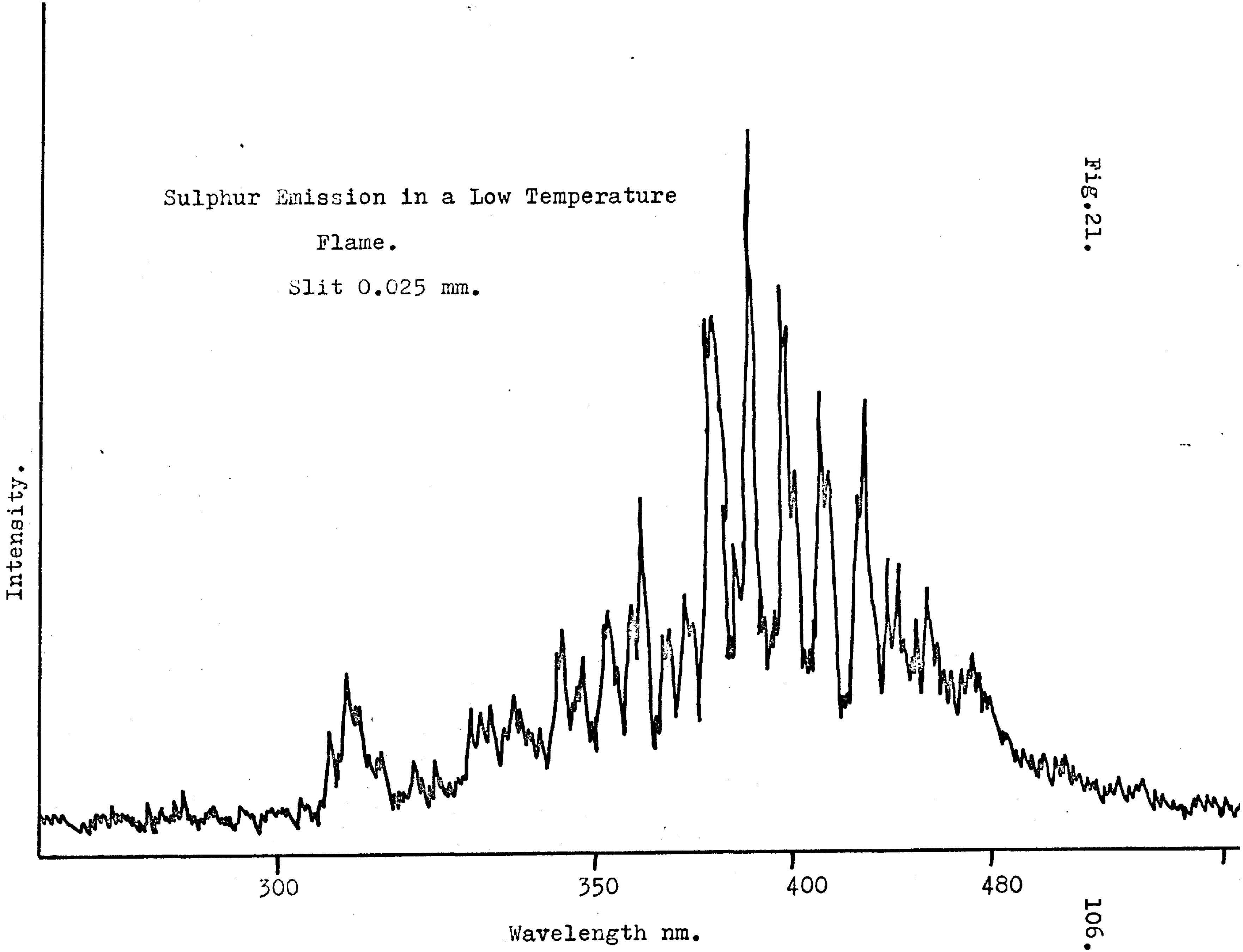
Wavelength (nm)	Relative intensity	Wavelength[155,156,157]* (nm)	Relative * intensity
430	3	430.13	5
436	4	436.82	10
445	4	449.58	6
485	4	485.05	5
540	7	-	-
616	10	-	-

III.xiii. Sulphur.

Sulphur is found to give a banded emission (fig.21) with band heads at the following wavelengths:

Wavelength (nm)	Relative intensity	Wavelength[135]* (nm)	Relative* intensity
350	4	350	3
355	4.5	355.5	4
359	4.5	359	3
364	5.5	364.5	7
374	7.5	374	9
384	10	384	10
394	7.5	394	10
405	5.5	405	9
415	6.5	415	6
419	5.5	419.5	4
427	6.5	427	4
431	5	431	3

* Emission spectrum due to the S_2 species in a hydrogen diffusion flame.


Sulphur Emission in a Low Temperature Flame.

Slit 0.025 mm.

Fig.21.

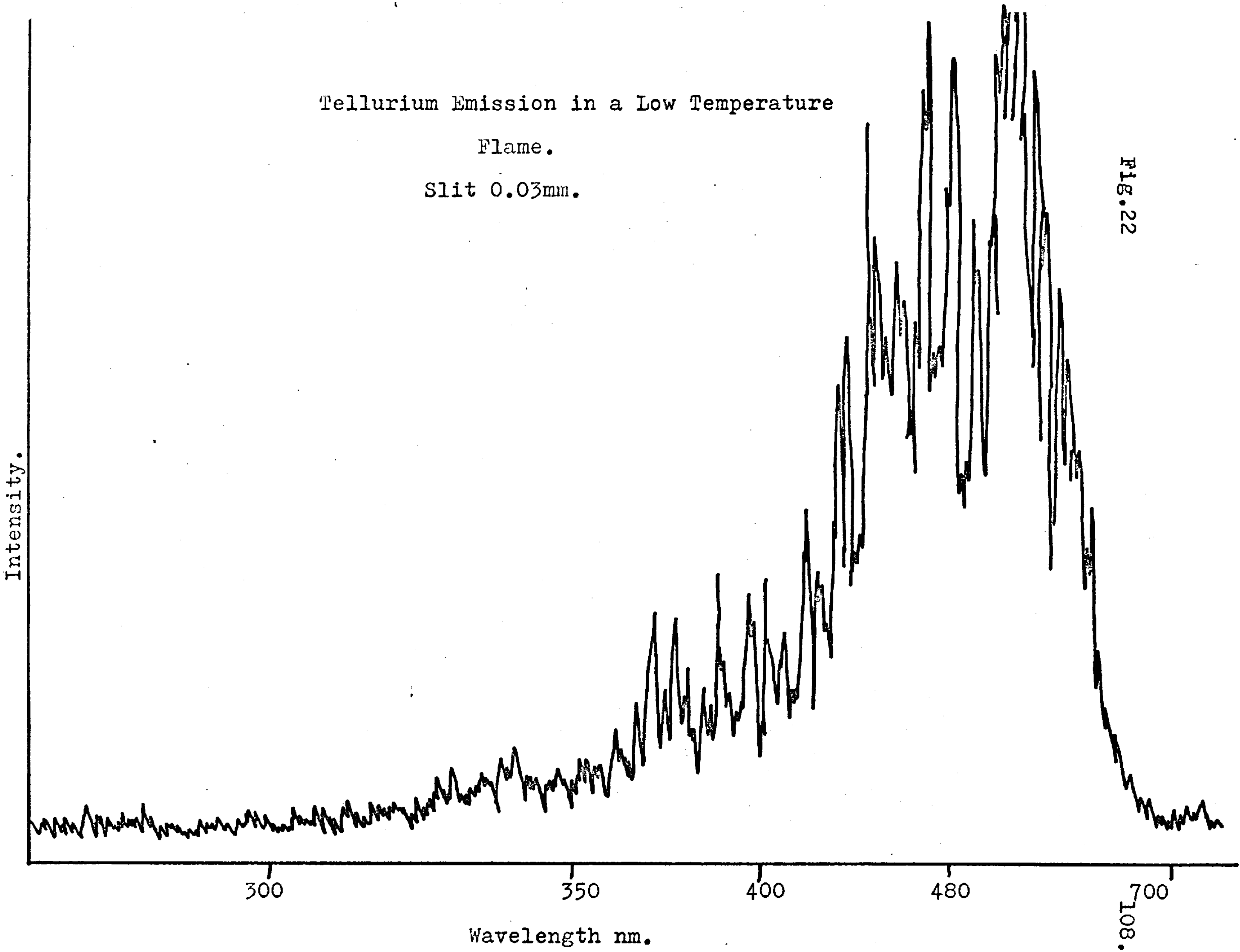
III. xiv. Tellurium.

Tellurium emits a complex banded system over the region 360-700 nm (fig.22) with a maximum at ca. 525 nm. The only reported continua appears to be due to the Te_2 species (occurring in a discharge tube[158]) over the region 490-640 nm and to the TeO species (also occurring in a discharge tube[154]) over the region 330-620 nm. It is not known which is the predominant species in the low temperature hydrogen diffusion flame.

III.xv. Tungsten.

Tungsten is found to emit a broad continuum over the region 440-700 nm with maxima at 590 and 622 nm (fig.23). A similar continuum is reported over the same region with maxima at 586.52, 589.86, 621.98, 626.02, and 630.33 nm for the WO species in an arc discharge[159,160].

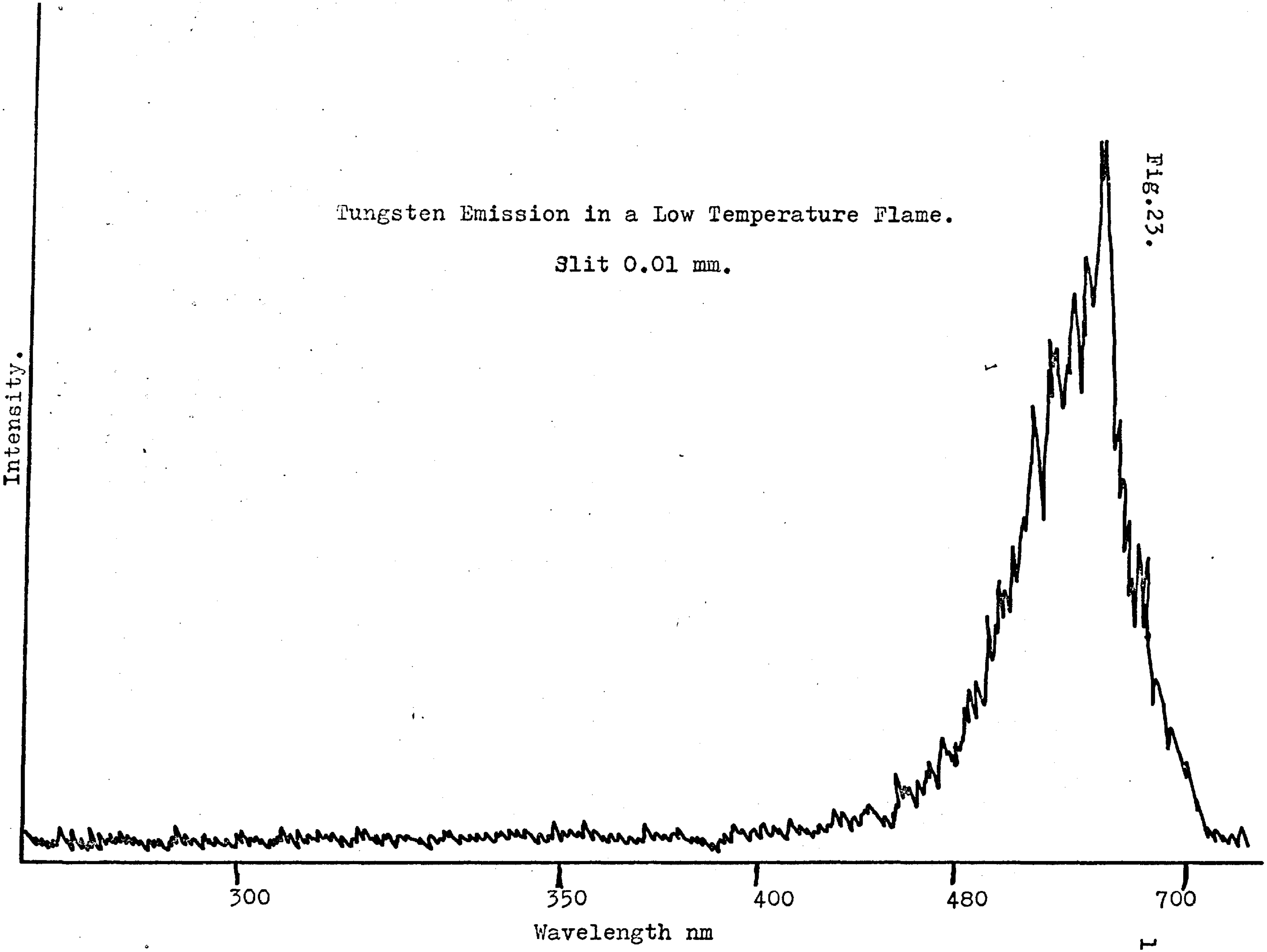
Each of the metal fluorides (except uranium) examined give rise to a specific molecular emission in the hydrogen diffusion flame. The emission for all elements except carbon is very intense and may be used for



Tellurium Emission in a Low Temperature Flame.

Slit 0.03mm.

Fig.22



Tungsten Emission in a Low Temperature Flame.

Slit 0.01 mm.

Fig.23.

qualitative purposes providing the metal fluorides are separated first on a gas chromatographic column. The very low background and noise given by the flame used in this study is advantages and could allow for the use of wide band-pass filters to achieve maximum sensitivity for all elements.

The predominant emitting species have been identified in all instances except for Ge and Re. For the elements As, Se, and Te it is probable that more than one species is responsible for the emission observed, e.g. the oxide and the diatom. It is considered unlikely that any of the emissions observed can be attributed to particulate matter such as incandescent elemental or oxide particles.

The following wavelengths should provide optimum results for both qualitative and quantitative purposes:

Sb at ca. 580nm; As at 460 (or 580) nm; B at 580 (548) nm; C at 560 nm; Ge at 458 nm; I at 616 nm; Mo at 580 (622) nm.; P at 528 nm; Re at 525 nm; S at 374, 384, 394, 436, and 452 nm; Si at 616 nm; Te at 525 nm; and W at 622, (or 590) nm.

lV. Evaluation of the Spectroscopic Detector.

The wavelength of maximum emission for each individual element is determined by interpreting the molecular emission obtained in the low temperature flame. Armed with this information it is possible to establish whether these emissions are analytically useful. For it is hoped that by the careful selection of wavelength, at which to monitor, it will be possible to distinguish between differing elements and thus produce a selective detector.

If the outlet from the reactor-injection vessel is connected directly to the inlet capillary in the burner head it is possible to evaluate the reactor-injection system, without the introduction of a third variable, namely, the gas chromatographic column. To be analytically useful the system must form the fluorides quantitatively and the reactor-injection vessel must not suffer from any of the problems exhibited by the Juvet and Fisher system. It is to establish this that a series of calibration curves are plotted for each individual element.

The E.H.T. supply is set to provide sufficient voltage to ensure that the signal given by the largest weight, in each series of samples, remains on-scale and the dark current and background radiation are backed-off on the chart recorder. The flow-rates of the carrier gas (nitrogen) and of the nitrogen and hydrogen to the burner are adjusted to 0.1, 4.7, 2.6, litres/minute respectively.

The weighed samples are placed in the reaction vessel and the reactor-injection vessel is evacuated to less than 1 torr and the chlorine trifluoride is introduced. The sample boat is then heated to dull red heat ($600^{o}C$) with the radio frequency generator and maintained at this temperature for a period of one minute. The radio frequency generator is then switched off and the products are swept directly to the flame by the nitrogen carrier gas. The emission signals are monitored at the optimum wavelength for each element and are compared to the signal obtained for a blank determination of just chlorine trifluoride.

IV.i. Optimum Slit Width.

The E,H.T. supply provides 1150 volts and a series of similar samples of boron are weighed (196µg.) and placed in the reaction vessel. The signal is recorded, at 548 nm, for each sample at differing slit widths.

Slit width (nm).	Signal/noise ratio.
0.1	2
0.2	24
0.4	40
0.6	9.5
0.8	5.3

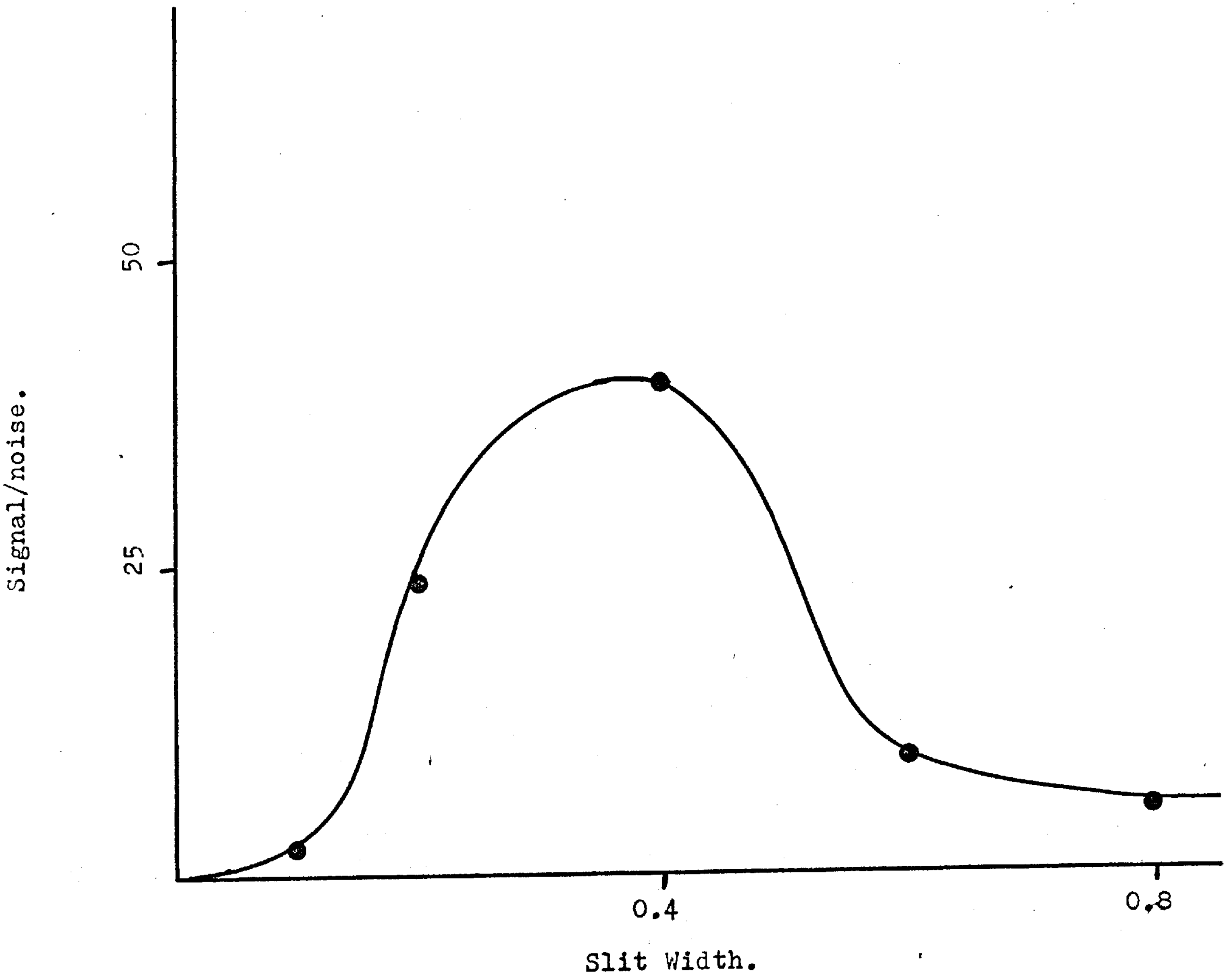
From the curve which shows the relationship between the signal/noise ratio and slit width (fig.24) it may be seen that 0.4mm is the optimum slit width.

IV.ii. Arsenic.

It is found that 460nm is the best wavelength at which to monitor. The slit is set at 0.4 mm and the E.H.T. supply provides 1100 volts.

Weight (µg).	Signal.
58.4	20
106.3	30
124.7	39
149.7	47
189.0	60

Fig.24.



It may be seen (fig.25) that the relationship between the weight of the arsenic and the signal is rectilinear.

IV.iii. Antimony.

The monochromator is set at the optimum wavelength, 580 nm, and the slit is adjusted to 0.4 mm. The E.H.T. supply is set at 1000 volts.

Weight (µg).	Signal.
45.5	5
90.5	10
131.8	14.5
214.5	25
259.8	30

The signal is found to be proportional to the weight of antimony (fig.25).

IV.iv. Boron.

The band at 548 nm is the best wavelength at which to determine boron. The slit is adjusted to 0.4 mm and the E.H.T. supply is set at 1100 volts.

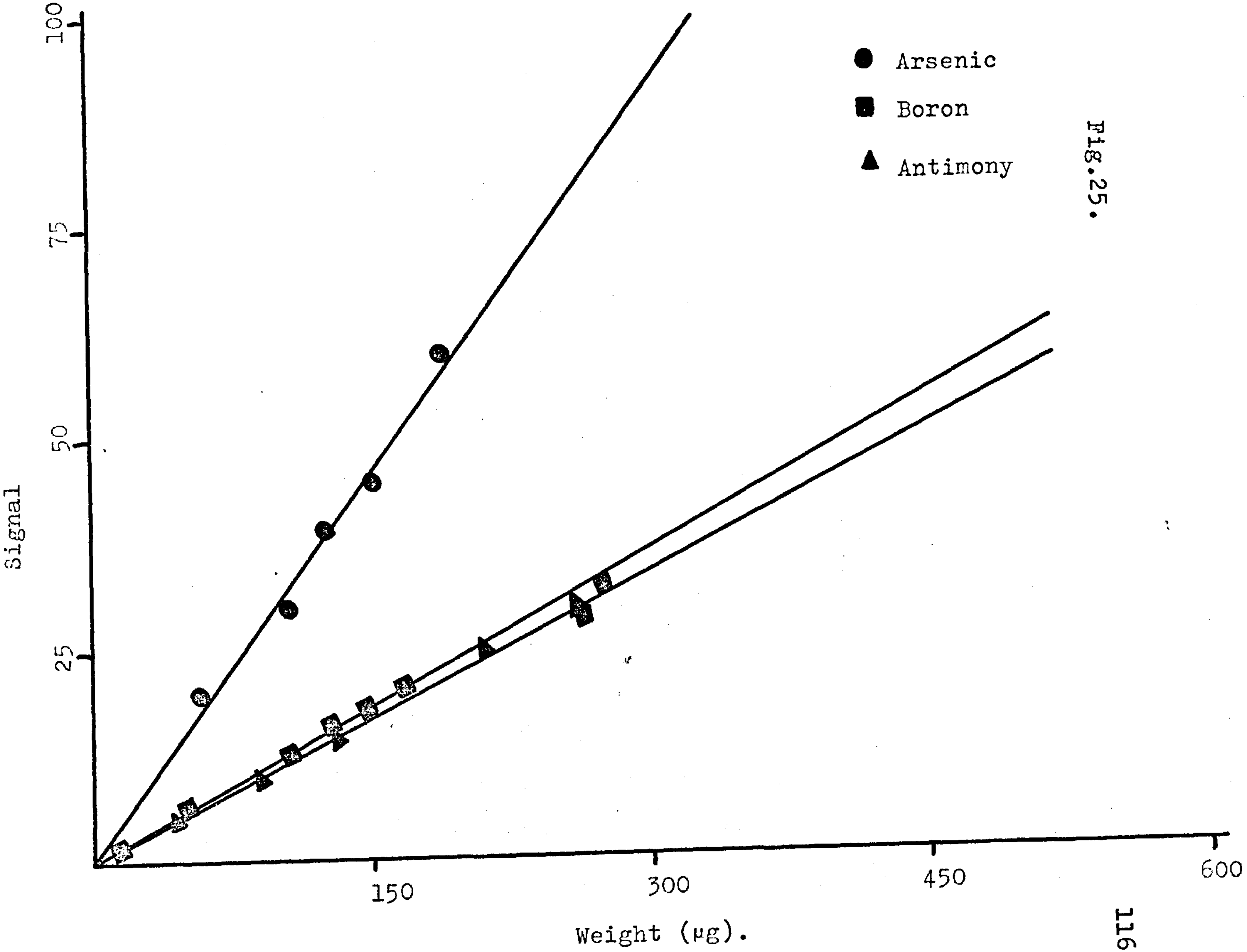

● Arsenic
■ Boron
▲ Antimony
100
75
50
25
Signal
150
300
450
600
Weight (µg).

Fig.25.

Weight (µg).	Signal.
13.8	2
49.4	6
105.0	12
125.0	15
144.6	16
170.6	20
258.0	28
272.9	32

From fig.25 it may be seen that the intensity of the emission is proportional to the weight of boron.

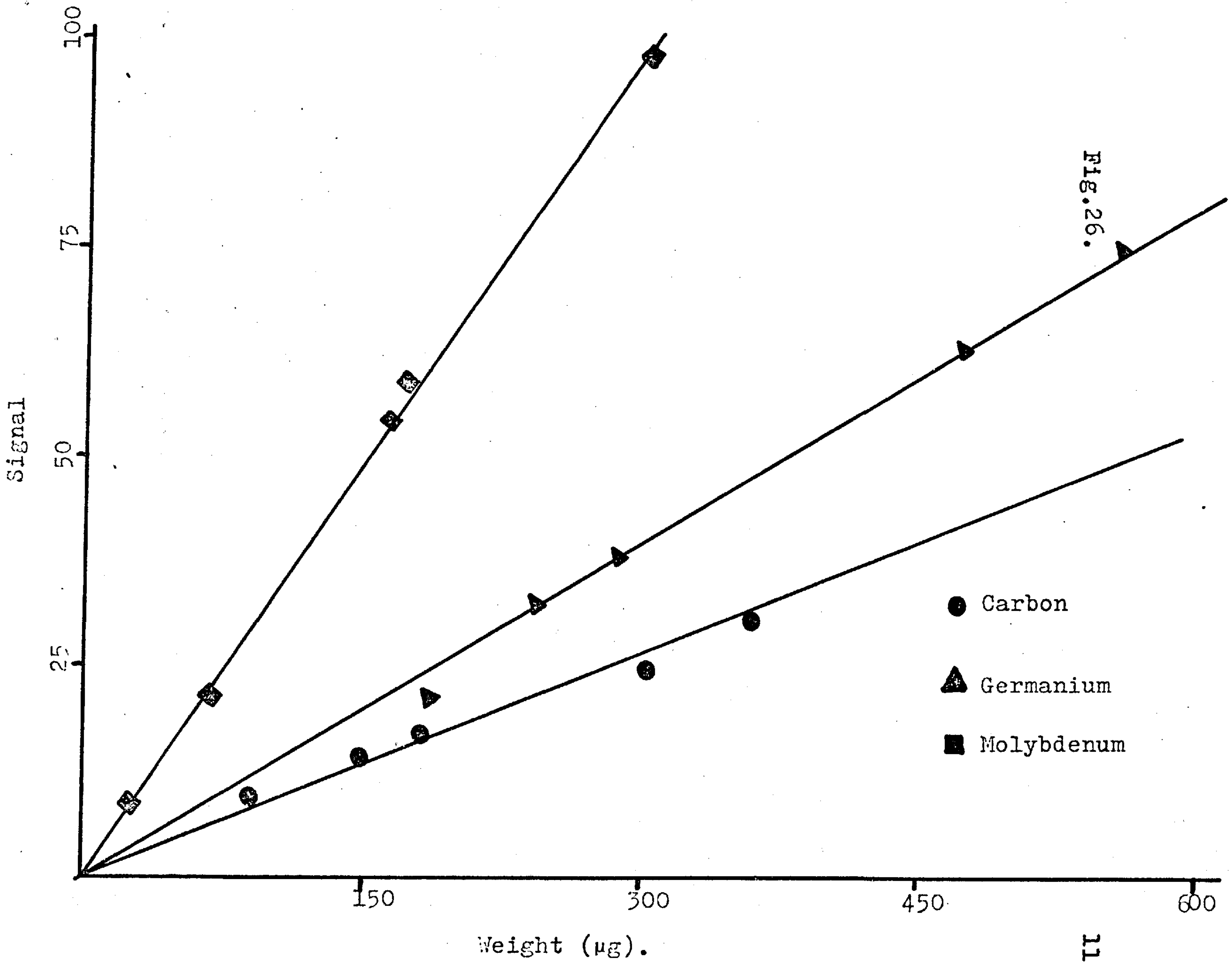
IV.v. Carbon.

The signal is recorded at 560 nm which is the maximum of the continuum emitted by carbon. The slit is set to 0.4 mm and the E.H.T. supply provides 1100 volts.

Weight (µg).	Signal.
90	9
158.4	14
182.7	16
304.7	25
360.0	31

It may be seen (fig.26) that the relationship between the weight of carbon and the signal is rectilinear.

Fig.26.


100
75
50
25
Signal
150
300
450
600
Weight (μg).
● Carbon
▲ Germanium
■ Molybdenum

IV.vi. Germanium.

The monochromator is set at 458 nm which is the maximum emission for germanium. The slit is adjusted to 0.4 mm and the E.H.T. supply is set to provide 1100 volts.

Weight (μg).	Signal.
188.5	21.5
243.0	33
285.0	37
473.8	63
558.0	75

It may be seen (fig.26) that the signal is proportional to the weight of the germanium.

IV.vii. Iodine.

No calibration is obtained for iodine as it is very difficult to weigh and it is difficult to transfer this element.

IV.viii. Molybdenum.

The monochromator is set at the band head at 622 nm. The slit is adjusted to 0.4 mm and the E.H.T. supply provides

1000 volts.

Weight (μg).	Signal.
25.6	9
68.2	22
168.4	54
175.8	58
304.0	95

The signal is found to be proportional to the weight of molybdenum (fig.26).

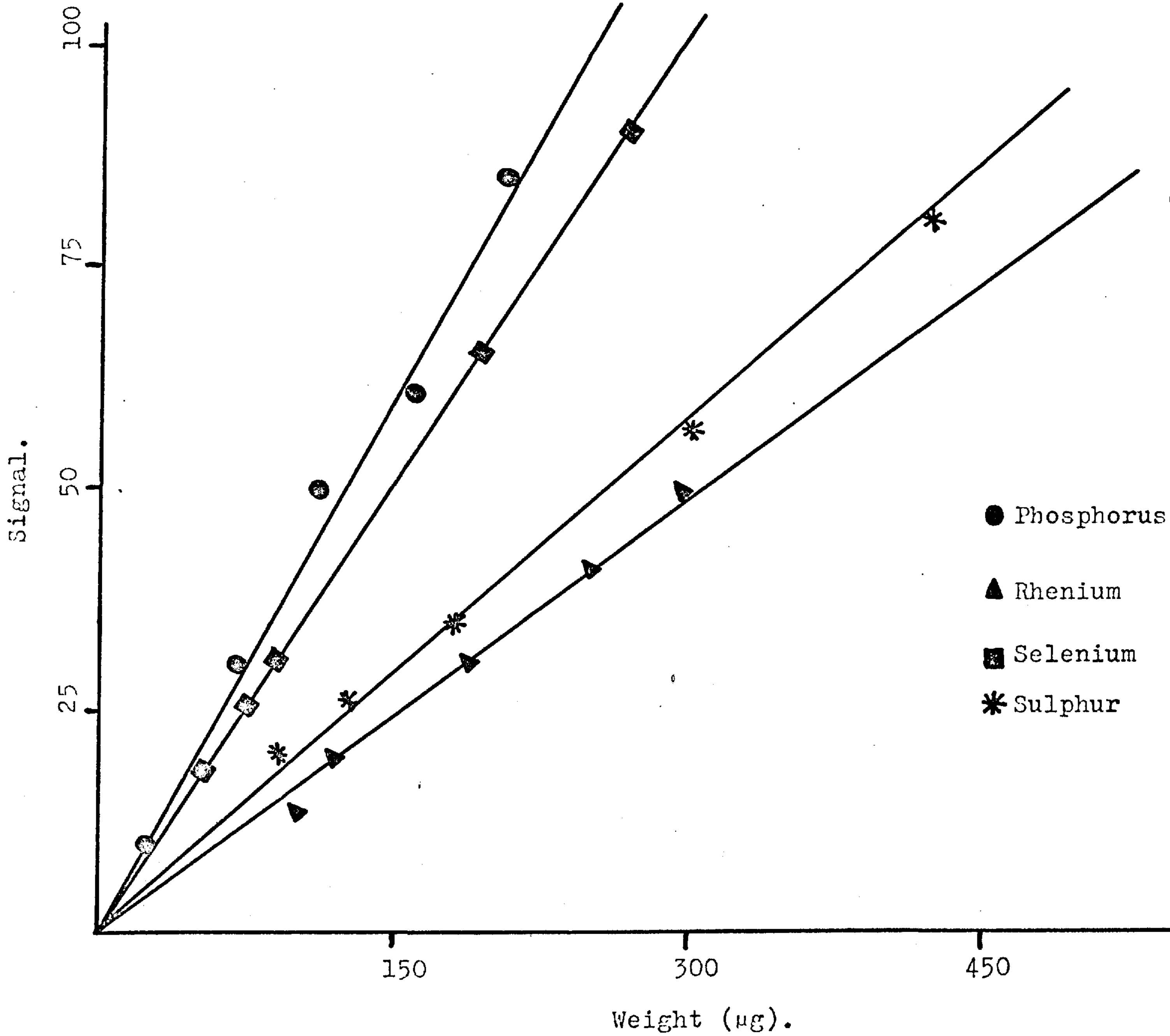
IV.ix. Phosphorus.

The signal is recorded at 528 nm which is the maximum of the continuum emitted by phosphorus. The slit is set to 0.4 mm and the E.H.T. supply provides 800 volts.

Weight (μg).	Signal.
23.6	10
68.6	30
108.6	50
157.9	60
205.3	85

It may be seen that the intensity of the emission is proportional to the weight of phosphorus (fig.27).

Fig.27.


Signal.
100
75
50
25
150
300
450
600
Weight (µg).
● Phosphorus
▲ Rhenium
▨ Selenium
✱ Sulphur

IV.x. Rhenium.

The monochromator is set at the optimum wavelength, 525 nm, and the slit is adjusted to 0.4 mm. The E.H.T. supply is set at 1000 volts.

Weight (μg).	Signal.
102.0	14
120.0	20
185.5	31
246.8	42
293.8	50

It may be seen that (fig.27) that the relationship between the concentration of the rhenium and the signal is rectilinear.

IV.xi. Selenium.

It is found that 394 nm is the best wavelength at which to monitor. The slit is set at 0.4 mm and the E.H.T. supply provides 900 volts.

Weight (μg).	Signal.
56.6	16.5
73.0	24.5
96.0	30
198.0	65
270.0	90

The signal is found to be proportional to the weight of selenium (fig.27).

IV.xii. Sulphur.

The monochromator is set to monitor at 384 nm which is the most intense band head for sulphur. The slit is set at 0.4 mm and the E.H.T. supply provides 900 volts.

Weight (μg).	(Weight)^2.	Signal.
9.51	90.6	20
11.1	123.4	25
13.3	178.6	35
17.46	305.1	57
20.04	419.6	80

The signal is found to be proportional to the square of the weight of the sulphur (fig.27).

IV.xiii. Silicon.

The signal is recorded at 436 nm which is the optimum band head. The slit is set to 0.4 mm and the E.H.T. supply provides 1000 volts.

Weight (μg).	Signal.
53.3	14.5
65.1	19.5
85.1	25
143.8	40
160.7	47

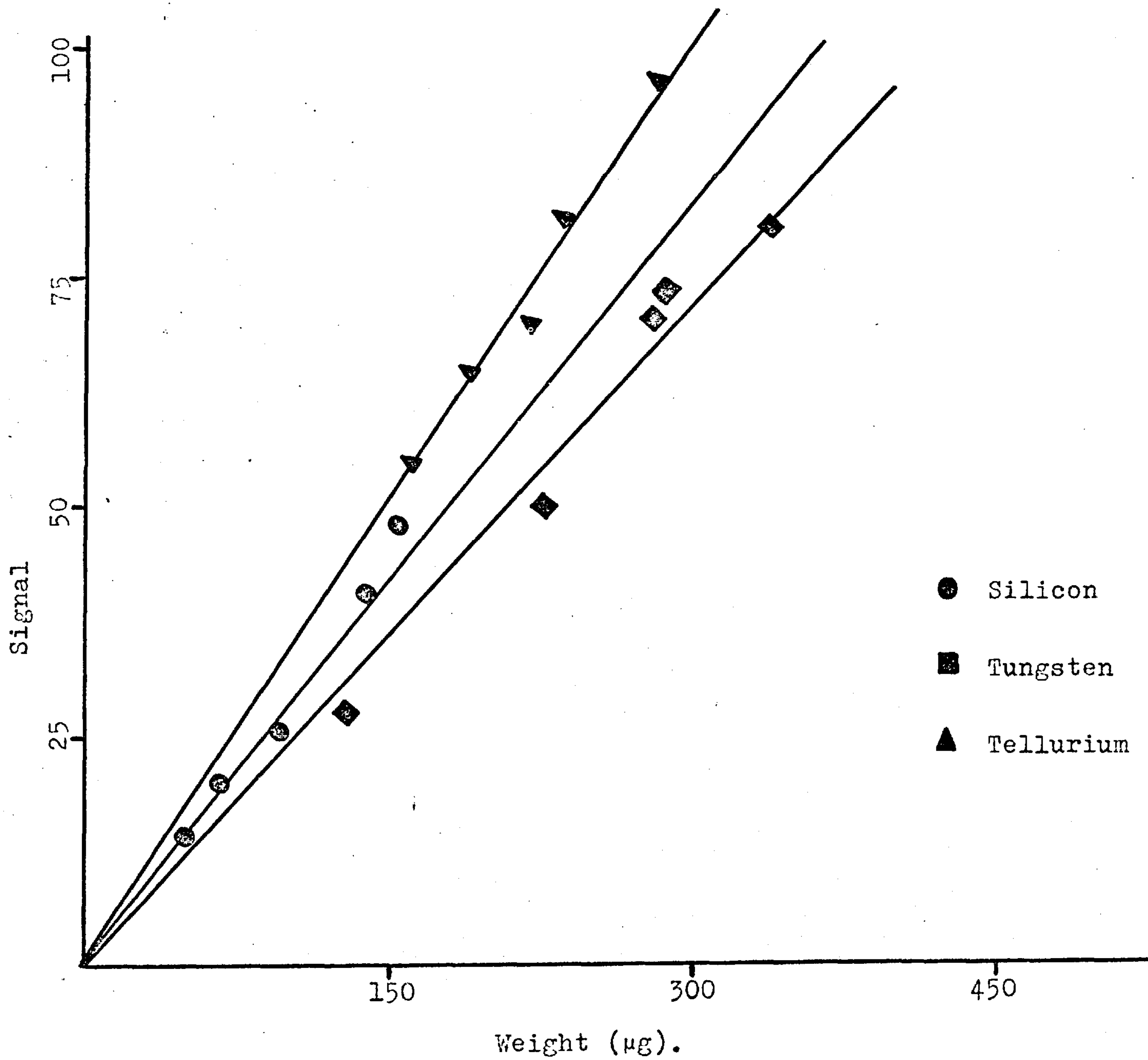
From fig.28 it may be seen that the intensity of the emission is proportional to the weight of silicon.

IV.xiv. Tellurium.

The monochromator is set at 525 nm which is the maximum of the continuum emitted by tellurium. The slit is set to 0.4 mm and the E.H.T. supply provides 900 volts.

Weight (μg).	Signal.
166.7	55
185.0	66
206.5	70
232.7	82.5
266.0	95

It may be seen that (fig.28) the relationship between the weight of the tellurium and the signal is rectilinear.



100
75
50
25
Signal
150
300
450
600
Weight (µg).
● Silicon
▨ Tungsten
▲ Tellurium

Fig.28.

IV.xv. Tungsten.

It is found that 622 nm is the best wavelength at which to monitor. The slit is set at 0.4 mm and the E.H.T. supply provides 800 volts.

Weight (μg).	Signal.
125	27
230.5	50
282.8	68
292.0	70
349.0	80

The signal is found to be proportional to the weight of tungsten (fig.28).

For all the elements except sulphur it may be seen that there is a linear relationship between the signal and the quantity of sample. No detection limits are given as it is impossible to weigh samples any smaller than 10-50 μg. The addition of a solid inert diluent to the element, which would enable smaller quantities of the element to be examined, was not attempted as it was expected that these diluents would retain the fluorides by absorption.

Chapter 3.

The Use of the Spectroscopic Detector in a Gas Chromatographic System.

I. Introduction.

The separation of volatile fluorides requires that a careful examination of the column packing materials is made, for, as these fluorides are so corrosive the use of most of the common materials is precluded. This problem of the reaction of the sample with the column packing material is not unknown in other more straight forward separations by gas liquid chromatography, but in these cases it is the solid phase which is the reactive agent. For ideally, in gas liquid chromatography, the solid phase should be chemically inert and should not participate in the elution process. However, in order to maintain upon its surface the thin coherent film of liquid phase necessary for efficient partitioning, the support must possess some adsorptive properties and it is the heterogeneity of these that is the cause of many of the problems encountered in practice. The adsorption of solute molecules at the liquid-solid interface may lead to changes in the retention and in extreme cases molecular rearrangement[161]. A study of the effect of the adsorption of solute and liquid phase molecules upon retention data has also been reported[162,163,164].

The separation of these fluorides has been successful on perfluorinated materials and generally Kel-F oils or waxes on PTFE. supports have been the most successful.

II. The Chromatographic System.

With the development of a detector which is selective to most of the elements under discussion it is possible to compare and contrast the signals it produces with that of a more conventional commercial detector.

Pye Series 104 gas chromatographic equipment is used for the separation of these fluorides. A katharometer was chosen as it is a non-destructive detector which enables the two detectors to be used in tandem. The katharometer was modified by replacing the normal tungsten filaments by nickel filaments (Gow Mac, Ltd.) which are only slowly attacked by the volatile fluorides. It was found that only after eighteen months of continual use the filaments had to be replaced as the signal became noisy.

The carrier gas is controlled by a pressure controller and the pressure is measured on a pressure gauge. Helium is chosen as the carrier gas as it is found that the signals from the katharometer for some of the fluorides are negative which makes it very difficult to interpret the chromatograms. The carrier gas is dried by passing it through an absorber containing activated molecular sieve (Linde type 4A) and all organics are removed by a similar absorber containing activated granular charcoal. This gas is then split into two, one side is connected directly to the reactor-injection vessel and hence through the chromatographic column to the sample arm of the katharometer, and the other side is connected directly to the reference arm of the katharometer via a rotameter. The sample outlet from the katharometer is fed directly into the flame via the burner inlet capillary. The flow-rates to the burner head are controlled and measured with rotameters (nitrogen 4.7 litres/min., hydrogen 2.6 litres/min.).

The reactor-injection system is operated in a similar way to that previously described, and the flow-rate through the column is adjusted to 50 mls/min. with the flow-rate through the reference side of the katharometer adjusted to a similar rate by the use of the rotameter.

The column, which is used for all the chromatographic separations, is made from stainless steel (22', 1/4"o.d.) and contains Kel-F oil No 10 on Hostaflon (PTFE., 15% w/w). This column was packed under vacuum at the temperature of liquid nitrogen which ensures that the PTFE. is not crushed. This column is chemically conditioned by passing a mixture of chlorine trifluoride and helium through it for one hour. The conditioning is checked at the start of each day by passing successive equal samples of chlorine trifluoride through it until the response of the katharometer is constant. All the connections throughout the chromatographic system are made with stainless steel couplings (Swagelok, Ltd.).

In all the figures of this chapter the response of the katharometer is shown as a continuous line with that of the spectroscopic detector as a dotted line.

III. The Effect of Radio Frequency Heating on Pure Samples of Chlorine Trifluoride.

Once the column has been chemically conditioned it is possible to investigate the purity and the retention time for the separation of chlorine trifluoride. The reactor-injection vessel, which is of known volume (5ml.), is filled with chlorine trifluoride and this sample is swept onto the column by the carrier gas when the gas sampling valve is rotated. It was found that providing the column is properly conditioned and that no radio frequency is applied only one peak is eluted which is due to chlorine trifluoride, (fig.29a.). However, if the empty nickel sample boat in the reaction vessel is heated to 600°C

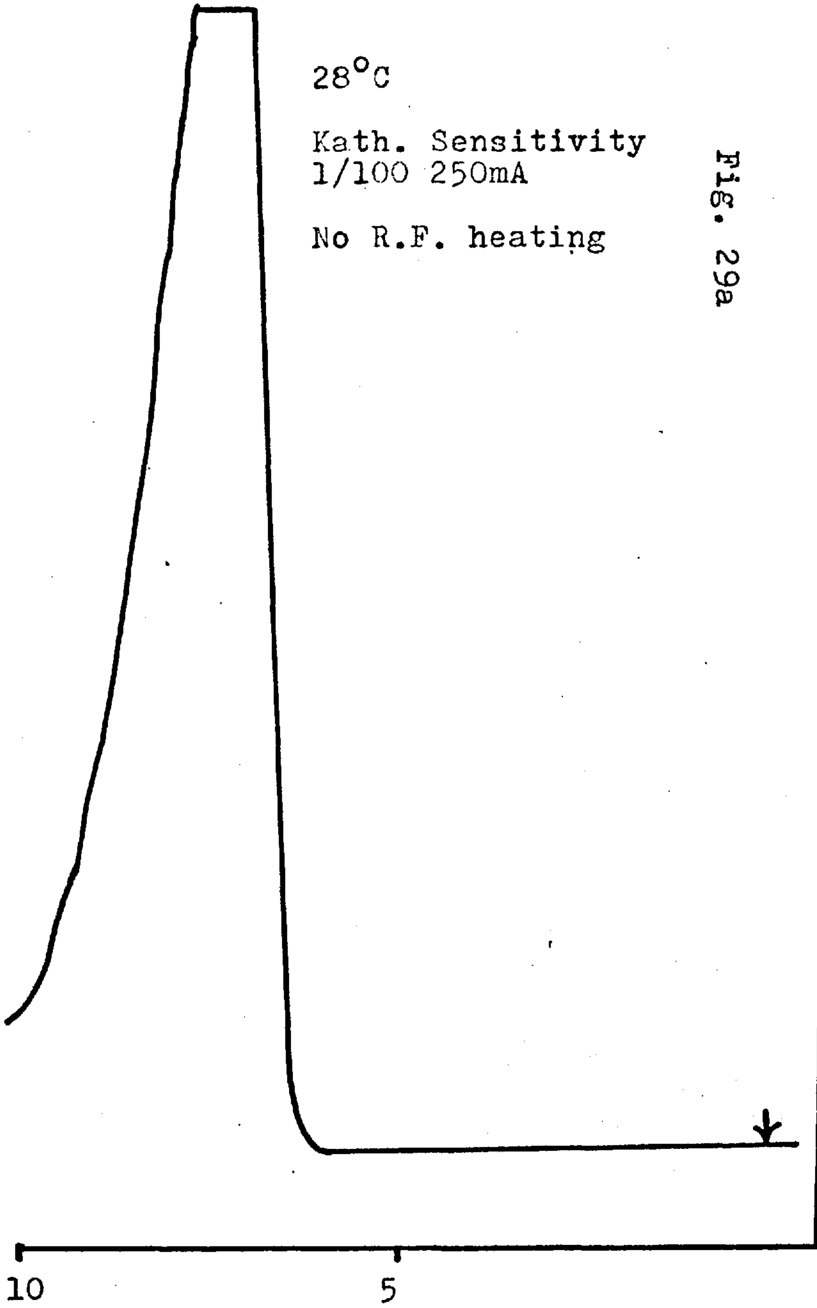


Fig. 29a

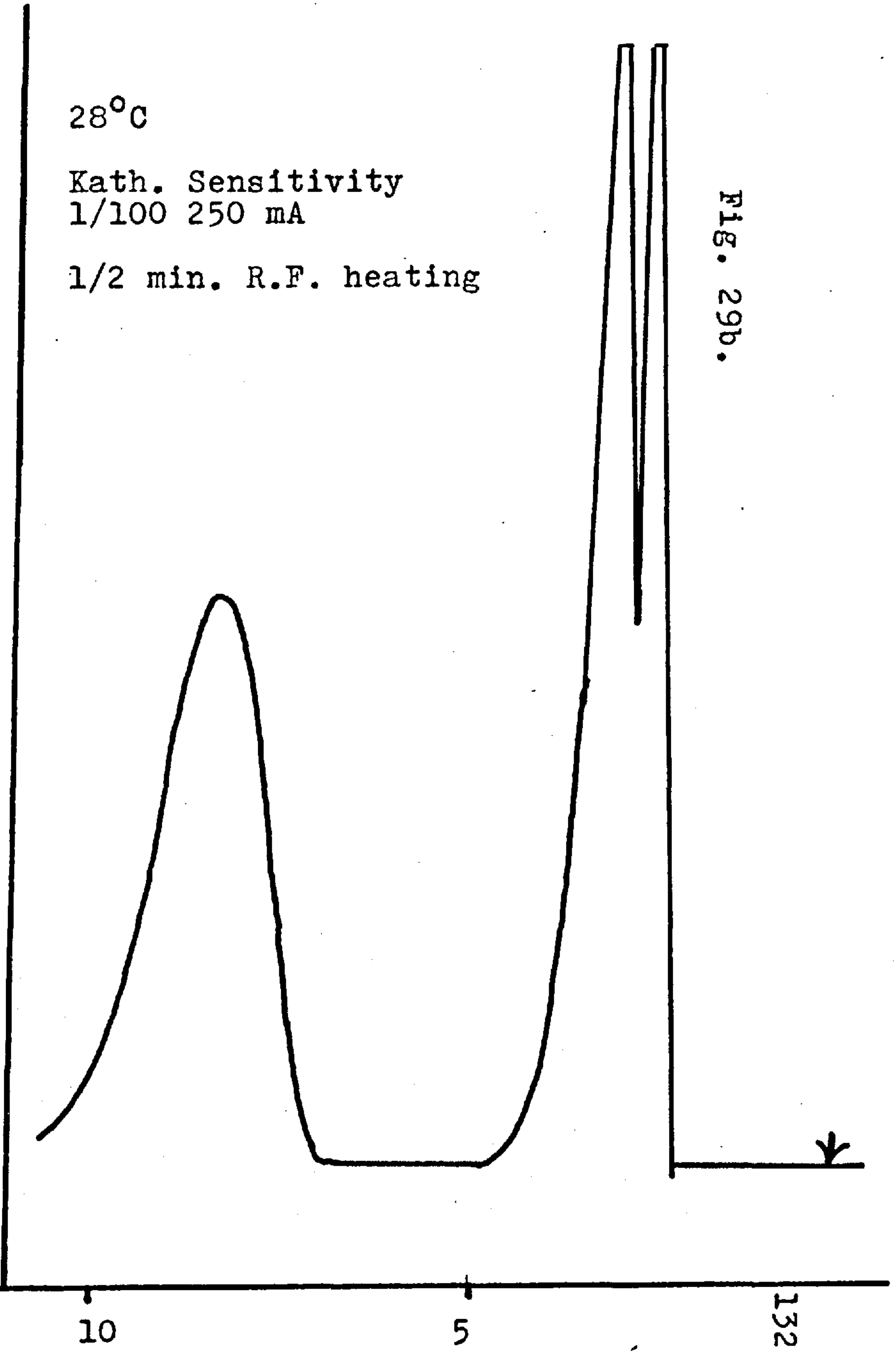


Fig. 29b.

Time (min).

by the radio frequency heater this energ is sufficient to dissociate the chlorine trifluoride into chlorine and fluorine. It was found that if the time which the radio frequency heater is applied is varied then the ratio of the products of the dissociation of chlorine trifluoride changes (fig. 29b, 30a, 30b). From these results it may be seen that the dissociation reaches an equilibrium mixture after about one minute so, as a general rule the radio frequency heater is only applied for one minute. This study was carried out using the katharometer.

IV. The Separation of Tungsten, Molybdenum and Rhenium.

IV.i. Column temperature 75°C.

A column temperature of 75°C was chosen as it has been previously reported[126] that at this temperature tungsten may be separated from molybdenum and tunsten from rhenium.

This investigation was started by separating a blank sample of chlorine trifluoride which had been subjected to radio frequency heating for one minute, this was to

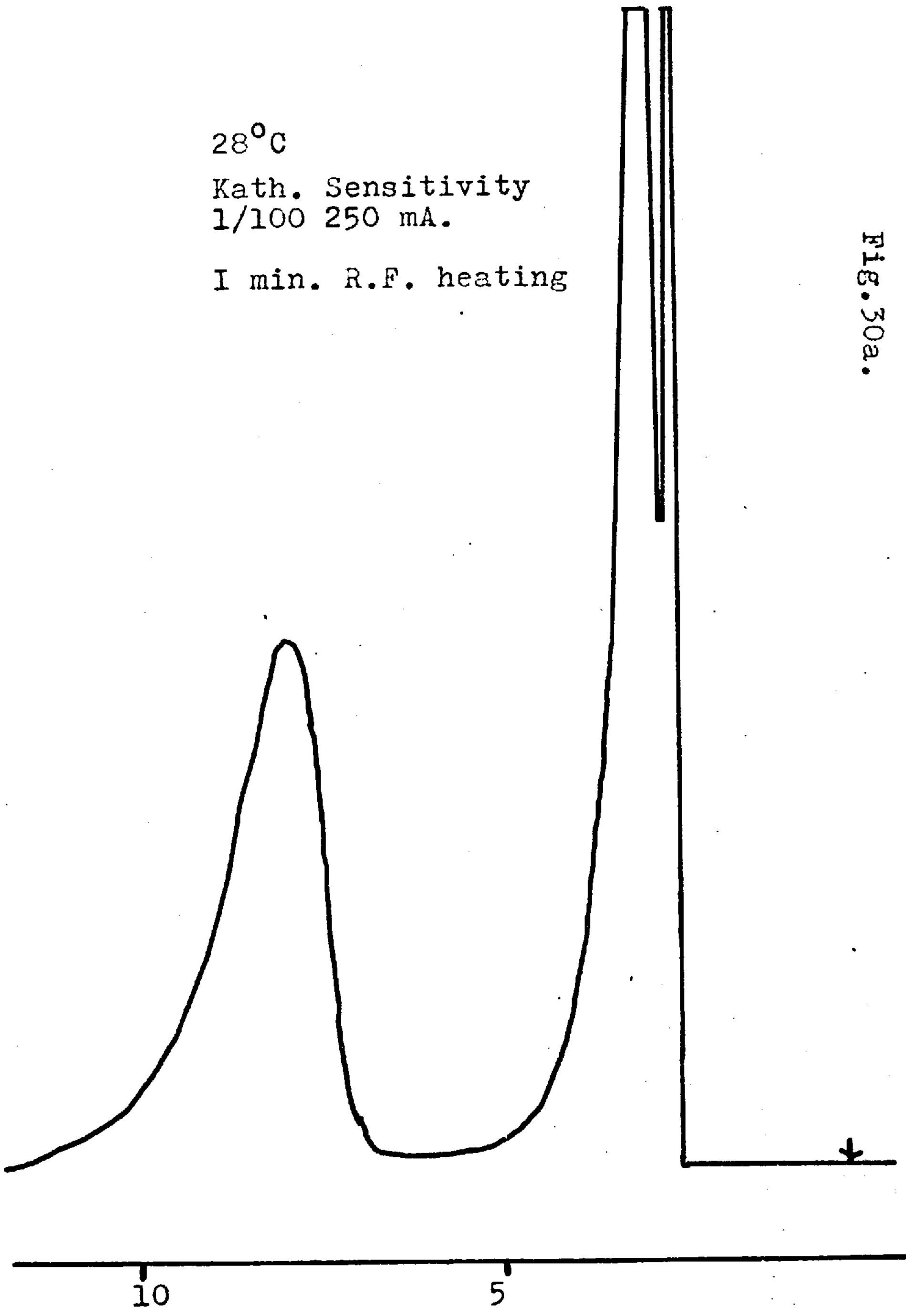


Fig. 30a.

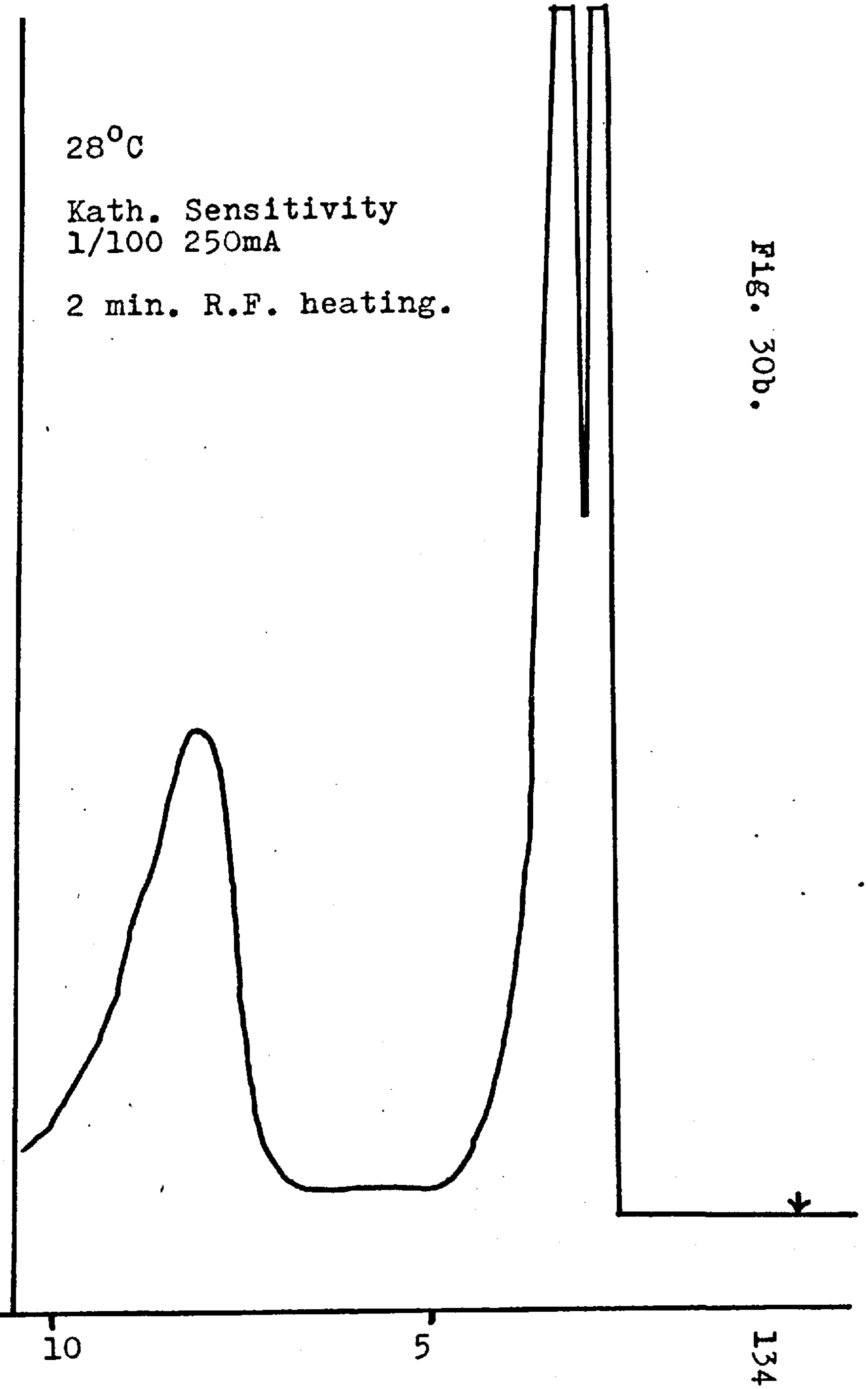


Fig. 30b.

Time (min).

establish the retention times of the chlorine trifluoride and its dissociation products. A comparison of the response of the katharometer with that of the spectroscopic detector is shown (fig. 31a, 31b) and from this it may be seen that the spectroscopic detector fails to respond to chloride trifluoride, fluorine and chlorine at 622 or 525 nm.

Separations of molybdenum, rhenium, and tungsten from the reaction products were made separately, once the 'blank' chromatogram had been obtained, in order to establish the retention times of these elements. The spectroscopic detector is set to monitor at 622 nm for tungsten and molybdenum and 525 nm for rhenium. It was found that in order that a response is shown by the katharometer for these elements, samples ca. 500μg. are required which means that the sensitivity of the spectroscopic detector must be reduced. From the results obtained (fig. 32, 33, 34) it may be seen that the spectroscopic detector only responds to the metal fluoride. At this temperature it is impossible to separate molybdenum and rhenium but yet possible to separate molybdenum and tungsten and rhenium and tungsten (fig.35,36).

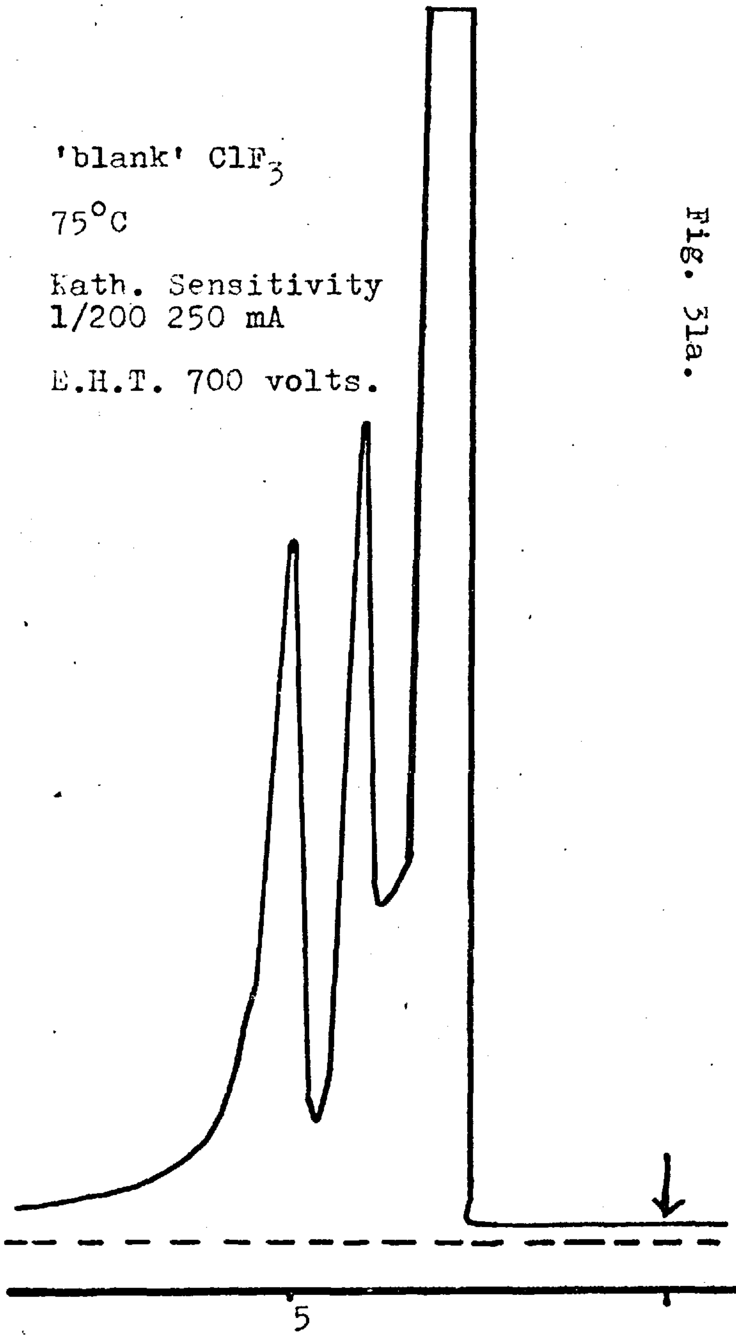


Fig. 31a.

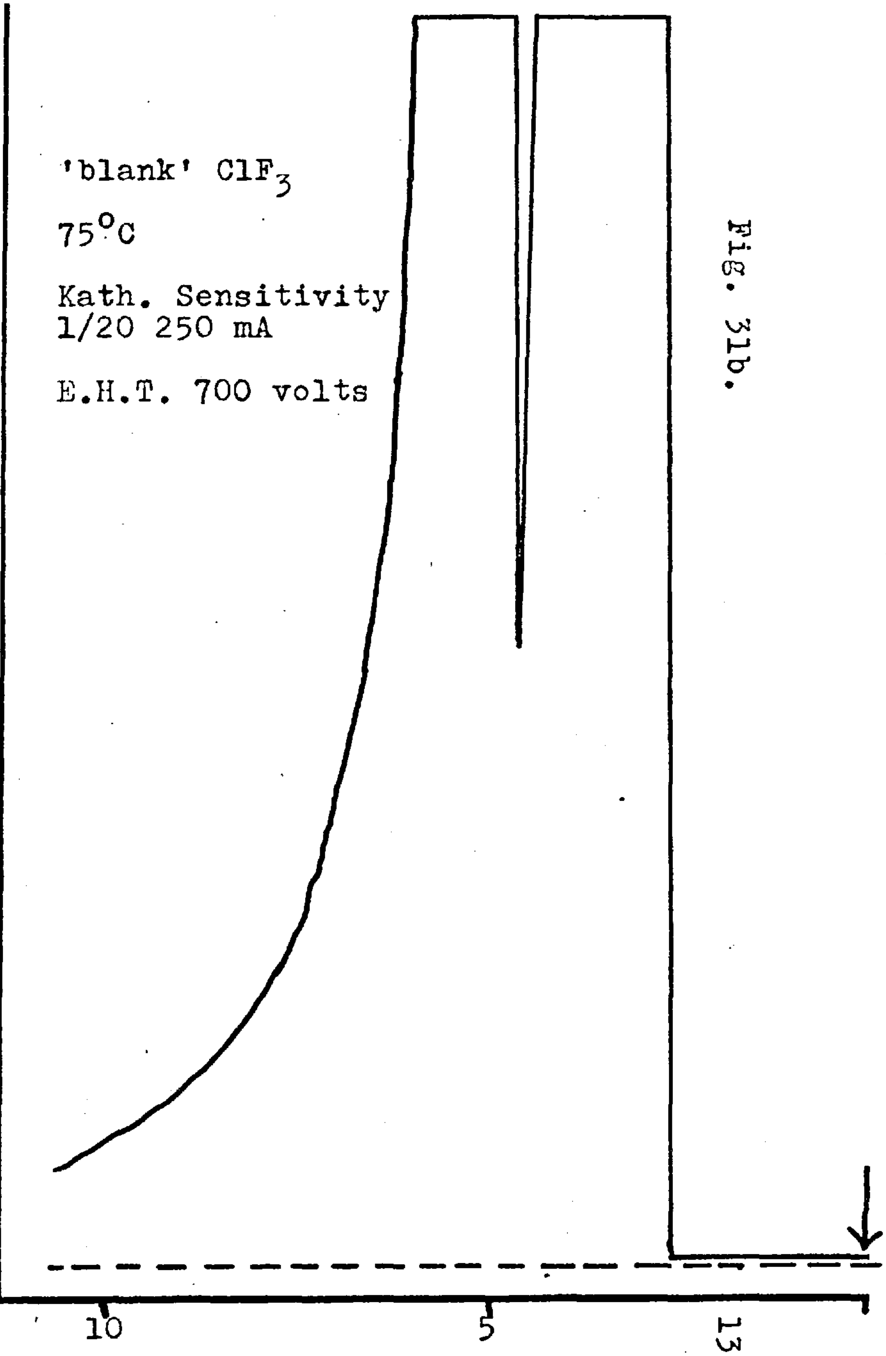


Fig. 31b.

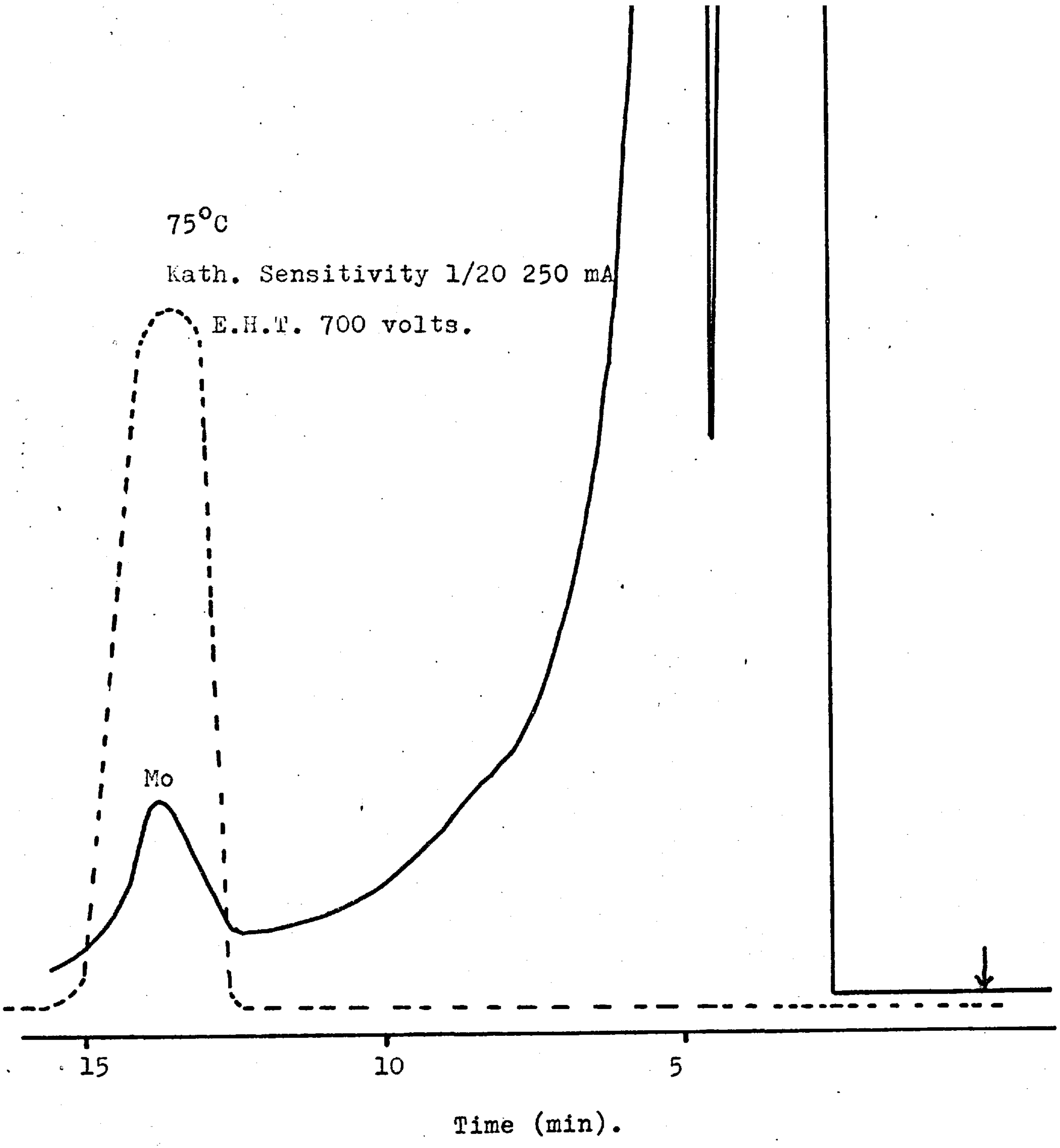

75°C
Kath. Sensitivity 1/20 250 mA
E.H.T. 700 volts.
Mo
15
10
5
Time (min).

Fig.32.

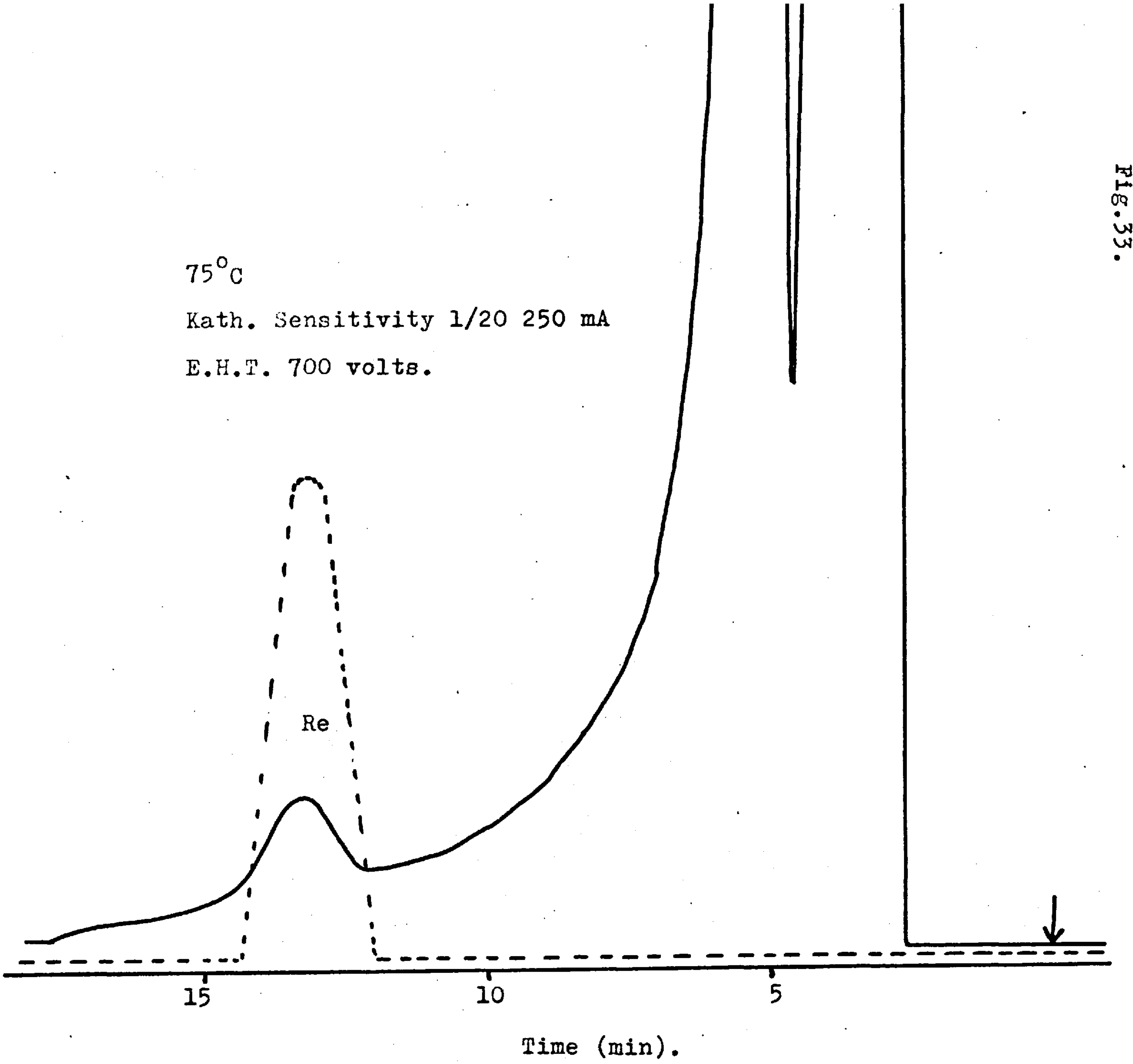

75°C
Kath. Sensitivity 1/20 250 mA
E.H.T. 700 volts.
Re
15
10
5
Time (min).

Fig.33.

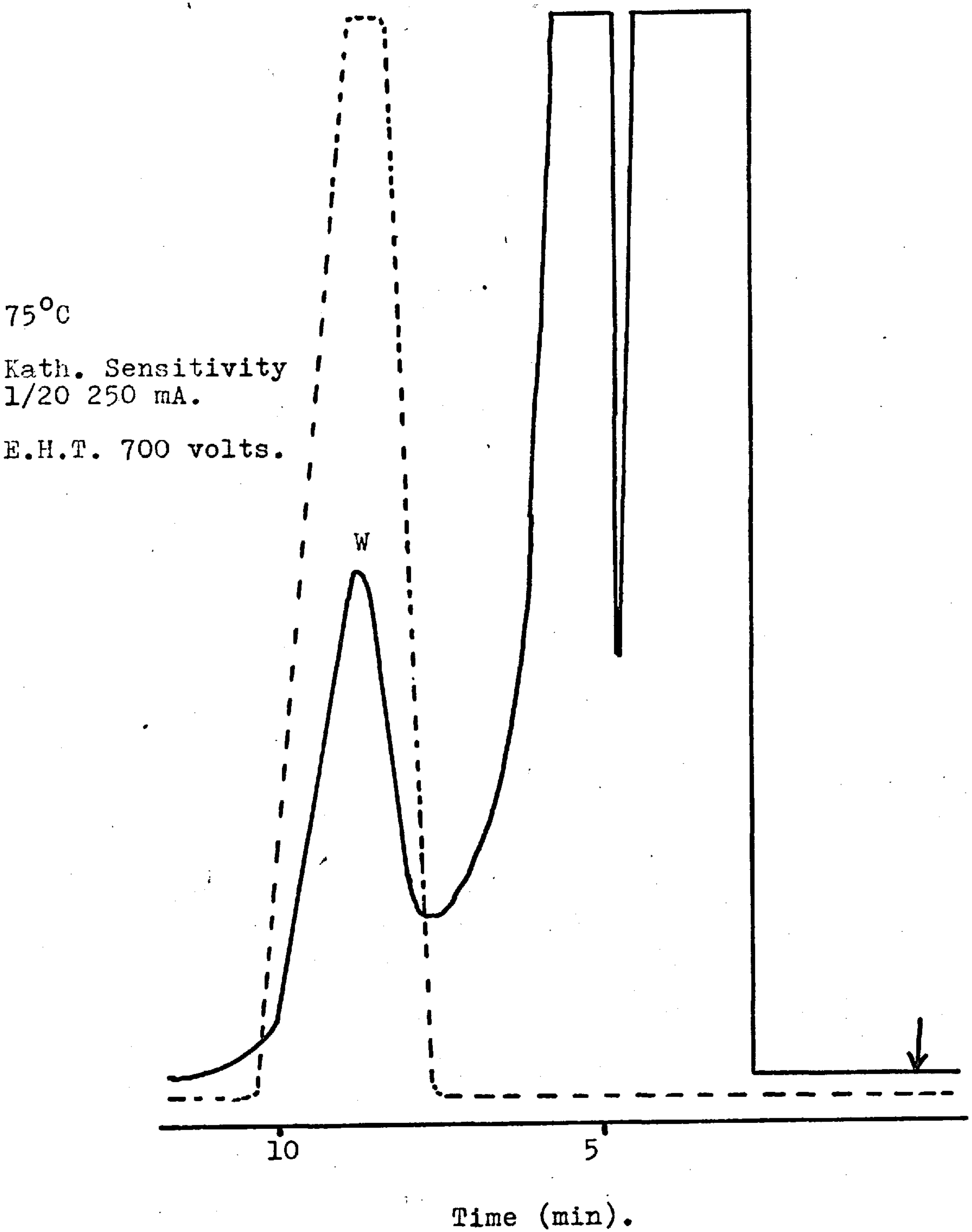


Fig 34.

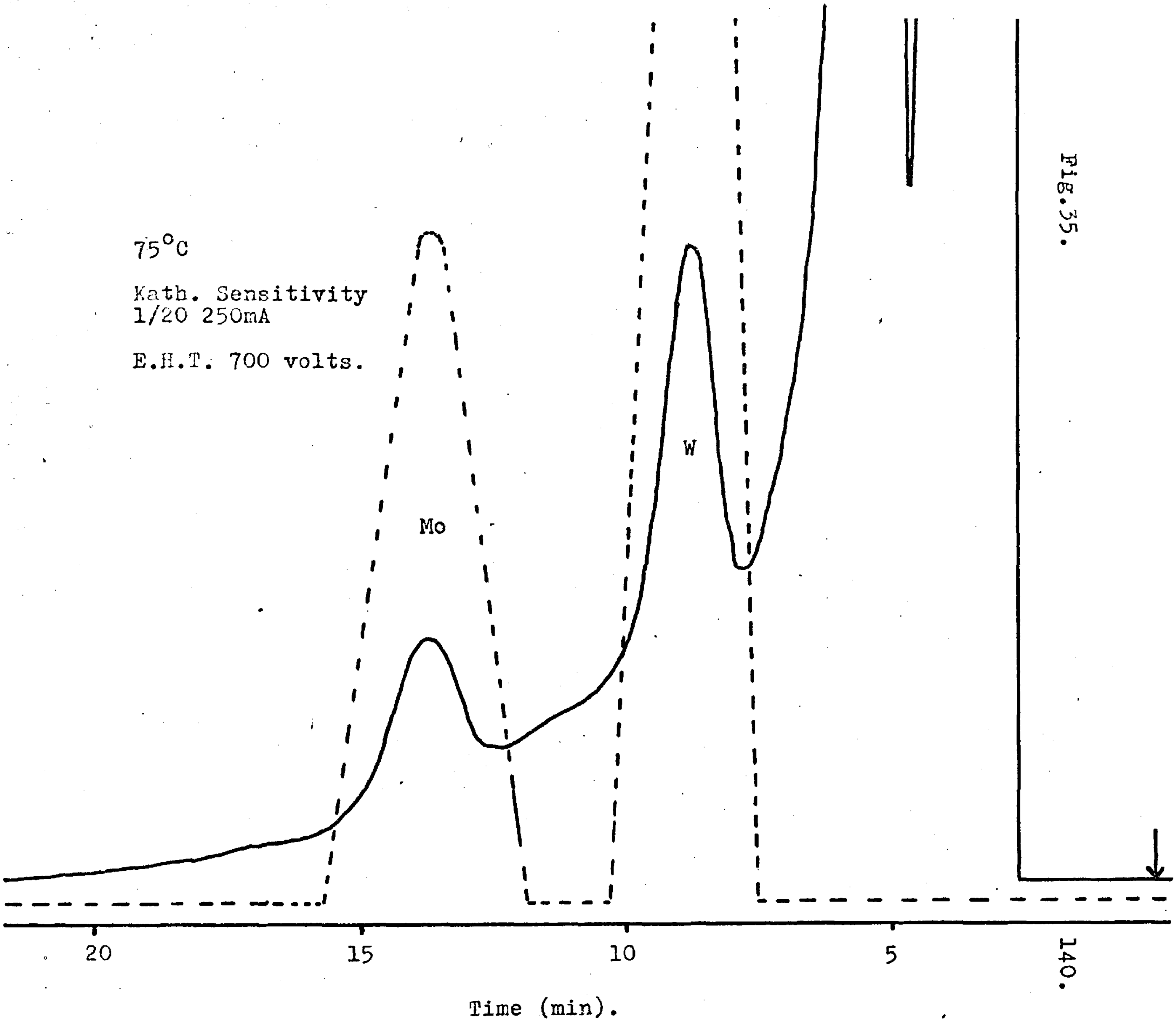
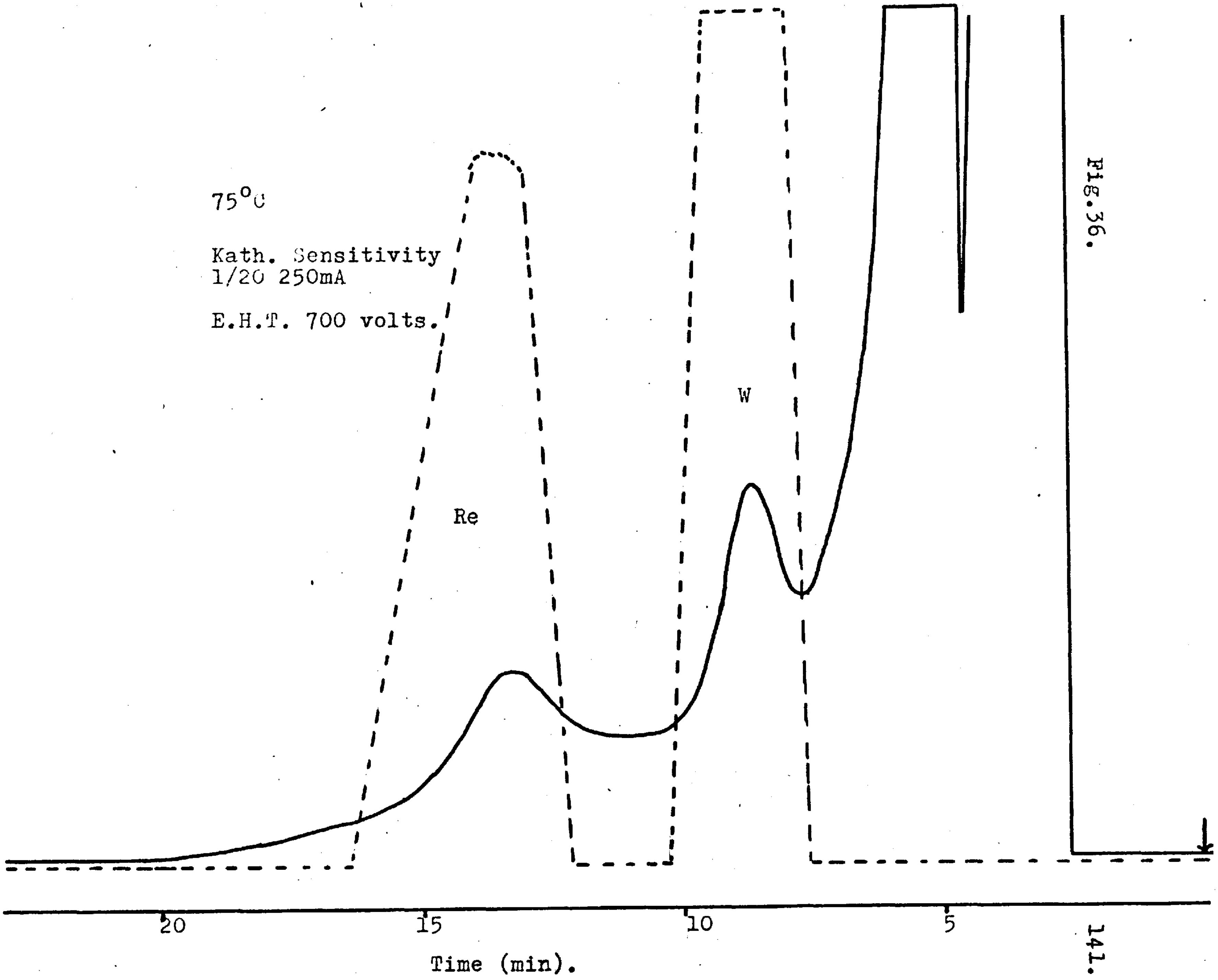

75°C
Kath. Sensitivity
1/20 250mA
E.H.T. 700 volts.
Mo
W
20
15
10
5
Time (min).

Fig.35.



75°C

Kath. Sensitivity
1/20 250mA

E.H.T. 700 volts.

Fig.36.

However, as tungsten, molybdenum and rhenium emit their maximum radiation in a similar region of the spectrum selectivity may only be obtained by consideration of the retention times.

IV. ii. Column temperature 55°C.

The 'blank' separation of chlorine trifluoride, chlorine and fluorine was determined (fig. 37) at this lower temperature and similar separations of rhenium, tungsten and molybdenum from the excess chlorine trifluoride and other fluorinated reaction products were also obtained (fig. 38, 39, 40). However, it may be seen that rhenium and molybdenum still have similar retention times.

IV. iii. Column temperature 45°C.

The flow-rate through the column was reduced from 50 ml/min. to 30 ml/min. as well as the column temperature from 55 to 45°C. With these conditions further separations were obtained (fig. 41, 42, 43, 44) but rhenium and molybdenum still had the same retention time.

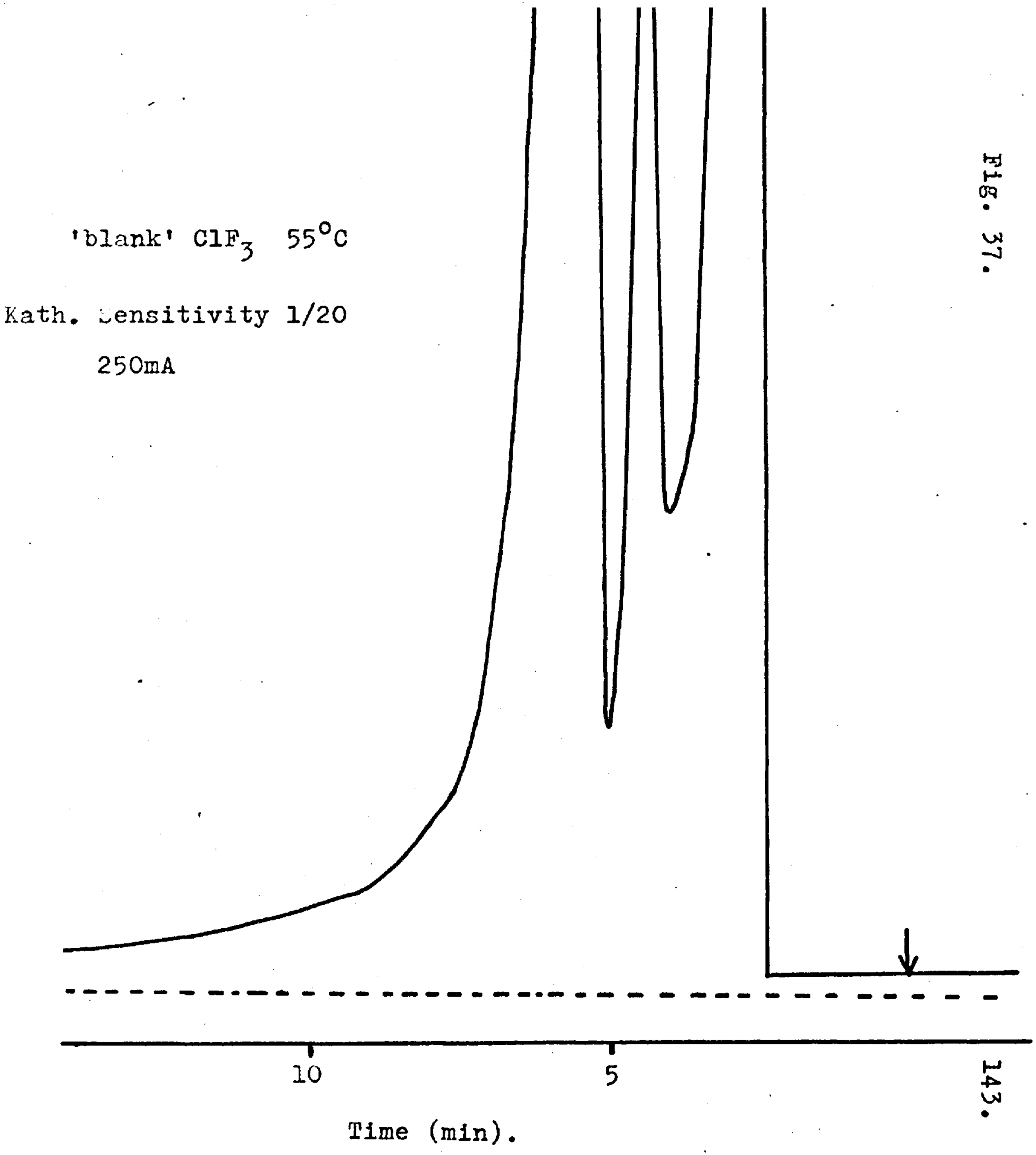


Fig. 37.

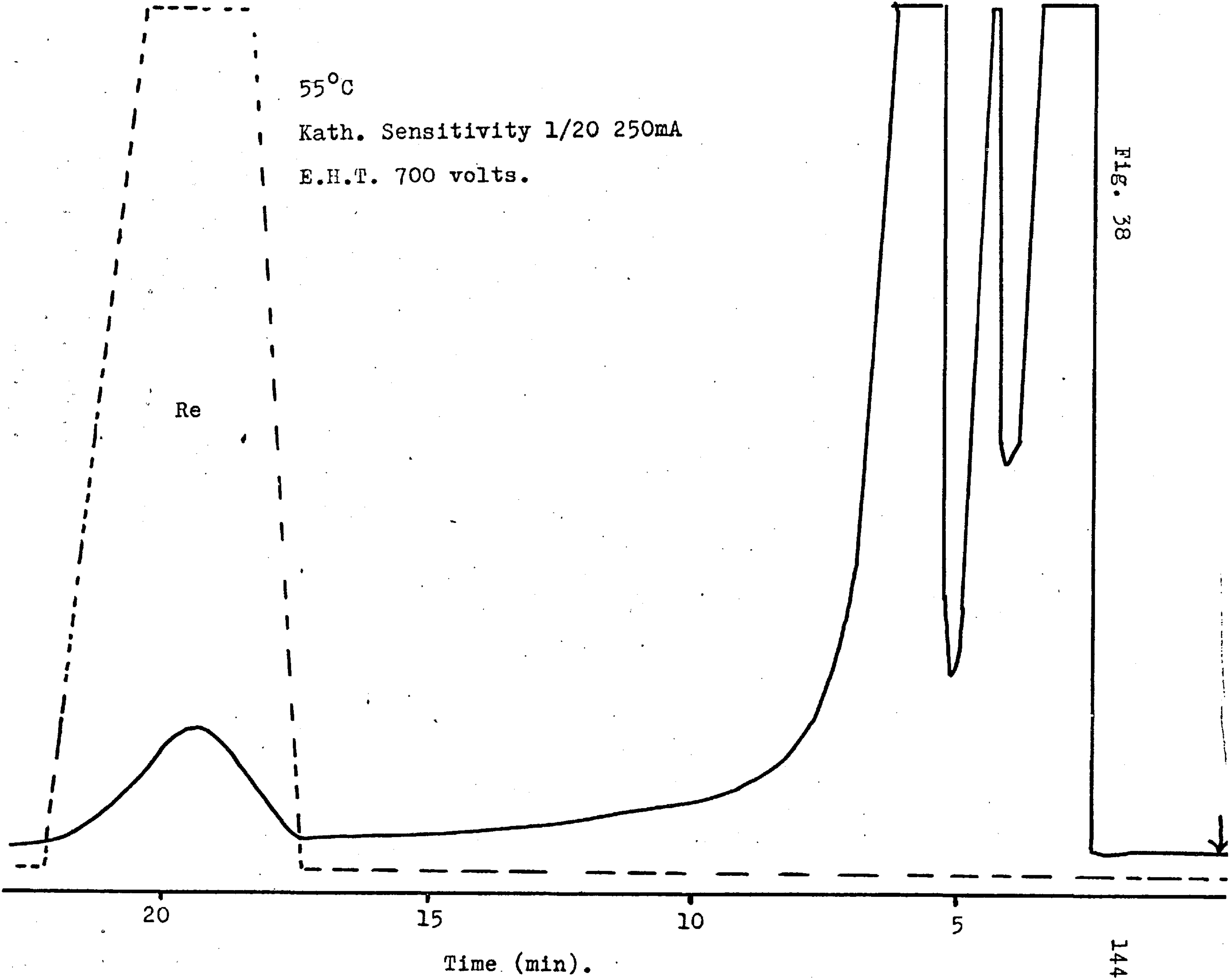

55°C
Kath. Sensitivity 1/20 250mA
E.H.T. 700 volts.
Re
20
15
10
5
Time (min).

Fig. 38

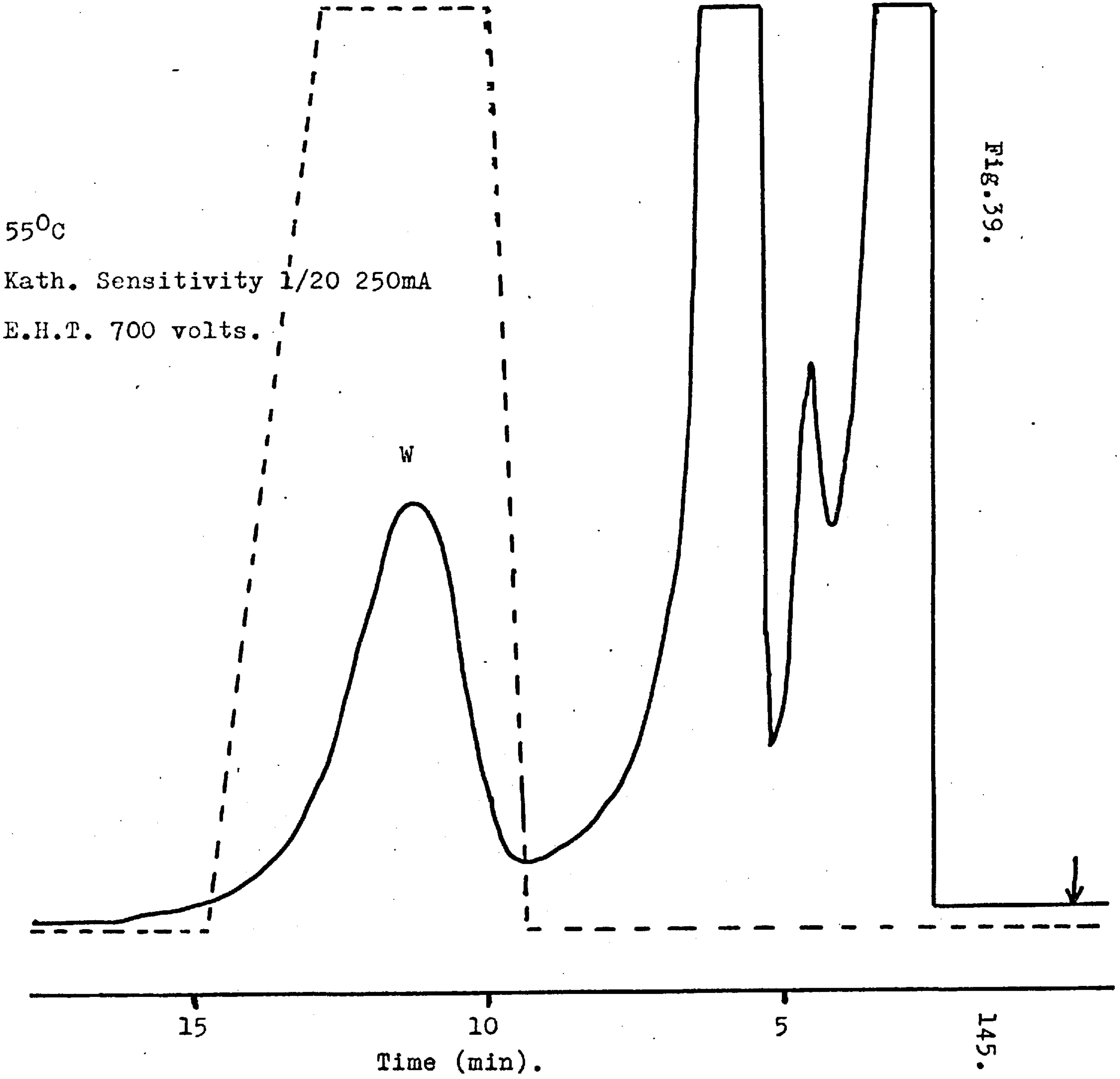

55^{0}C
Kath. Sensitivity 1/20 250mA
E.H.T. 700 volts.
W
15
10
5
Time (min).

Fig.39.

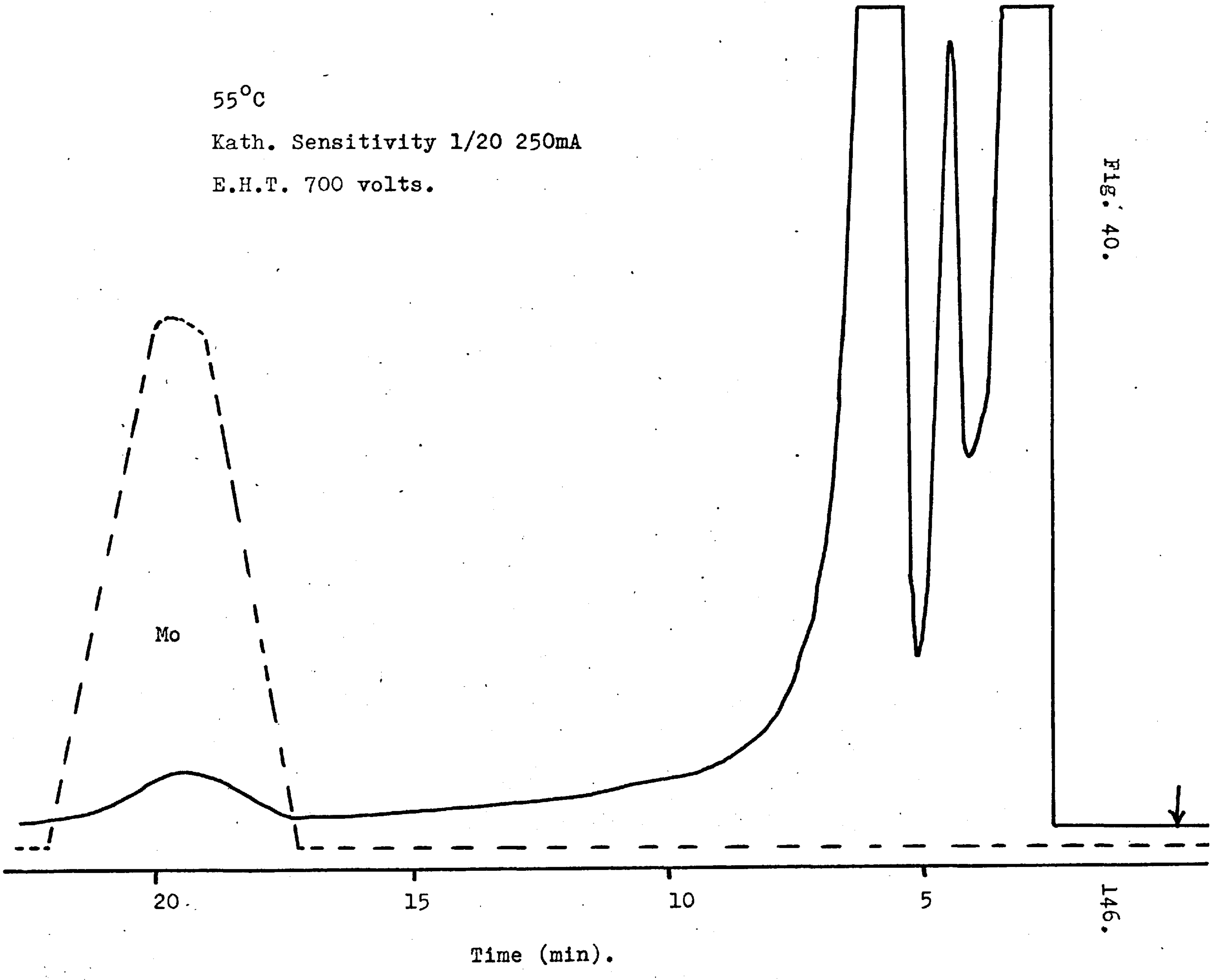
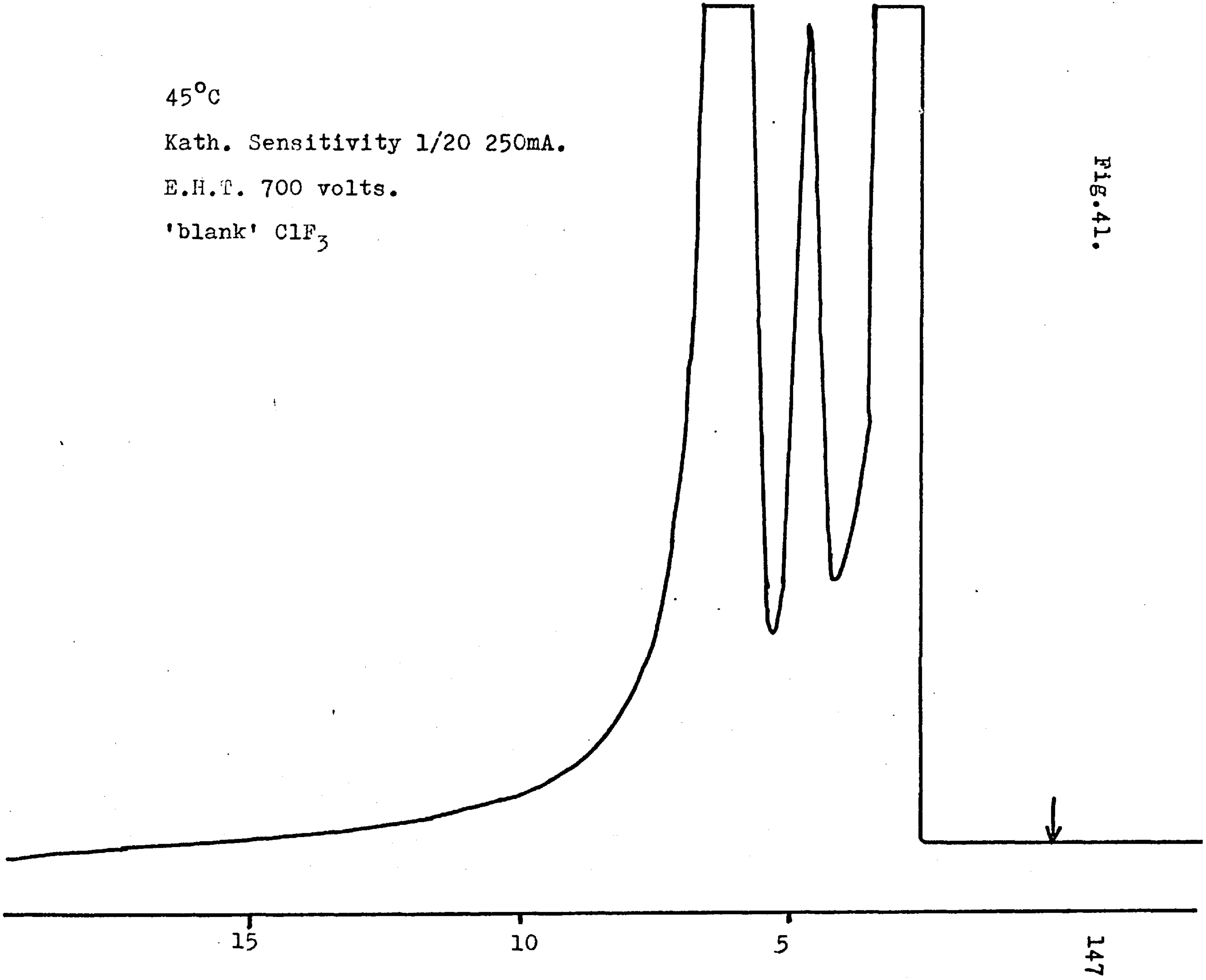

55°C
Kath. Sensitivity 1/20 250mA
E.H.T. 700 volts.
Mo
20
15
10
5
Time (min).

Fig. 40.



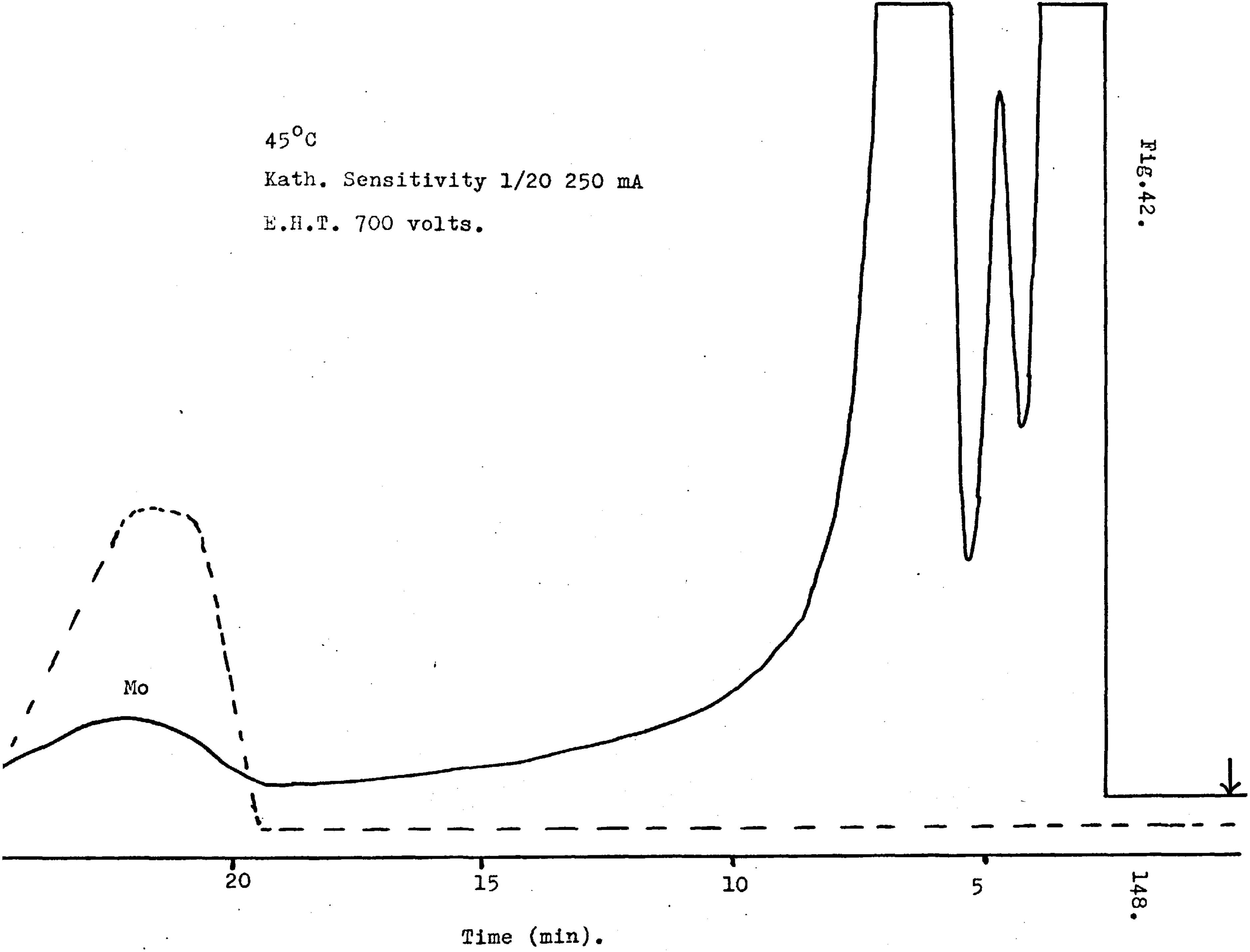
45°C

Kath. Sensitivity 1/20 250mA.

E.H.T. 700 volts.

'blank' ClF_3

Fig.41.



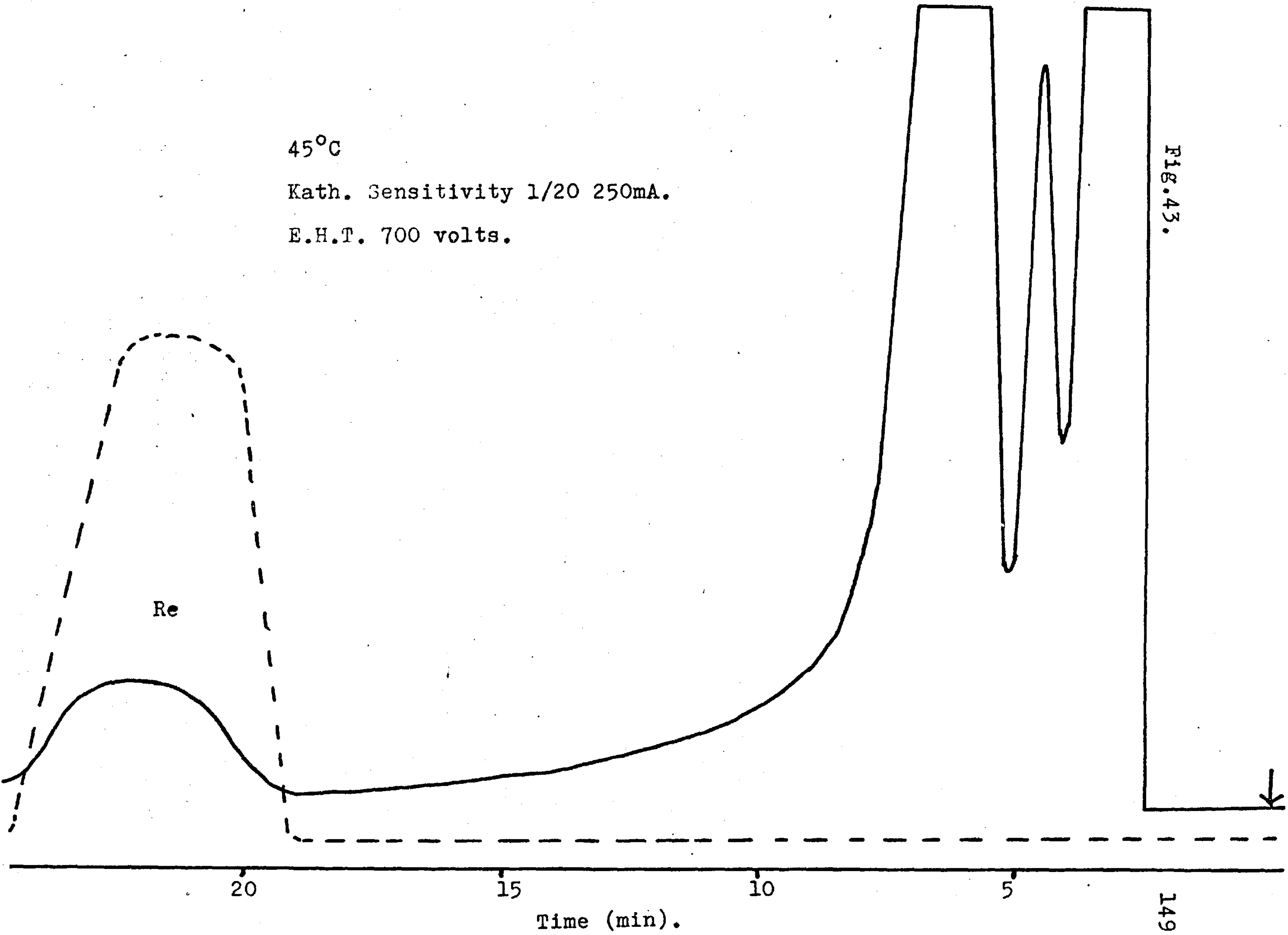
45°C

Kath. Sensitivity 1/20 250 mA

E.H.T. 700 volts.

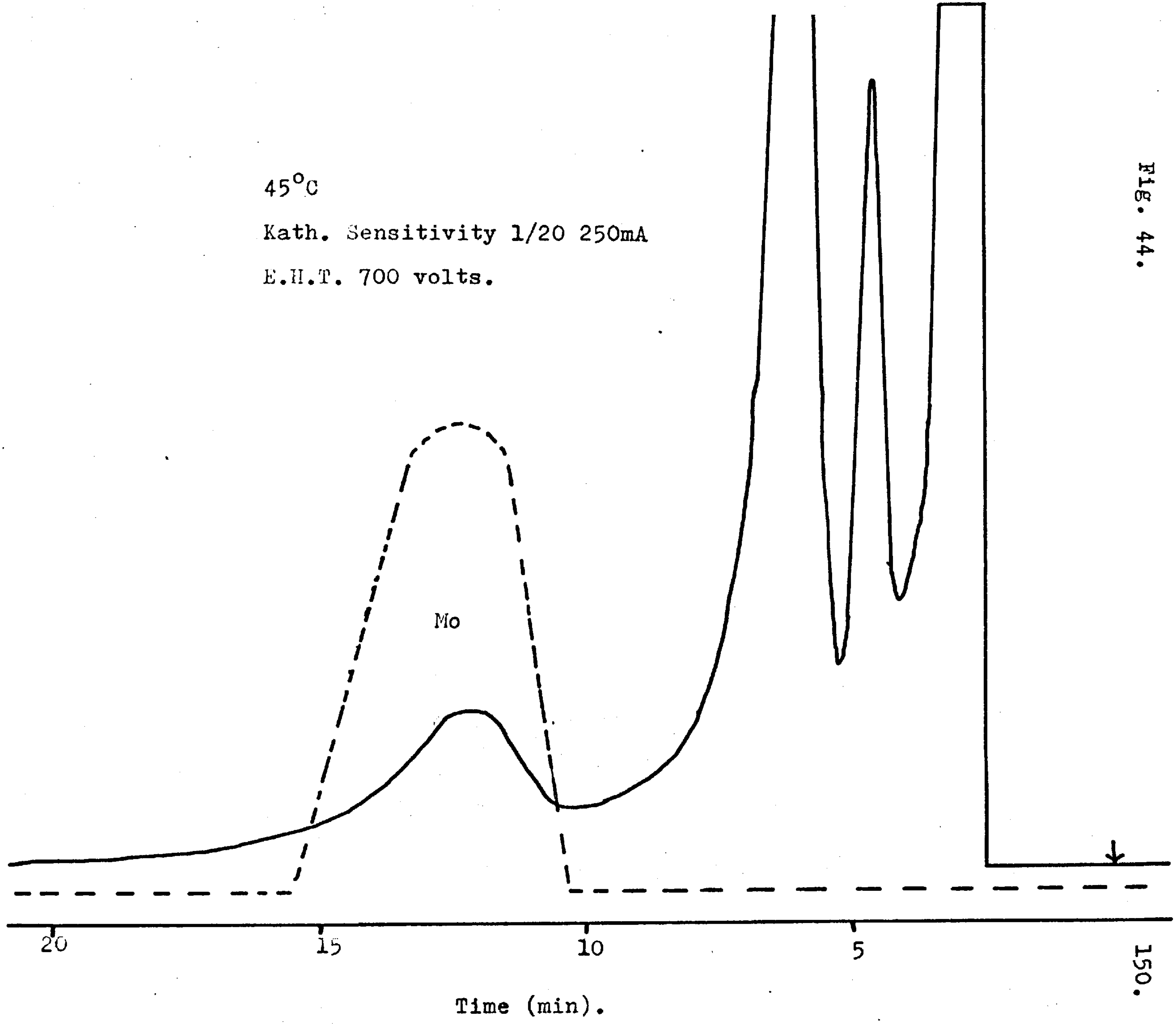
Fig.42.

Fig.43.


45°C

Kath. Sensitivity 1/20 250mA.

E.H.T. 700 volts.



45°C

Kath. Sensitivity 1/20 250mA

E.H.T. 700 volts.

Fig. 44.

Even lower column temperature and lower flow-rates were examined but the peaks due to molybdenum and rhenium became so broad that it is difficult to interpret the chromatograms. It is however, possible to distinguish between rhenium and molybdenum if two equal samples are run consecutively with the spectroscopic detector set at 525 nm and 622 nm. If rhenium is present the response at 525 nm will be greater than at 622 nm and the converse will be true for molybdenum. However, if the mixture contains both rhenium and molybdenum then it is impossible to determine their individual concentrations by this method.

IV. iv. Calibration curves obtained from the spectroscopic detector and the katharometer.

A series of samples of known weight for each element are separated by the chromatographic system at 75°C with a carrier gas flow-rate of 50 ml/min. The photomultiplier is adjusted to 650 volts and the slit width to 0.4 mm with the sensitivity of the katharometer set at 1/10 and the bridge current at 250 mA. The signals obtained from the katharometer and the spectroscopic detector are shown below.

Tungsten.

Weight µg.	Katharometer response.	Spectroscopic response. at 622 nm.
324.4	7.5	31
592.6	15.7	54
604.8	16.0	55
863.6	29.0	83
907.0	31.0	90

Molybdenum.

Weight µg.	Katharometer response.	Spectroscopic response. at 622 nm.
357.5	3.5	19
419.7	4.1	26
602.0	8.7	35
616.0	8.8	39
908.7	11.3	60

Rhenium.

Weight µg.	Katharometer response.	Spectroscopic response. at 525 nm.
473.8	4.9	21
535.9	5.8	26
731.3	7.5	35
897.6	8.9	41
924.7	9.3	45

Calibration curves for these results are shown (fig. 45)

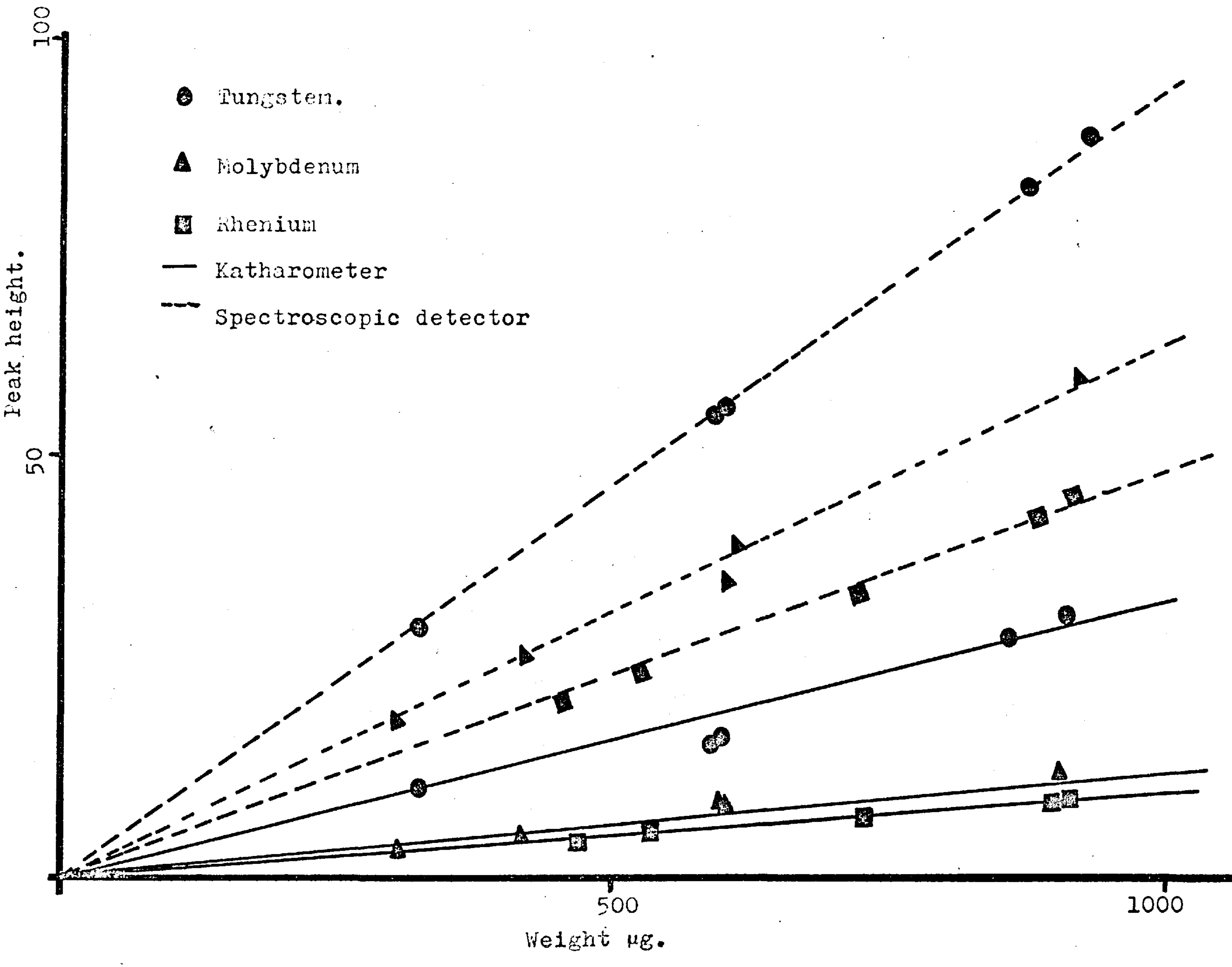

● Tungsten.
▲ Molybdenum
■ Rhenium
— Katharometer
--- Spectroscopic detector
100
50
Peak height.
500
1000
Weight μg.

Fig. 45.

and all of them show a rectilinear dependence between signal and the weight of sample. These curves also show that if the spectroscopic detector is used after separation on a gas chromatographic column then the sensitivity of this detector increases by at least one order of magnitude. This is due to the fluorides taking a longer time to pass through the flame as they are eluted in the form of broad peaks. This theory is substantiated by the fact that the sensitivity of tungsten is not increased as much as that for rhenium and molybdenum.

V. The Separation of Boron, Phosphorus, Selenium, Silicon, Sulphur and Tellurium.

This group of elements form fluorides so easily that no radio frequency heating is necessary. In fact, the reaction is so exothermic that this energy is sufficient to dissociate the excess chlorine trifluoride into chlorine and fluorine. These elements have never been successfully separated under any conditions for even at the extreme temperature of -77°C, where the column packing materials (Kel-F oil No. 10

on Kel-F moulding powder) operate as a gas solid chromatographic phase, boron and silicon were not separated from fluorine[126].

Since it is found that the heat of reaction dissociates the excess chlorine trifluoride the 'blank' chromatogram of pure chlorine trifluoride is subjected to radio frequency heating even though when individual elements are determined no radio frequency heating is used. This is carried out in order that there is no mistaken identification of the chromatograms obtained.

V. i. Column temperature 23°C.

The separation was first attempted at an ambient temperature with the spectroscopic detector set at 548 nm for boron, 528 nm for phosphorus, 394 nm for selenium, 384 nm for sulphur, 436 nm for silicon and 525 nm for tellurium. It was found that at this temperature that these elements are split into two groups the first group which consists of boron, silicon, and phosphorus are eluted with the fluorine (fig. 46a, 46b) whereas sulphur, selenium, and tellurium are eluted as a shoulder on the

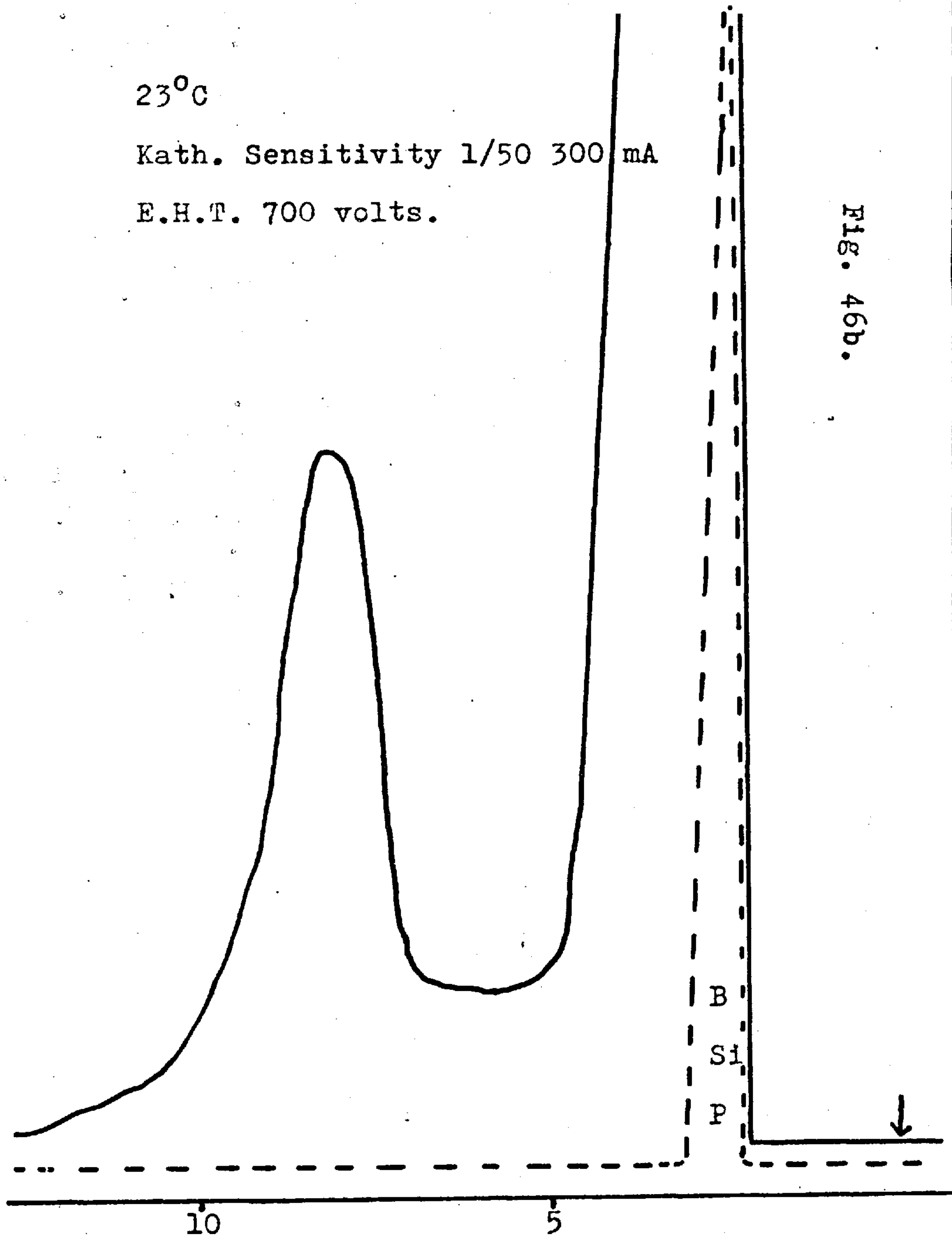


Fig. 46b.

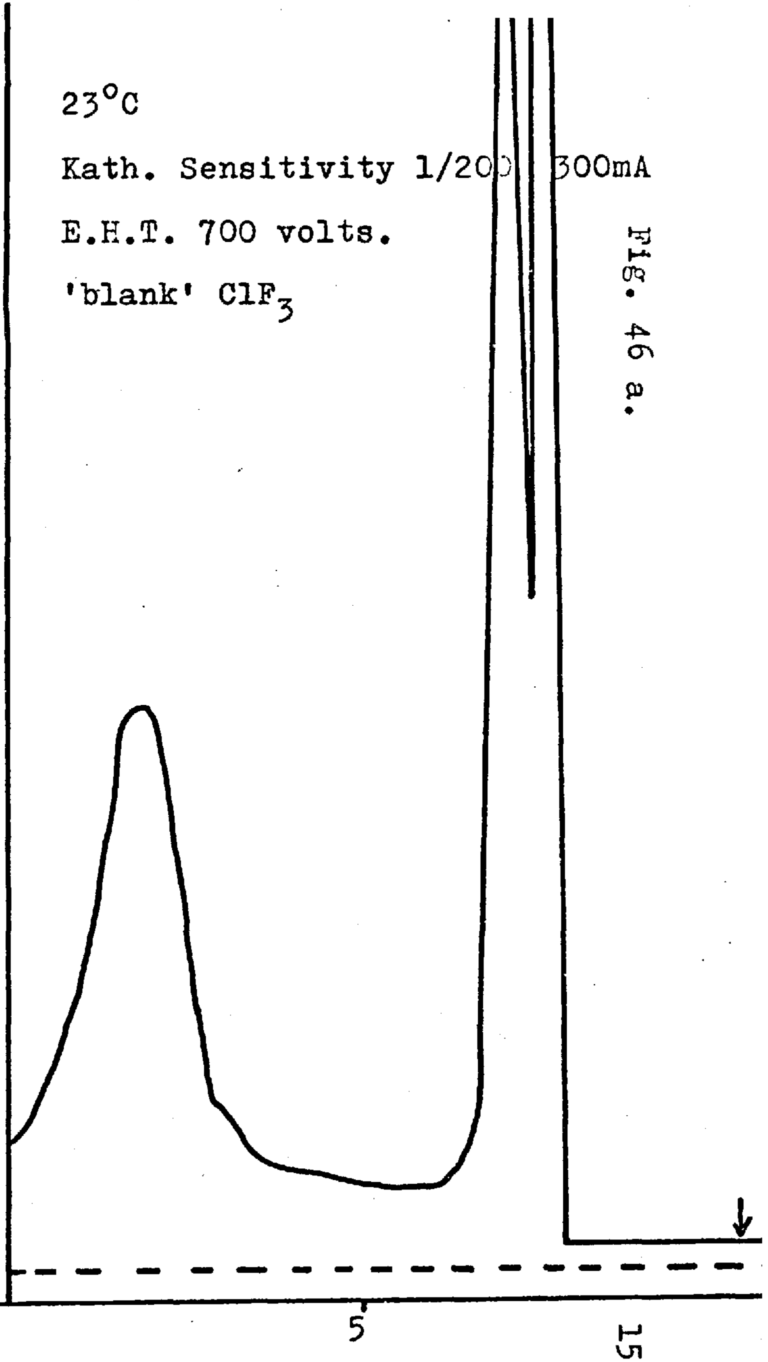


Fig. 46 a.

Time (min).

peak due to chlorine (fig. 47a, 47b).

V.ii. Column temperature -6°C.

In order that this temperature may be obtained the analyser oven is replaced by an ice-salt freezing mixture whose temperature was adjusted to -6°C by varying the ratio of salt to ice. This temperature is chosen as it is the temperature at which Kel-F oil No.10 starts to solidify and at this temperature this stationary phase will have the most effect on the degree of separation of the mixture. However, it was found that although the separation of the two groups was increased the separation of the groups into their individual components was not affected (fig. 48, 49a, 49b). The peak due to either sulphur, selenium and tellurium was better defined.

It is possible to obtained some selectivity between sulphur, selenium and tellurium and boron, silicon and phosphorus by careful choice of wavelengths. Sulphur and selenium may be distinguished from tellurium by comparing the intensities of equal samples of the elements at 384 nm and 525 nm, for tellurium will give a greater signal at

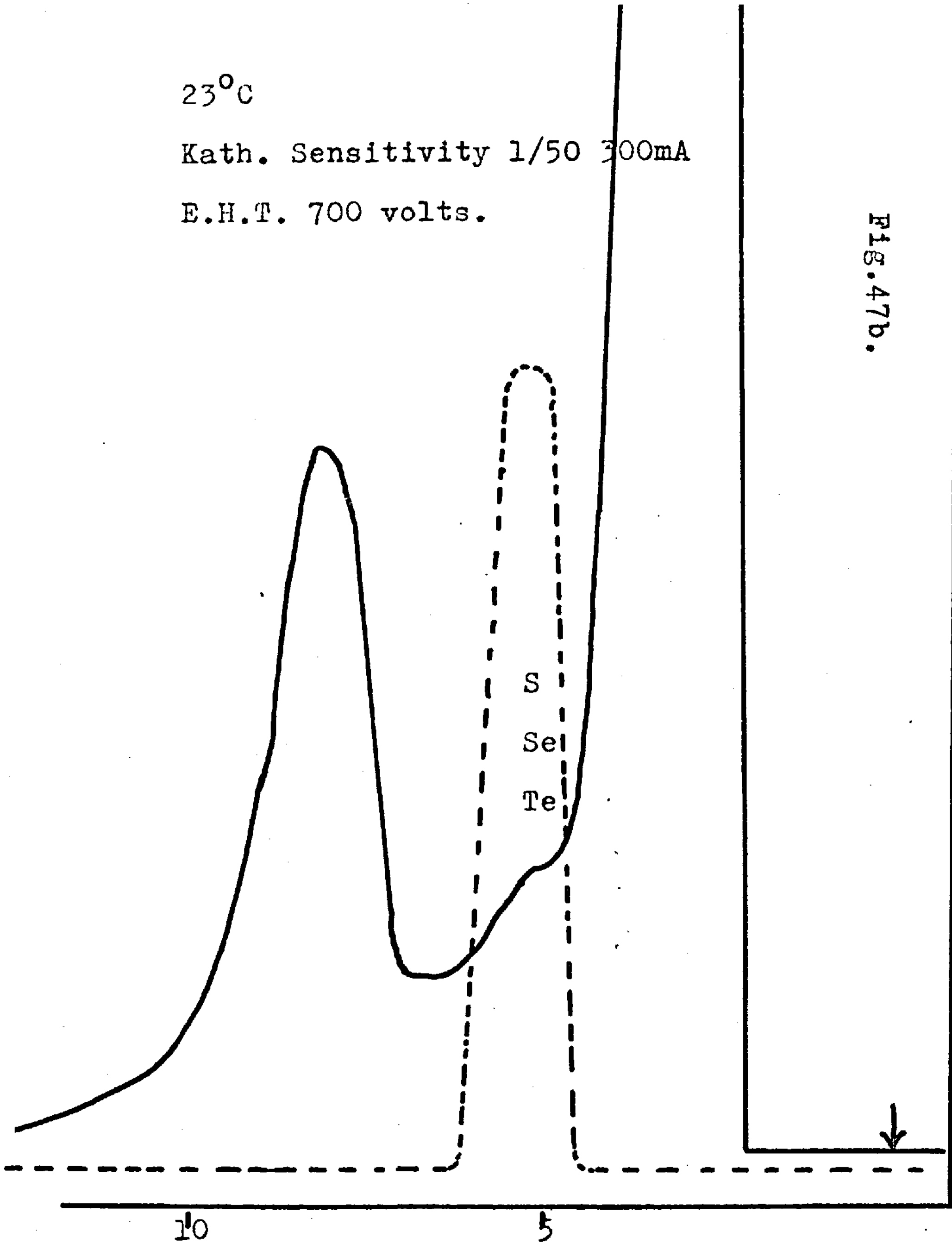


Fig.47b.

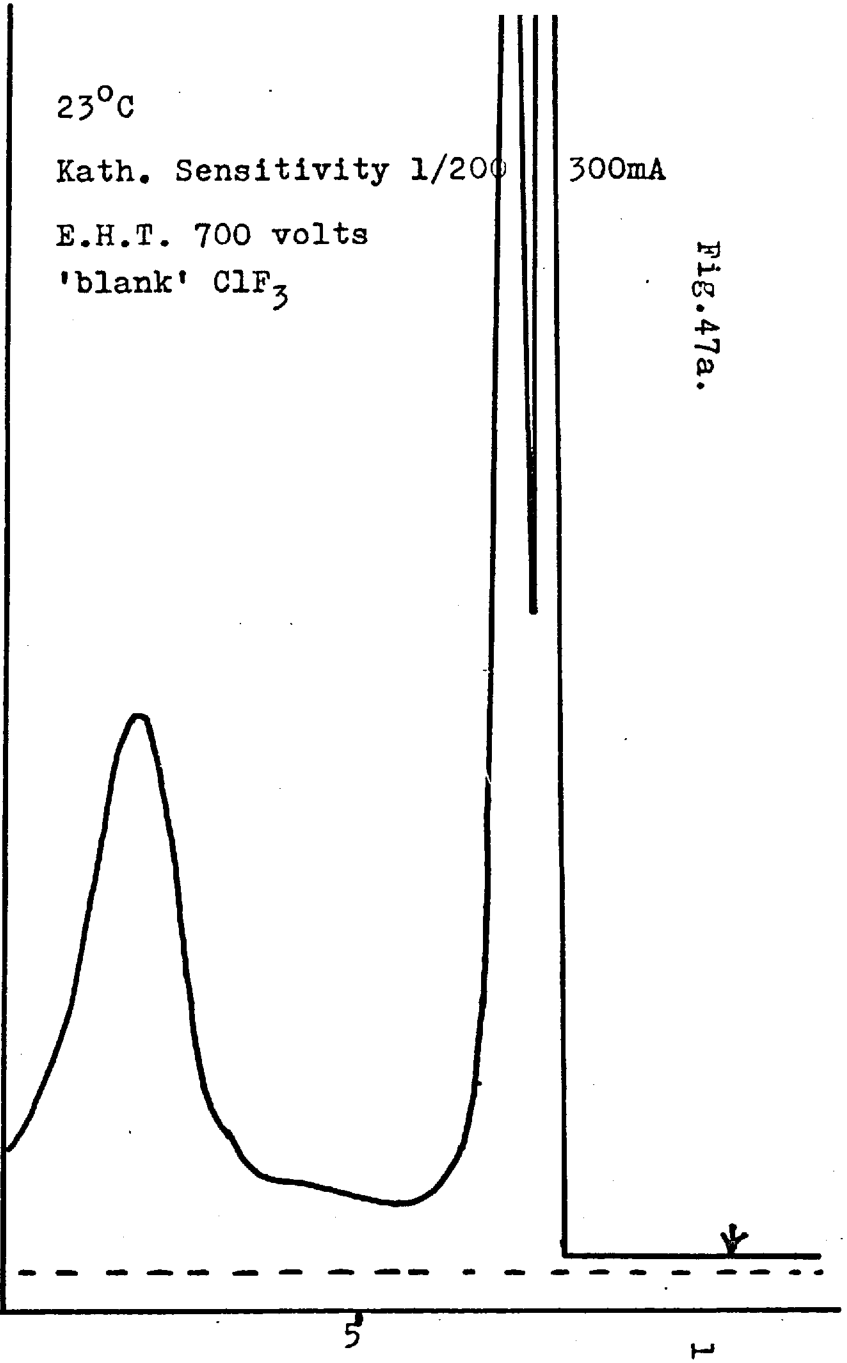


Fig.47a.

Time (min).

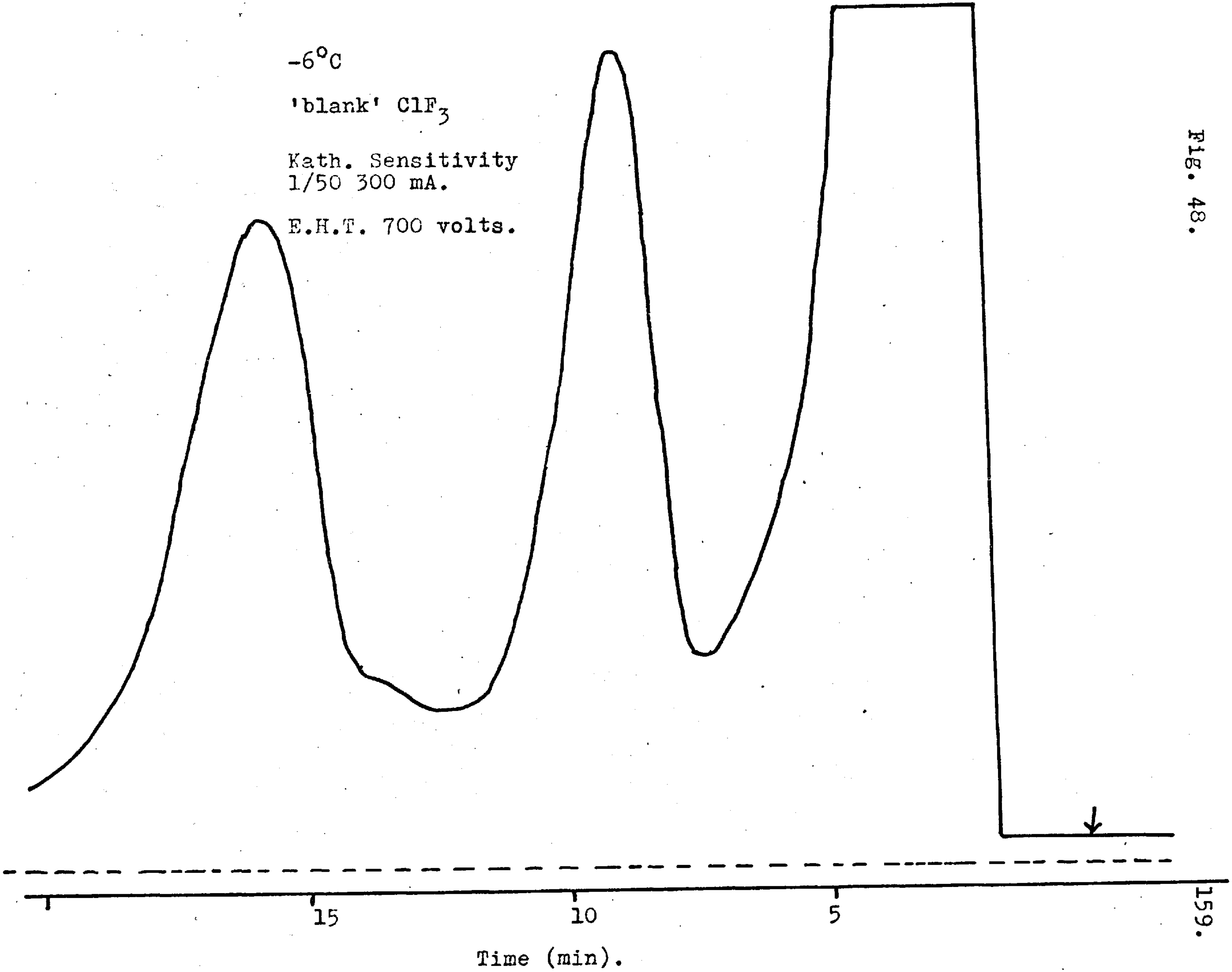

-6°C
'blank' ClF_3
Kath. Sensitivity
1/50 300 mA.
E.H.T. 700 volts.
15
10
5
Time (min).

Fig. 48.

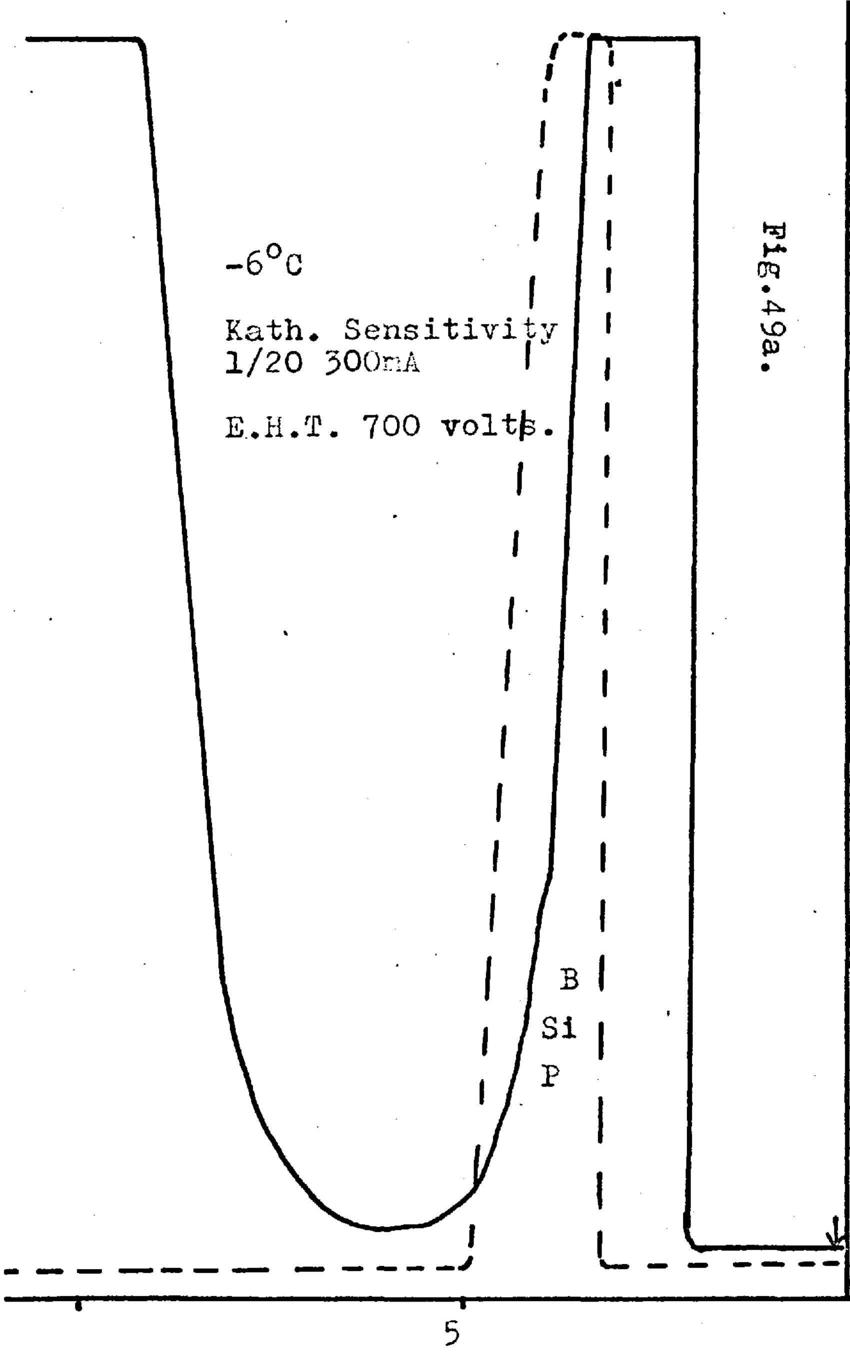


Fig.49a.

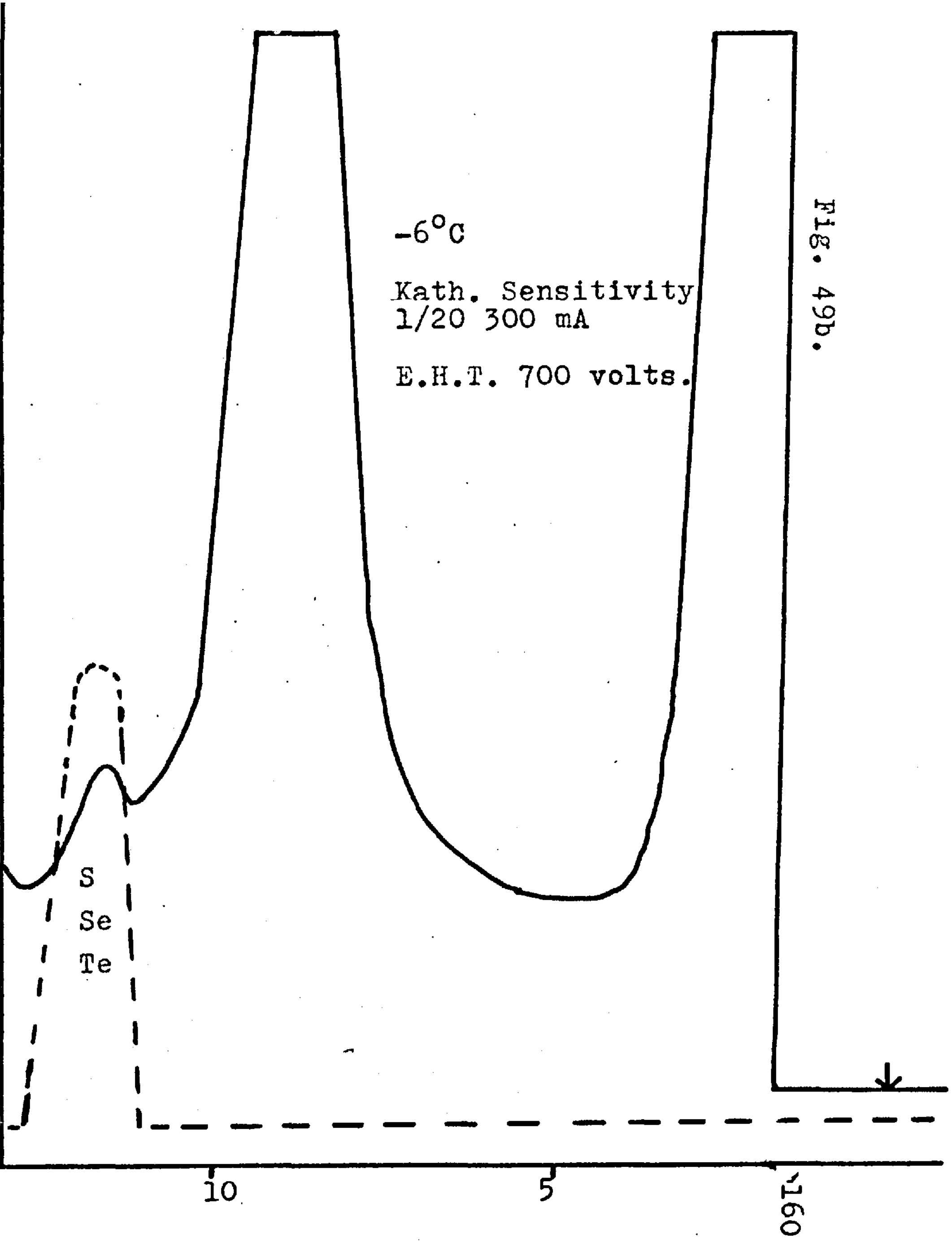


Fig. 49b.

Time (min).

525 nm than at 384 nm whereas for the other two the converse will be true. Sulphur may be distinguished from selenium if equal samples are measured after chromatographic separation at 384, and 394 nm and if the intensities of emissions at 384, and 394 nm are approximately the same the peak is due to selenium whereas if the signal at 384 is greater than that at 394 nm. the peak is due to sulphur.

Similarly, it is possible to distinguish between boron, silicon and phosphorus by comparing the intensities of equal samples at 528, 548, and 436 nm. If the maximum intensity is at 528 nm the peak is due to phosphorus, or if it is at 548 nm it is due to boron , and finally if the maximum is at 436 nm the peak is due to silicon.

However, if the mixture contains more than one element from each group it is impossible to determine the concentration of each component by this method.

V. iii. Other column packing materials.

As all these compounds form fluorides which are gases at ambient temperatures it was decided to try and separate them by gas solid chromatography which is the more usual method of separation for gases. Two materials were chosen Poropak G and activated alumina.

Poropak G was tried first and as this material is a cross-linked polystyrene molecule it was decided to try and partially fluorinate it by reacting it with chlorine trifluoride diluted with helium. However, this was found to be too vigorous as the cross-linking was broken down by the fluorinating agent with a result that this material gradually vaporised into various volatile fluorocarbon fragments.

Alumina which had been activated by placing it in an oven at 600°C for twenty-four hours was packed into a stainless steel column (12', 1/4" o.d.). This column was then chemically conditioned with chlorine trifluoride but the chlorine trifluoride was absorbed by this material and as a result the alumina glowed red hot. This is probably due to the fact that alumina has a large number of active OH sites which will hydrolyse the chlorine trifluoride. These active sites were reduced by a small loading of Kel-F oil No. 10 (2%w/w) on this alumina but a similar effect was obtained. Fluorosilicone oil was tried in place of Kel-F oil with a similar lack of success.

The only answer would be to use a system with the column at -77°C but due to the manufacturers delay in supplying a vacuum dewar of sufficient size to take the chromatographic column this separation was not possible.

It has, however, been shown that for these separations the spectroscopic detector shows a marked improvement over the katharometer since it has inherrent sensitivity and selectivity. If a complete gas chromatographic separation of these elemental fluorides could be obtained this detector would show tremendous advantages over conventional detectors.

Chapter 4.

A Polarographic Detector for Carbonyl Compounds.

It is important to have accurate methods of analysis for aldehydes and ketones as these compounds have wide industrial uses. Aldehydes are used in the production of some thermosetting resins such as phenyl-formaldehyde (Bakelite, Bakelite Ltd.), melamine-formaldehyde (Melolam Ciba Ltd.), urea-formaldehyde (Aerolite, Ciba Ltd.), polyesters, and polyurethanes, and they are also used in the preservation of tissue protein (formalin). Certain aldehydes and ketones have medicinal uses as hypnotics i.e. paraldehyde, chloral, and some alkyl aryl ketones, whilst others are used in the perfume (muscone and civetone) and flavouring (vanillin) industries. The major use of these compounds is in the paint industry where they are used as solvents (acetone, methyl ethyl ketone, methyl n-pentyl ketone, and cyclohexanone).

The analysis of mixtures which are suspected of containing aldehydes or ketones is generally carried out using either twin-column plots or Kovat indices techniques but a much more elegant approach to this problem of functional group analysis in gas chromatography was suggested by Hoff and Feit[165]. In this technique the gaseous sample to be analysed is reacted witha classification reagent in the syringe used to inject the sample onto the gas chromatographic column. Depending upon the type of pretreatment, the carbonyl compounds are either removed, or chemically converted, and a comparison of the resulting chromatogram with that obtained for an untreated sample, makes it possible for rapid identification of the peaks due to carbonyl compounds. Reagents and conditioned have been devised for a wide range of functional groups; a summary of the section relevent to carbonyl group analysis is shown (table 3).

Another method for the determination of aldehydes and alcohols is based on the principle of a gas diffusion

Reagent.	Composition.	Vol. of reagent.	Syringe vol.	Reaction time.	Purpose of reagent.
hydroxylamine	4g. NH_2OHHCl in 50ml. H_2O.	5	2	3	removes carbonyl compounds.
sodium borohydride.	1g. $NaBH_4$ in 2ml. H_2O	5	2	3	removes carbonyl compounds produces corresponding alcohols.
potassium permanganate	sat. soln in H_2O.	5	2	3	removes aldehydes leaving ketones. produces ketones from sec. alcohols.

Table 3 .

fuel cell.[166] The cell consists of a silver oxide electrode as an anode with a predetermined equilibrium rest potential, and it is used in a differential circuit. The electrolyte is potassium hydroxide. This electrochemical detector has a high selectivity for primary and secondary alcohols, as well as for aldehydes and providing the flow rate does not exceed 1 ml/sec. there is complete anodic oxidation of the detected substances to the respective carboxylic acids or ketones. Apart from the detector which is selective to carbonyl compounds[88,89] polarography has been completely ignored in detection systems for gas chromatography.

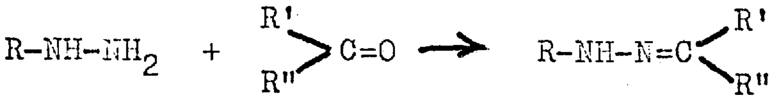
The present study of the development of a selective detector for carbonyl compounds is based on the polarographic reduction of the azomethine derivative. This derivative is formed by passing the separated carbonyl compounds, as they elute from the chromatographic column, into a buffered supporting electrolyte containing the carbonyl reagent.

The direct polarographic determination of carbonyl compounds is frequently complicated by the occurence of interfering side reactions such as hydration or acetal formation and it has been shown[167,168,169] that this class of compound can be more easily determined after conversion to the corresponding azomethine derivative eg. with hydroxylamine or semicarbazide hydrochloride. The reduction of the azomethine =C=N- group in semicarbazones and Girard reagent T occurs by an overall 4-electron process involving fission of the =N-N= bond initially, followed by the saturation of the resulting imine:

Girard reagent T (trimethylglycylhydrazide).

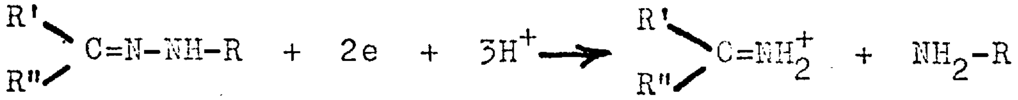
$$(NH_2.NH.CO.CH_2.N^+(CH_3)_3)\ Cl^-$$

Condensation.

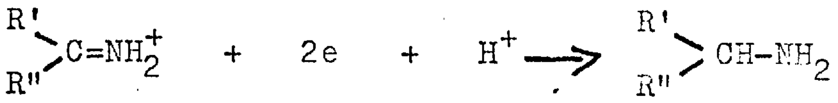


$$R\text{-}NH\text{-}NH_2 \quad + \quad {}^{R'}_{R''}\!\!>C=O \longrightarrow R\text{-}NH\text{-}N=C\!\!<^{R'}_{R''}$$

Proposed Reduction Mechanism.



$$ {}^{R'}_{R''}\!\!>C=N\text{-}NH\text{-}R \quad + \quad 2e \quad + \quad 3H^+ \longrightarrow {}^{R'}_{R''}\!\!>C=NH_2^+ \quad + \quad NH_2\text{-}R$$



$$\begin{matrix}R' \\ R''\end{matrix}\!\!>C=NH_2^+ \quad + \quad 2e \quad + \quad H^+ \longrightarrow \begin{matrix}R' \\ R''\end{matrix}\!\!>CH-NH_2$$

The advantage of semicarbazide hydrochloride and Girard reagent T over the more reactive nucleophile 2,4-dinitrophenylhydrazine is that these reagents are non-electroactive, consequently large excesses can be employed. The reduction waves for semicarbazones and Girard reagent T derivatives occur at much more positive potentials and are also better developed than the corresponding aldimines and ketimines, used by Mairanovskii et al[88,89].

As the azomethine group is reduced via the protonated complex the polarographic waves show a conventional dependence upon pH. The region over which the diffusion current shows its maximum limiting current extends from pH 1 to 4.5. As the rate of formation of the derivative is maximal at ca. pH 4, it is convenient to use the carbonyl reagent buffered to pH 4.5 as the supporting electrolyte with the derivative being formed "in situ" when the carbonyl is added.

In the present work the selection of the optimum condition for the formation of the azomethine derivative has been based on the results of previous studies in our laboratories on the polarographic reduction of carbonyl compounds [168, 169].

II. Design of the Polarographic Detector.

First of all Girard reagent T derivatives were prepared for the alkanals under discussion to find the potential at which the current is limiting for all these alkanals. This was carried out in a Kalousek cell and the potential between the dropping mercury electrode (D.M.E.) and the saturated calomel electrode (S.C.E.) was applied by a controlled potential recording polarograph (Metrimpex OH 102). The best potential for these alkanals is found to be -1.32 volts. Further studies were performed to establish the optimum pH, percentage ethanol, and the rate of formation of the derivatives.

A rectilinear dependence of the limiting current as a function of concentration is observed over the range 5µM/ml to 50µM/ml. (fig.50).

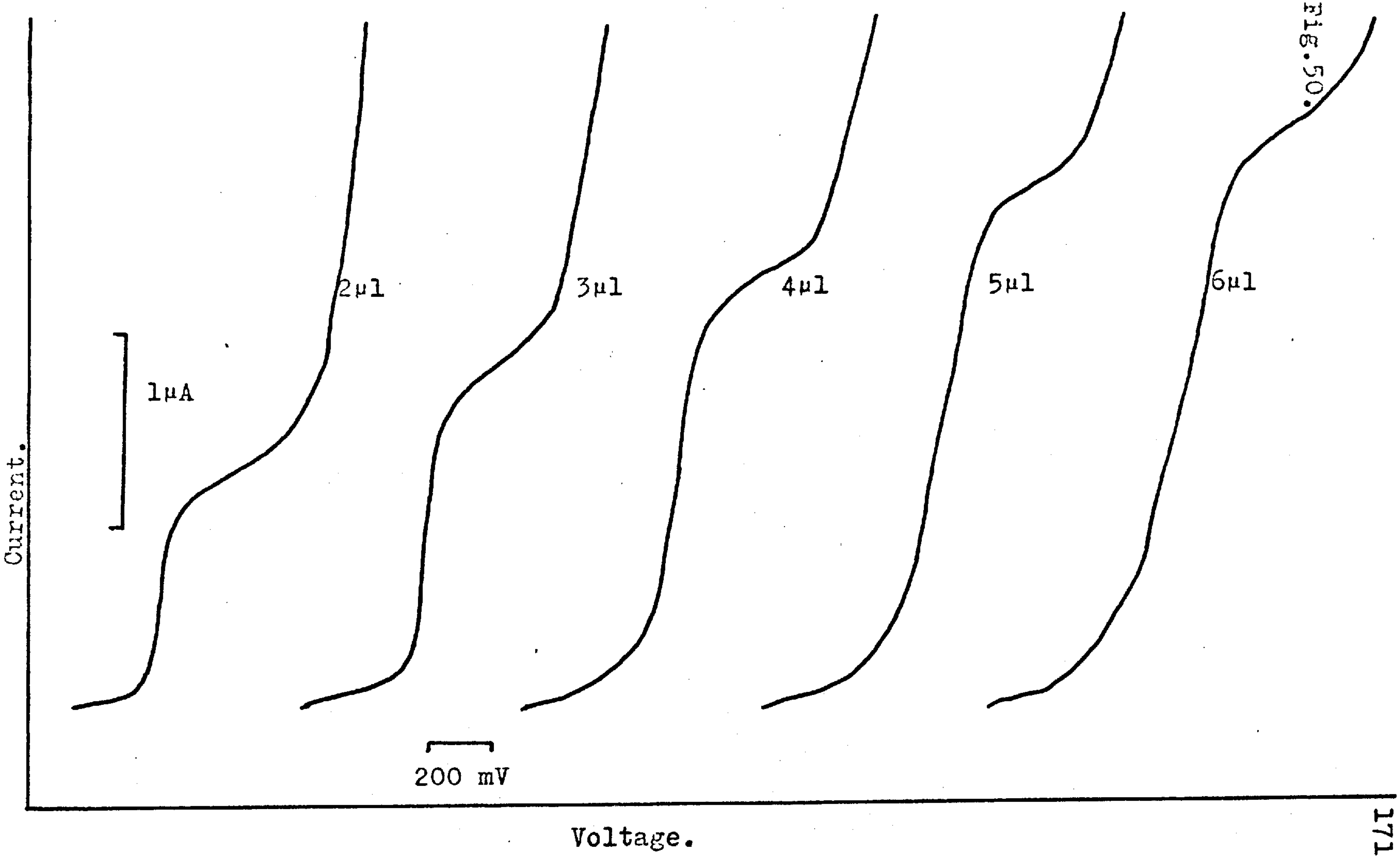


Fig.50.

II.i. Design of the Absorber.

The design of the absorber is critical as it is imperative for the derivatives to be formed instantaneously and to rapidly form a homogeneous mixture in the polarographic cell. Several designs were examined the first is where the eluent is forced through a glass sinter plate in the base of the cell into the absorbing solution. However, it is found that since the rate of formation of the derivative is so rapid it occurs within the sinter itself and none of the derivative reached the solution. A similar problem occurs when a small glass sinter is fused into the end of a glass inlet tube. A gas sparged absorber was tried next in which the capillary tip of the inlet tube is optically ground to fit the base of polarographic cell so that the gas is forced through a small annular orifice. The maximum carrier gas flow rate which could be attained without detrimental effects on the efficiency of the gas chromatographic separation, however, is insufficient to make this device work effectively. The most efficient design of absorber was found to be a stainless steel capillary (20 thou i.d.) fused into the end of a pyrex inlet tube. To check that there is quantitative dissolution of the eluent the limiting currents are compared when successive samples are introduced directly into the cell, the outlet tube, and the injection port. Providing the outlet tube is heated to the temperature of the injection block quantitative recovery is obtained (ie. 100% absorption of the carbonyl compounds).

II. ii. Choice of Electrodes.

In the first part of this study a normal dropping mercury electrode was used. However, various problems were encountered. The carrier gas bubbles adversely affected the drop time of the electrode and the drop time and the drop life is random. Also it is possible for carrier gas bubbles to be trapped on the electrode and this equally affected the response of the detector. It was, therefore, decided to use a Smǒler dropping capillary. The angle between the tip of the capillary and the main body of the capillary was varied between 30 to 90° and after exhaustive studies a Smǒler capillary with the tip at 90° was adopted. This capillary has a more rapid drop rate which shortens the response time and enables the solution to be stirred continuously without any detrimental effect on the detector response. It is found that the absorption and equilibration of the solution is enhanced by the use of a magnetic stirrer which revolved at 20 r.p.m. A saturated calomel reference electrode is used which has a glass sinter at its boundary with the solution under investigation.

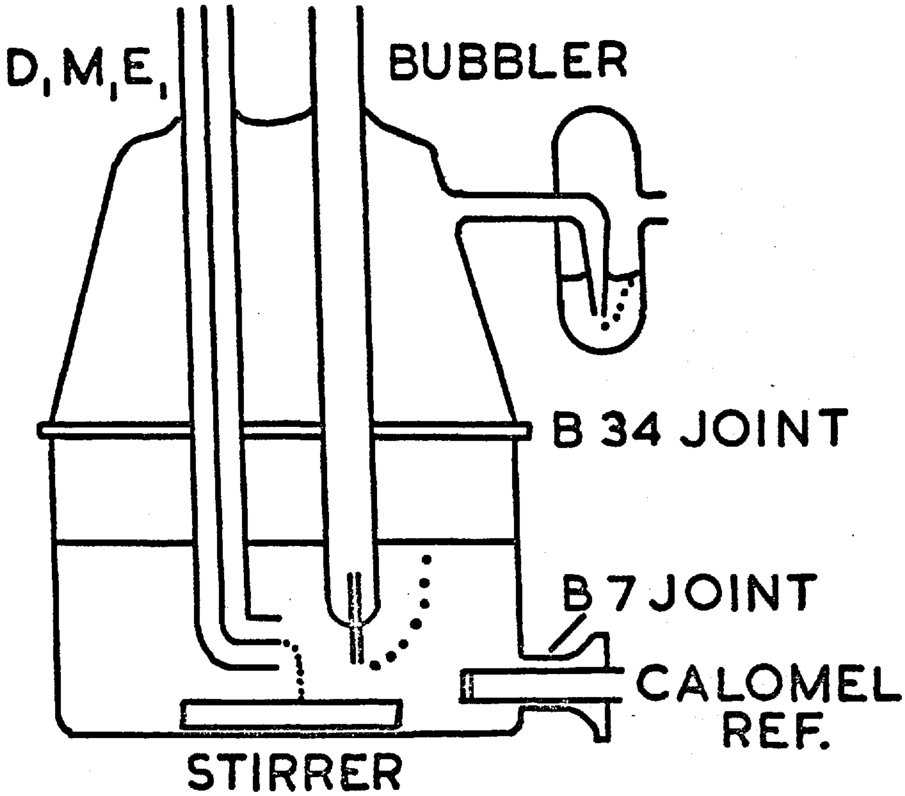
II.iii. Polarographic Cell.

This consists of an optically flat bottomed cell with a B 34 conical top (fig. 51). The indicating electrode and the absorber are ground to fit the cell top (cf. a glass hypodermic syringe) which enables their depth to be varied. The calomel reference electrode enters the cell at the base via a B 7 socket and is sealed by a PTFE. stopper.

III. The Chromatographic System.

A development gas chromatograph is used throughout this work. For the initial development of the chromatographic separation a flame ionisation detector is used,

Fig. 51.



subsequently, this is replaced by the polarographic detector in series with a katharometer. Nitrogen is the carrier gas used for the initial studies with the flame ionisation detector and helium is used for the studies using the katharometer with the polarographic detector in tandem. The potential required by the polarographic detector is supplied by a Cambridge General Purpose Polarograph and the signal is displayed on a 0-10 mV chart recorder.

III.i. The Separation of an Awkward Carbonyl Mixture.

The first problem was to establish the optimum chromatographic conditions for the separation of carbonyl compounds. It was, therefore, decided to choose a mixture which had been reported only being separable with difficulty on nitrobenzene or 2-nitrobiphenyl stationary phases[170] . This mixture consists of ethanal,propanal, propenal, dimethyl ketone, 2,4-butanedione, butanal, and 2-methyl propanal. Several stationary phases were examined at different flow rates and different temperatures: versamid, dinonyl and di-2-ethyl hexyl phthlates and carbowax 20M. The first three gave incomplete separation but with Carbowax 20M on chromosorb W (15% w/w) a complete separation is achieved (fig.52 table 4.).

Table 4.

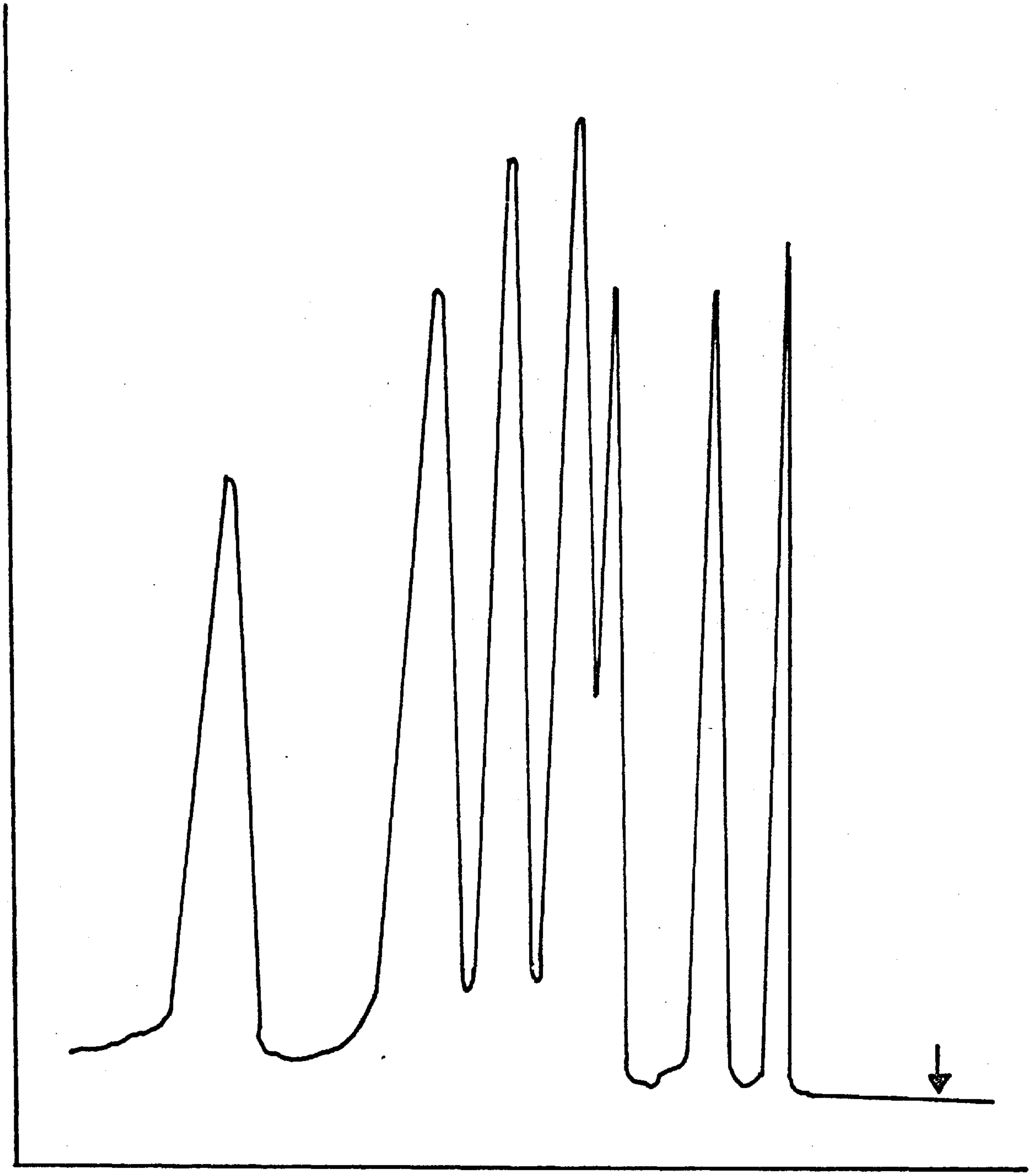
Compound.	Retention time (min).
ethanal	2.38
propanal	3.38
propenal	4.88
dimethyl ketone	5.50
butanal	6.38
2-methyl propanal	7.50
2,3-butanedione	10.63

Carrier gas nitrogen, flow rate 20ml/min., Dead volume 44ml., column temperature 140°C, Injection temperature 225°C, flame ionisation detector.

III. ii. Kovât Indices for an Homologous Series of Alkanals.

It was then decided to establish the retention data for an homologous series of alkanals (C_2-C_{10}) and an homologous series of alkanes (C_2-C_{15}). With this information it is possible to calculate the Kovât indices for the alkanals. This data is obtained by separating the mixtures on a column containing Carbowax20M on chromosorb W at three differing temperatures and also

Fig.52.



Time.

the temperature dependence is found (fig, 53, 54, 55. table 5, 6.).

Table 5.

Compound	Retention time (min). 150°	175°	200°
ethane	0.07	0.10	0.13
propane	0.12	0.16	0.19
butane	0.20	0.25	0.28
pentane	0.35	0.37	0.40
hexane	0.69	0.60	0.56
heptane	1.19	0.96	0.80
octane	2.11	1.50	1.15
nonane	3.50	2.35	1.79
decane	5.93	3.72	2.42
undecane	10.10	5.88	3.63
dodecane	18.20	9.37	5.60
tridecane	29.40	15.00	8.50
tetradecane	51.40	24.00	12.00
pentadecane	88.20	36.00	18.00

Carrier gas nitrogen, flow rate 25 ml/ min., dead volume 30 ml., Injection temperature 225°C, flame ionisation detector.

Compound.	Retention times (min).			Kovat Indices (I).			Temperature dependence dI/dT	
	150°	175°	200°	150°	175°	200°	150-175°	175-200°
ethanal	1.28	1.00	0.87	715	715	720	0.0	+0.2
propanal	2.08	1.52	1.21	805	805	815	0.0	+0.4
butanal	3.30	2.30	1.81	880	890	885	-0.4	-0.2
pentanal	5.55	3.60	2.45	987	990	985	-0.12	-0.2
hexanal	9.15	5.56	3.53	1070	1085	1085	-0.6	0.0
heptanal	14.95	8.56	5.14	1170	1180	1175	-0.4	-0.2
octanal	24.59	13.12	7.80	1270	1280	1280	-0.4	0.0
nonanal	40.25	20.40	11.00	1370	1380	1375	-0.4	-0.2
decanal	66.75	31.90	16.40	1460	1480	1480	-0.8	0.0

Carrier gas nitrogen, flow rate 25 ml/mn., dead volume 30 ml., Injection temperature 225°C, flame ionisation detector.

Table 6.

Fig.53.

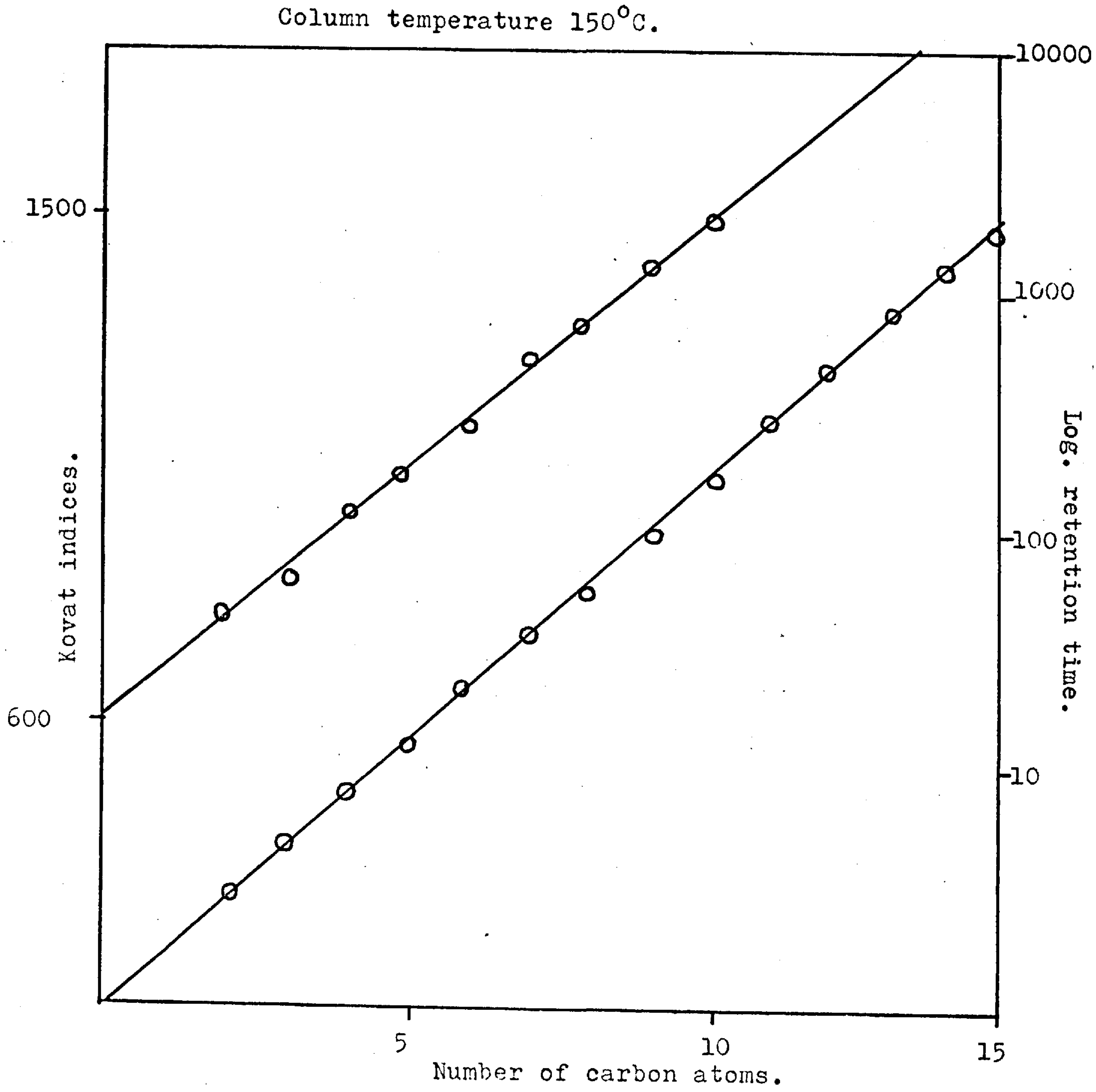

Column temperature 150°C.
1500
600
Kovat indices.
10000
1000
100
10
Log. retention time.
5
10
15
Number of carbon atoms.

Fig. 54.

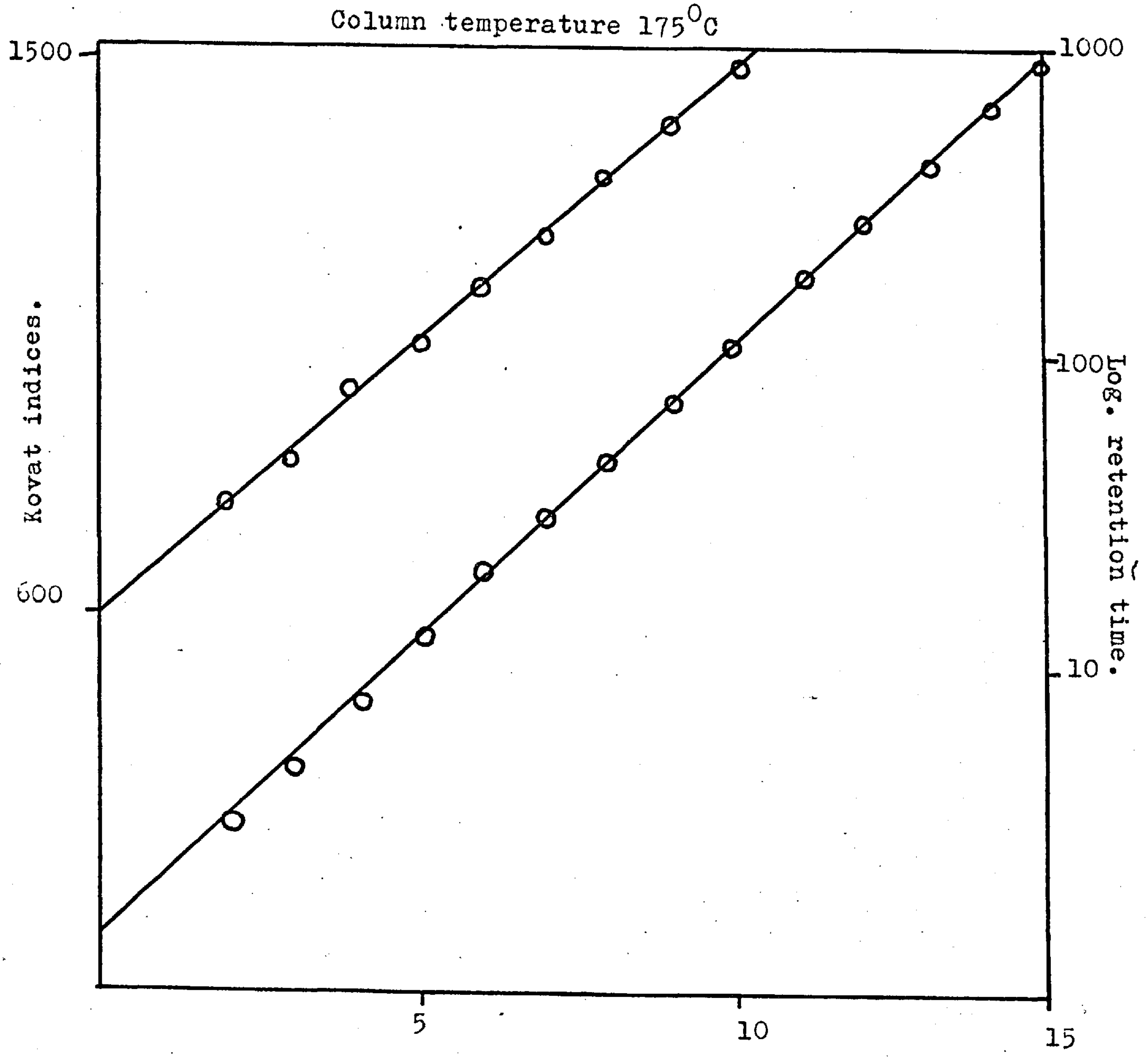
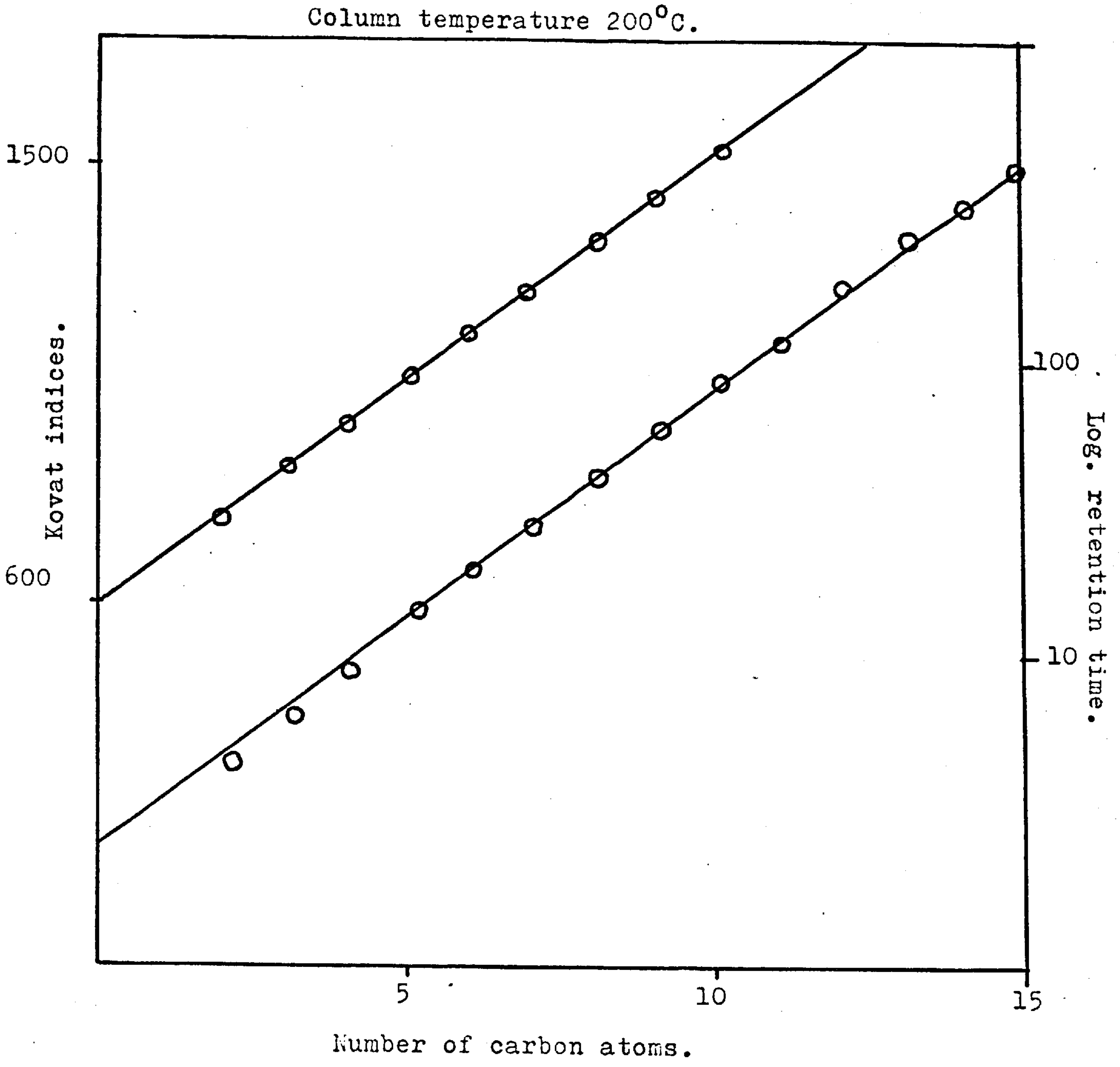

Column temperature 175^{0}C
1500
600
Kovat indices.
1000
100
10
Log. retention time.
5
10
15
Number of carbon atoms.

Fig. 55.


Column temperature 200°C.
1500
600
Kovat indices.
100
10
Log. retention time.
5
10
15
Number of carbon atoms.

IV. The Use of the Polarographic Detector.

The outlet from the katharometer is connected to the bubbler in the polarographic detector by a brass coupling. The polarographic detector is filled with the carbonyl reagent and the supporting electrolyte.

2.5 ml. acetate buffer (pH 4.55, 0.2M acetic acid, 2.0M sodium acetate).

1.0 ml. Girard reagent T (1M aqueous).

7.5 ml. ethanol (analytical reagent grade).

3.9 ml. distilled water.

0.1 ml. Triton X100 (0.1% aqueous, maximum suppressor).

The carrier gas (helium) is allowed to bubble through the polarographic cell for 5 minutes before the sample is injected, this is to ensure that there is no dissolved oxygen in the solution.

The polarographic response for an homologous series of alkanals (C_2-C_9), after separation on a column containing carbowax 20M on chromosorb W at 150°C, is shown with the response of the katharometer which is in series prior to the polaographic detector (fig.56). From a comparison of the two signals it is evident that the rate of formation of the derivative is extremely fast and that the limiting factor is the equilibration of the solution. The katharometer is also useful in that it indicates the presence of any non-electroactive species in the eluent.

IV.i. Interferences.

Clearly, a polarographic detector will respond to any electroactive species which is reducible at the potential applied. When the presence of an electroactive non-carbonyl containing substance is suspected this can be confirmed by a comparison of the detector response both in the presence and absence of the Girard reagent T which should be the same if it is present. Several potential interferences were studied (table 7). No unexpected results were obtained.

This detector may be used for the detection of other functional groups providing that they can be selectively

Fig. 56.

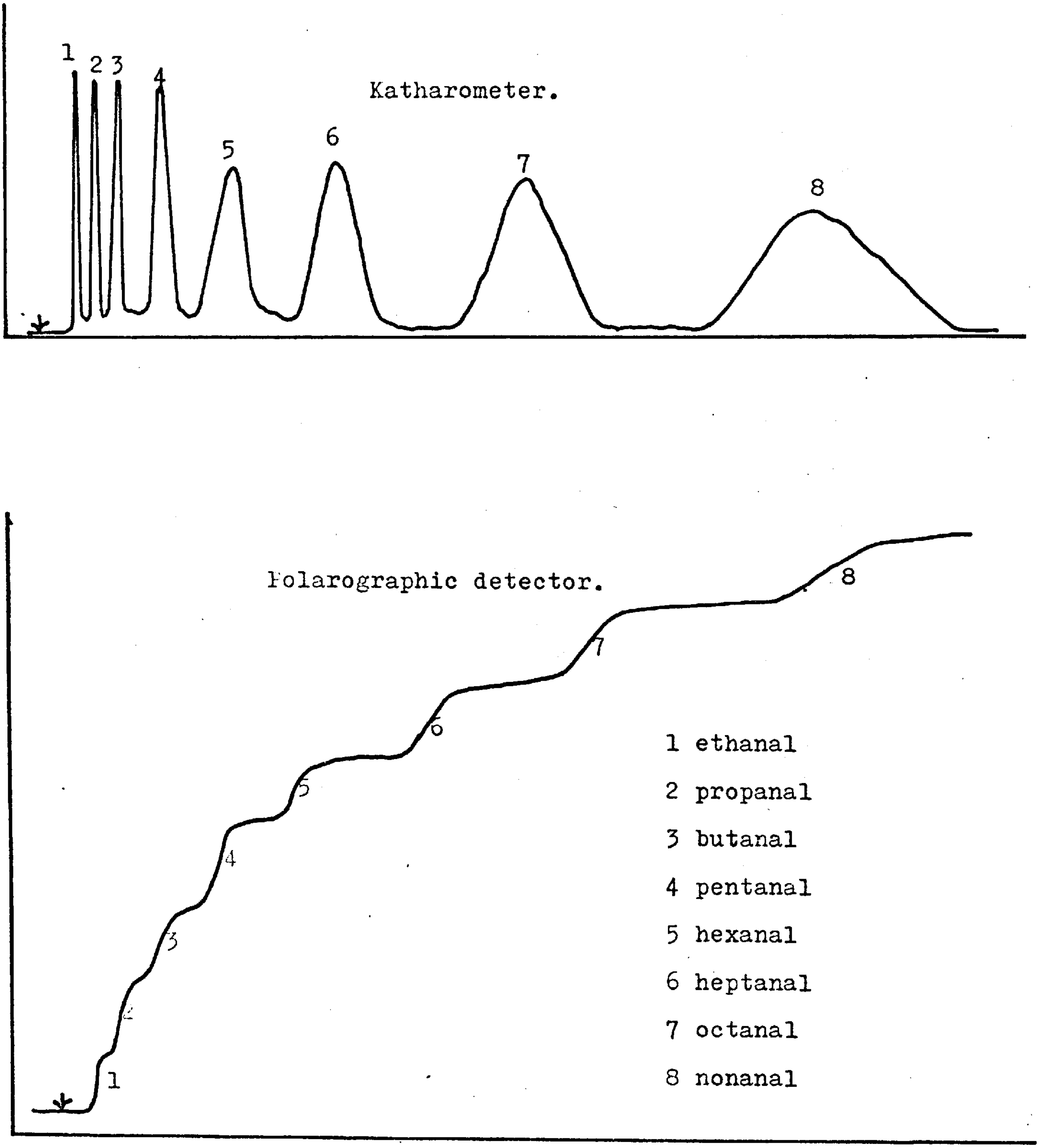

Katharometer.
1
2
3
4
5
6
7
8
Polarographic detector.
1
2
3
4
5
6
7
8
1 ethanal
2 propanal
3 butanal
4 pentanal
5 hexanal
6 heptanal
7 octanal
8 nonanal

Table 7 .

Compound.	Interference.	Compound.
unsaturated alcohols.	none	allyl alcohol
unsaturated esters	none	allyl acetate
saturated ester	none	ethyl acetate
primary amines	none	butylamine
nitriles	none	methyl cyanide
ethers	none	diethyl ether
aromatic hydrocarbons	none	toluene
alkanes	none	pentane
alkenes	none	pentene
nitro compounds	slight	nitromethane
alkyl halides	slight	bromopentane
acyl halides	slight	acetyl chloride

reduced at a chosen potential without interference from other electroactive groups. It is possible that this detector sensitivity may be increased by at least two orders of magnitude if the quantity of the supporting electrolyte and cell dimensions are reduced.

Chapter 5.

Conclusions and Suggestions for Future Work.

This project has shown that it is possible to develop a spectroscopic detector, based on molecular emissions in a low temperature hydrogen diffusion flame, which shows some selectivity and yet is insensitive to chlorine, fluorine, and chlorine trifluoride. It has also been shown that even if the separation is not very efficient the selectivity of the detector may compensate for this ineffective separation. With the development of a reactor-injection system which does not appear to suffer from any disadvantages it would appear possible to extend this artificial study using pure elements to the analysis of alloys, ores, and other metalurgical samples. For in theory it should be possible to leech out all the elements which form volatile fluorides from other elements which form non-volatile fluorides in any sample but it will be probably found that these volatile fluorides will tend to form non-volatile complexes which will lead to erroneous results.

If capillary columns containing Kel-F oils are used it is possible that all the fluorides could be separated with ease. However, this would mean that the reactor-injection vessel would have to be redesigned so that its volume is reduced by at least two orders of magnitude and even then the majority of the sample would have to be vented to the atmosphere.

The problem of weighing out small samples can be overcome if a solution of the element is prepared and an aliquot of this solution is placed on the sample boat. The solvent is then evaporated off before it is reacted with chlorine trifluoride. This would not be possible in the cases of non-metals whose compounds are very volatile as the process of evaporation of the solvent would possibly lose some, if not all, of the sample.

Some other work was done in the evaluation of other detection systems which are suitable for monitoring these corrosive fluorides. It was found that the use of microwave emissive detectors at atmospheric or at reduced pressure might have some future use providing it is possible to vent the fluorine and chlorine trifluoride before it reaches this detector, for these molecules attack hot silica rapidly. The result of this attack is that the transparent tubing goes opaque and there is continuous background emission due to silicon. Also this detector must be used with much smaller samples than the spectroscopic detector as the elements soon plate out on the walls of the silica tubing and this results in the background radiation increasing. This detector would, however, be much more selective than the spectroscopic detector as atomic emissions are observed.

Preliminary studies of other detectors based on flames were also made and it was found that chlorine, fluorine, and chlorine trifluoride did not increase the background radiation due to air/acetylene and nitrous oxide/ acetylene flames. It was found that as these flame can be used then selective detection systems based on Atomic Absorption Spectroscopy or Atomic Fluorescence Spectroscopy are possible for use in gas chromatography.

It is also possible that the Electron Capture detector may be used to detect these fluorides providing that suitable materials of construction are found.

Similarly it has been shown that electrochemical detectors based on plarography can be successfully used as selective detectors of organic molecules in gas chromatography. This idea has considerable scope in functional group analyses providing that suitable non-electroactive reagents are available which are selective to certain groups.

So to conclude this study it would seem that the use of a micro-reactor-injection vessel followed by separation on a capillary column with detection by a microwave emissive detector would possibly be the best method for the analysis of elements which form volatile fluorides.

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