THE EXAMINATION OF THE TAR ACID EXTRACT FROM A LOW TEMPERATURE COAL TAR BY GAS-LIQUID PARTITION CHROMATOGRAPHY.

A thesis submitted to Glasgow University in fulfilment of the requirements of the Degree of Doctor of Philosophy

by

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The bulk of the work in Part 3 of this thesis has been submitted to the Journal of Applied Chemistry for publication in the following papers:-

Gas-Liquid Chromatography, Part I:- Retention Volume Data of Certain Tar Acids.

Irvine, L., and Mitchell, T.J. (In Press).

Gas-Liquid Chromatography, Part II:- Analysis of the Alkali Extract of a Low Temperature Coal Tar.

Irvine, L., and Mitchell, T.J. (Submitted).

Summary.

Gas-liquid partition chromatography is presented as a method for the analysis of the tar acid extract from a low temperature coal tar. The historical development of the technique is outlined and a description given of the essential features of the apparatus. The theory of gas chromatography is briefly stated and applications of the method are described.

The construction and use is described of a gas-liquid chromatography apparatus in which temperature control is maintained by an electrically-heated air jacket.

Preliminary experimental work determined the results obtainable with the apparatus at relatively low column temperatures (Ca.100°C). The adaptations necessary for high temperature work are discussed.

Optimum working conditions are enumerated for the examination of thirty tar acids ranging in boiling point from 180-250°C and the application of additional flash heating at the entry of the chromatographic column is described.

Retention time data is given for thirty tar acid control samples and chromatograms for two coal tar xylenol fractions.

The use is then described of a vapour-heated

gas-liquid partition apparatus and retention time data is given for the tar acid control samples at 183°C, 155°C and 135°C. The examination of the tar acid extract from a low temperature coal tar has been made. The analysis was confined to the fraction 230-250°C distilled from the extract. This distillate was sub-divided by gas-liquid chromatography into six fractions, in each of which probable compounds were indicated by retention time data and confirmed by infra-red spectroscopy.

CONTENTS.

1. INTRODUCTION.

1.1. Summary.

The importance of tar acids in industry is dealt with briefly. The production of low temperature tar is discussed and the possibilities for research into the utilisation of its constituent materials.

Gas chromatography is presented as a method for the analysis of the tar acid extract from a low temperature coal tar. The historical development of the technique is outlined and a description given of the essential features of the apparatus. The theory of gas chromatography is briefly stated and applications of the method are described.

1.2. The Importance of Tar Acids in Industry.

In 1955, the quantity of tar acids used commercially was approximately 2.2 per cent of the total tar produced (3 million tons).

About 12,800 tons of carbolic acid and nearly 52,000 tons of refined cresylic acid were produced from U.K. coal tar in 1954. Demand for phenol is increasing for phenolformaldehyde plastics and as a starting material in adipic acid manufacture leading to nylon. Phenol is also important in the manufacture of salicylates, insecticides and dyestuffs and is used for the preparation of oil additives for use in the petroleum industry. The relatively small amount of phenol in conventional coal tars has been insufficient to supply all the demands, and increasing quantities of phenol are being synthesised from benzene.

In future years, coal tar may be made to yield more phenol, partly because of work carried out on dealkylation of higher phenols[1], but chiefly through processing the low temperature tars produced as by-products in the manufacture of smokeless fuels. Low-temperature carbonisation of coal gives a higher tar yield than high-temperature carbonisation and extends the range of chemicals obtainable by pyrolysis of coal.

Coal tar is still the main source of cresols and xylenols. The major use of cresols is in the plastics industry. Other outlets are as ore-flotation chemicals, disinfectants, and in the manufacture of dyes and inks. Xylenols are used as intermediates for plasticisers, antiseptics, fungicides and dyestuffs.

Tar Acid Research.

The chemical structure of the tar acids isolated from a high temperature tar (vertical retort) has been studied by the Coal Tar Research Association. In the boiling range 180 - 250°C., 34 individual phenols were isolated and identified.

The National Coal Board have for some years been carrying out extensive research on smokeless fuel production. The subsequent increased yield of tar also provides scope for research, particularly in the utilisation of the greater range of chemicals present. Analysis of the tar is therefore important and for this purpose it is convenient to divide the tar into acidic, neutral and basic fractions.

This thesis describes the analysis of the tar acid fraction of a low-temperature coal tar. Such a fraction is very complex and the compounds present require a high degree of separation for their identification to be possible.

The technique of gas-liquid chromatography has therefore been employed.

1.3. Gas Chromatography.

1.3.1. Introduction.

The term gas chromatography describes all chromatographic methods in which the traditional moving liquid phase or solvent is replaced by a moving gas. Separations effected by gas chromatography therefore depend upon repeated distribution of the substances to be separated between the moving gas and the stationary phase packed into the column. The term gas-solid chromatography describes the technique in which the fixed phase is an adsorbent solid (e.g. charcoal, zeolites), while the term gas-liquid partition chromatography is used where the fixed phase is an absorbent liquid held in an inert supporting material.

The substances being separated are carried through the chromatographic column by the moving gas, and mainly at temperatures below their critical temperatures so that they are technically vapours. The term vapour is extended to describe all the substances separated on gas chromatographic columns, although some may in fact be gases. The term gas is then restricted to the description of the mobile phase.

Gas-liquid partition chromatography is the analytical technique which was used for the analysis of the tar acid extract from a low-temperature tar.

1.3.2. Historical Background.

Adsorbent columns were used in the first gas chromatographic experiments. The sample to be analysed was introduced at the column inlet and then carried through the column in a stream of nitrogen, hydrogen or air. This process is called elution analysis as distinct from displacement analysis. The records obtained show a series of peaks of vapour concentration. If separation has been complete each peak represents a single pure component of the original mixture. The peaks in an adsorption chromatogram almost invariably have sharp "fronts" and diffuse "tails".

Displacement analysis is a modification of the gas-adsorption technique and was introduced by Claesson[2] in 1946. Here the components are displaced from the adsorbent by a displacer vapour present in constant concentration in the gas stream. The displacer vapour is chosen such that it is more strongly adsorbed on the packing than any of the components of the mixture to be separated. Chromatograms from displacement columns consist of a series of steps of vapour concentration. Each step corresponds to a pure component of the mixture, if separation has been complete.

The introduction of the gas-liquid partition technique by James and Martin[3] in 1952 was the most important advance in gas chromatography. They used a

stationary liquid phase of silicone fluid and stearic acid on kieselguhr as inert support to separate a large series of volatile fatty acids. The vapours were carried through the column in a stream of nitrogen (elution analysis), and the concentration of the emerging components in the carrier gas was determined and recorded by an automatic burette. Detection methods have since been considerably extended. Typical gas-liquid partition traces consist of a series of peaks. Again each peak represents a pure component if resolution has been complete. The component is identified by measurement of its retention volume, where

Retention Volume =	Volume of gas emerging from outlet of chromatogram in unit time	X	Time interval between introduction of sample and occurrence of appropriate peak on record.

Also, the peaks differ from those given by adsorbent columns since they are very nearly symmetrical. The elution method is always used in gas-liquid partition chromatography, displacement analysis being limited to adsorption chromatography.

Gas-liquid partition chromatography is the simplest in principle of the gas chromatographic methods as well as being the most efficient and convenient in practice.

1.3.3. Apparatus for Gas-Liquid Chromatography.

Various forms of apparatus have been used for gas-liquid chromatography.

In a typical apparatus the chromatographic column consists of a glass U-tube containing the inert support over the surface of which the stationary phase is spread as a thin film. The carrier gas obtained from a cylinder via reducing valves is passed through a fine pressure control device, a flowmeter, and a needle valve before flowing through the reference arm of a vapour detector and on to the chromatographic column. The sample is introduced at the U-tube entry and carried by the mobile phase through the column. The separated constituents emerging from the column in the stream of carrier gas pass through the registering arm of the vapour detector where their presence is detected and recorded automatically. The column outlet may be maintained at either atmospheric or reduced pressure. The chromatographic column is itself enclosed in an air jacket which is heated to a temperature suitable for the required analysis. If high boiling compounds are being examined, the vapour detector is also heated to prevent condensation of components in the registering arm.

The essential parts of the apparatus will now be considered separately.

(a) Chromatographic Column.

The column may be constructed in pyrex glass or metal. For most analytical purposes straight 4 ft. columns with an internal diameter of 4 mm. are satisfactory, although 6 ft. U-tube columns are also commonly used. Spiralled columns have been employed[4,5] to give additional length while retaining a compact form. For difficult separations long columns have been built up by joining a series of straight 4 ft. tubes together at top and bottom with short U-shaped lengths of capillary tubing[6].

(b) Mobile Phase.

The carrier gas should be inert to the vapours and to the fixed phase, free from vapours and readily obtained in good supply. Nitrogen was the mobile phase used by James and Martin[3] in their original experiments and is probably the most widely employed.

Some property of the vapours being analysed is used for their detection e.g. thermal conductivity, density. Therefore detection is made easier if the same property of the carrier gas differs appreciably from that of the actual vapours. Thus the sensitivity of many detectors is increased if hydrogen is used, since it has a higher thermal conductivity and lower density than nitrogen.

Other mobile phases which have been used include helium and carbon dioxide.

(c) Stationary Phase.

The fixed phase must be stable and essentially non-volatile at the column temperature. Consequently stationary phases with high molecular weights would be very satisfactory. However the lower viscosities given by fluids with low molecular weights increase the separating efficiency of the column. Therefore a balance has to be reached in practice.

The choice of stationary phase also depends on the chemical nature of the vapours to be separated.

(d) Inert Support.

For high efficiency the column should be well packed with small particles to give intimate contact between the two phases. There is little practical advantage in using particles below about 0.5mm. diameter otherwise the column resistance to gas flow is increased and the length restricted.

The material chosen is simply a mechanical support for the stationary phase and must be completely inert, both chemically and from the adsorption standpoint, to the vapours being analysed.

Materials such as "Kieselguhr" (Celite 535, 545), so far the most widely used support, have been found satisfactory. Others include "Sterchamol", a furnace insulation brick ground to particle size 30 to 100 mesh[7], sodium chloride[8] and even glass beads[9].

(e) Sample Introduction.

The sample must be applied to the column and volatilised as rapidly as possible, otherwise resolution of components will be poor.

Samples may be introduced directly to the column packing using a micropipette[3]. A micrometer syringe with which the sample is injected on to the column through a serum bottle cap[10] has also been found convenient. Both techniques are described in more detail in Part 2.

(f) Flow Measurement.

Several methods of gas flow rate measurement are available. Capillary and U-tube flowmeter[11], rotameter[10] or soap bubble device[3] have all been employed.

(g) Flow Control.

The identity of a particular constituent is generally established by measurement of its retention time (the time interval between introduction of sample and the occurrence of the appropriate peak on the record).

Therefore the carrier gas flow rate must be adequately controlled to give reproducible results. For this purpose a manostat has been designed by James and Martin[3] to ensure a constant pressure at the column inlet. Where reduced pressure is used at the column outlet, control is effected by suitable valves.

(h) Temperature Control.

Since a variation of 1°C in the operating temperature can alter the retention volume by about 5 per cent, control of column temperature must be as accurate as possible to obtain reproducible results.

The air jacket surrounding the chromatographic column may be heated either by electrical means or by a surrounding vapour jacket.

Heating provided by the vapour of a pure stable liquid gives more accurate temperature control, but electrical heating has the advantage that the temperature can be changed rapidly.

Both forms of heating are later described in more detail (Part 2 and Part 3).

(i) Vapour Detector.

Some form of vapour detector placed in the effluent gas stream from the column is used to follow and record separations by gas chromatography.

The detector is such an important part of a gas chromatography apparatus that a separate study has been made (Part 2) of the qualities required in a good instrument as well as of the types of detector available.

1.3.4. Theory of Gas-Liquid Partition Chromatography.

Work carried out on liquid-liquid partition chromatography by Martin and Synge[12] led these workers to suggest the use of gas-liquid partition chromatograms for analytical purposes.

In their original work Martin and Synge used silica gel saturated with water as one phase of a chromatogram, the mobile phase being some fluid immiscible with water, the silica acting merely as mechanical support.

Separations in a chromatogram of this type thus depend upon differences in the partition between two liquid phases of the substances to be separated, and not, as in all previously described chromatograms, on differences in adsorption between liquid and solid phases.

Although Martin and Synge used the new chromatogram mainly for protein chemistry, by employing suitable phase pairs, many other substances were found to be separable.

The phases were then termed mobile or moving phase, and stationary phase respectively.

The mobile phase need not be a liquid but may be a vapour, and it was suggested by Martin and Synge that very refined separations of volatile substances should be possible in a column in which permanent gas is made to flow over gel impregnated with a non-volatile solvent in which the substances to be separated approximately obey Raoult's Law.

This therefore led to the development of gas-liquid partition chromatography by James and Martin. The substance being separated is partitioned between the stationary liquid phase, supported by a suitable material, and the gaseous phase, which moves through the column.

The gas-liquid partition column has two main advantages over the ordinary liquid-liquid partition column:

(a) the lower viscosity of the mobile phase allows relatively longer columns to be used with a subsequent gain in efficiency.

(b) it is generally easier to detect changes in composition of a gas than of a liquid stream.

1.3.4.1. Retention Time and Retention Volume.

The relative rates at which different substances move through a gas-liquid partition column are dependent on the nature of the forces (e.g. Van der Waals forces, hydrogen bonding) involved in their solution in the stationary phase. Each component as it emerges from the column is recorded by a vapour detector as vapour concentration against time or volume of effluent gas. Qualitative identification of each recorded peak is then carried out by measurement of retention time or retention volume where:-

Retention Time (t) = time which elapses before the centre of the zone of the substance under consideration emerges from the column.

Flow Rate (F) = volume of gas emerging from outlet in unit time.

Retention Volume of the centre of the zone (V_R) = t x F

1.3.4.2. Gas Compressibility.

The theory of gas-liquid chromatography differs from that of the liquid-liquid technique, where a constant partition coefficient is assumed, only by virtue of the fact that the mobile phase is compressible and thus produces a gradient of gas velocity down the column.

James and Martin[3] have carried out the necessary modifications to the theory of Martin and Synge[12] (1941) to allow for this and their calculations are reproduced in Appendix I.

If a is the area occupied by the gas phase in any cross-section of the column, L the column length, p_1 the gas pressure at the column inlet and p_o the pressure of gas at outlet, then it has been shown that

$$V_R = \frac{2}{3} \frac{aL}{R_F} \frac{(p_1/p_o)^3 - 1}{(p_1/p_o)^2 - 1}$$

The R_F value is the normal chromatographic parameter and represents the rate of movement of the zone of the substance under consideration relative to the rate of flow of the moving phase.

It is also shown that as P_1/P_o tends to unity then $\frac{(P_1/P_o)^3 - 1}{(P_1/P_o)^2 - 1}$ tends to $\frac{3}{2}$ and V_R tends to the limiting retention volume $V_g^0 = \frac{aL}{k_F}$

$$\therefore V_R = \frac{2}{3} V_R^0 \frac{(P1/Po)^3 - 1}{(P1/Po)^2 - 1}$$

James and Martin tested the theory by comparing at four different pressures:

(a) theoretical and experimentally determined flow rate ratios,

(b) values obtained for V_R^0 for different compounds.

Satisfactory agreement was obtained.

1.3.4.3. Column Efficiency.

The chromatogram is closely analogous in its mode of operation to distillation and a useful picture of the chromatographic process is gained by employing the concept of the theoretical plate, introduced to chromatography by Martin and Synge[12].

The H.E.T.P. or "height equivalent to one theoretical plate" is the thickness of the layer in which equilibrium is established between the two phases.

Calculation of Column Efficiency.

Two equations have been derived by James and Martin for calculating the number of theoretical plates from the experimental curves. (See Appendix I).

Equation 1.

$$r = 2\pi \frac{h^2L^2}{A^2}$$

where r = No. of theoretical plates.
h = Peak height of vapour.
L = Distance from start of record to centre of peak.
A = Area under peak.

Equation 2.

$$r = \frac{4t^2}{T^2}$$

where t = Time taken for centre of zone to emerge.
T = Time taken for the middle 68.3 per cent of the zone to emerge.

Fair agreement has been found between results obtained by the two methods.

1.3.4.4. Factors Affecting the Degree of Separation.

(a) Column Efficiency.

Diffusion is much more rapid in the gas than in the liquid, therefore diffusion in the liquid phase will normally be the factor limiting efficiency. The column efficiency is increased with reduction in flow rate but lengthwise diffusion in the gas along the tube becomes relatively important at very slow flow rates, and reduction beyond a limiting value leads to a spreading of the vapour peak and a consequent reduction in efficiency. There is thus an optimum flow rate value.

Different columns of the same length show slight variations in the H.E.T.P., since it is difficult to reproduce the same uniformity of packing and of dispersion of the liquid phase even with the most careful technique.

The number of theoretical plates is proportional to the length of the column. James and Martin[3] have described 4 ft. columns with efficiencies varying from

700 to 1200 plates, while an 11 ft. column had a plate number of 2000, despite the dead space produced at the bends of the column by the method of construction.

When the limiting factor is diffusion in the liquid phase, the H.E.T.P. is inversely proportional to the diffusion constant. Therefore raising the temperature will increase the diffusion constant and produce an increase in efficiency.

The nature of the liquid phase will influence the efficiency of a column since the diffusion constant of the solute in the liquid phase will generally be inversely proportional to the viscosity of the liquid. Fluids of low viscosity are therefore recommended.

The ratio of length to diameter is very large with gas-liquid columns and moderate increases in diameter should be possible without appreciable effect on efficiency. In fact, James and Martin[3] found one 4 ft. column of diameter 1.2cm. had an efficiency of 850 plates, while with 4mm. diameter columns the efficiency varied from 700 to 1200 plates (at 100°C).

(b) Change of Retention Volume.

The separation factor is taken as the ratio of two retention times or retention volumes. It is therefore a measure of the separation of two peak maxima.

Since, in a homologous series, the higher members will have larger latent heats of vaporisation, their change of vapour pressure with temperature will be larger than with the lower members, and the factor of separation will decrease with rise in temperature provided the gas flow rate and inlet pressure are unaltered. This has been confirmed experimentally.

Two competing factors are now introduced. Raising the column temperature decreases the retention volume but increases the diffusion rates. If the same gas flow rate is maintained the former factor predominates, resulting in a decrease in efficiency. If, however, flow rate factor and retention volume factor are set off against one another by adjusting the flow rate to give a constant retention time, the plate number is increased by raising the column temperature[13].

Relative retention volumes can be altered by changing the nature of the stationary liquid phase[14]. The degree of separation should be high when the fixed phase is of a similar chemical nature to the vapours being analysed, since increased vapour solubility is possible. Hence paraffin has been recommended for hydrocarbon separations[15], benzyl-diphenyl[15] and picric acid-fluorene[7] for aromatics, and diglycerol for alcohols[7].

1.3.5. Quantitative Analysis in Gas Chromatography.

Quantitative estimates of the constituents of a mixture can be obtained from the recorded chromatograms.

For this purpose a detector which produces a stepped rather than a peaked chromatogram (see pages 26-37) is preferred since each step height measures directly the quantity of a particular constituent present.

With detectors which produce peaked chromatograms, the quantity of vapour is directly related to the area under the peak. The area may be measured by a planimeter, by cutting out the peak shape on suitable paper and weighing, or by multiplying peak heights by half band widths[16]. The most common method of quantitative analysis is to measure peak heights, since these are also proportional to quantity of vapour when small vapour samples are employed as in normal practice.

In the case of a detector which has a response depending on the nature of the vapour, calibration of peak height against percentage component must be carried out for each vapour being analysed.

Internal Standard and Internal Normalisation Technique.

It is difficult to introduce an exact quantity of a liquid sample, and also to reproduce exact operating conditions from analysis to analysis. These difficulties are overcome with the internal standard method[17] by adding

a suitable volatile compound in known proportion to the mixture. Peak heights are then referred to the peak height of the internal standard. In the internal normalisation method[16], areas of all the peaks present are added and the total area is normalised to 100 per cent. The ratios of individual areas to this total give percentage concentrations directly.

1.3.6. Comparison of Gas Chromatography with Distillation.

Analytical distillation is the most direct comparison with gas chromatography, for both methods involve repeated distribution between two phases one of which is gaseous. However the basic principle of separation is more efficient in the case of gas chromatography. In distillation the substances to be separated are required to fill the whole of the column, since they actually form the phases and an overlap fraction therefore exists. In gas chromatography, the mixture to be resolved is quite separate from the fixed phase which is already present in the column. No analogue of azeotrope formation has yet been found in gas chromatography.

In terms of theoretical plates, gas chromatography is also more efficient. A very good fractionating column is only capable of an efficiency of

a few hundred theoretical plates, while gas chromatography columns can have efficiencies of a few thousand theoretical plates.

The versatility of gas chromatography also makes it possible to change the order of a separation by alteration of the fixed phase. Gas chromatographic separations are also much more rapid than those by distillation being completed in minutes rather than hours. Also, normal operation requires much smaller sample quantities; these can be scaled up if preparative work is necessary.

1.3.7. Some Applications of Gas Chromatography.

The early experiments by James and Martin[3] involved the separation of volatile fatty acids. Complete resolution was obtained of all normal acids (and iso acids up to at least C_6) on a 4 ft. column and of all the isomers of valeric acid on an 11 ft. column.

The same technique was used by James, Martin and Howard Smith[14] for the separation and micro-estimation of ammonia and the methylamines and by James[18] for the separation of volatile aliphatic amines and of the homologues of pyridine.

Ray[10] applied the technique to the separation of mixtures of hydrocarbons, alcohols, ethers, esters, aldehydes and ketones using "dinonyl" phthalate as stationary phase and thermal conductivity for detection. Using the same fixed phase Ray[19] separated propane, propylene and the C_4 hydrocarbons.

Bradford, Harvey and Chalkley[17] used G.L.P.C. to obtain sixteen clear chromatographic peaks from a petroleum fraction, the separation very much facilitating the subsequent identification of thirty-two components.

Pollard and Hardy[20] have studied the factors affecting the order of elution of halogenated methanes while Evans and Tatlow[21] have applied gas chromatography to organic fluorine chemistry.

Grant and Vaughan[22] have used the technique to determine the distribution of aromatic compounds in coal tar naphthas.

In a completely different field Glueckauf and Kitt[23] have employed gas chromatography for the separation of hydrogen isotopes.

Whitham[24] has used the technique for the analysis of petroleum products and has introduced liquid samples up to 3ml. to a large scale unit with a column bore of 1.27cm.

Comments.

Since the introduction of the gas-liquid partition technique by James and Martin in 1952, the applications of the subject have become extremely numerous.

The technique has become invaluable in both research and industry for qualitative identifications and routine quantitative analyses.

1.4. Choice of Technique for Analysis of Tar Acid Extract.

The tar acid fraction for analysis in this work may contain more than 30 components. Consequently if infra-red or mass spectrometric methods were employed, these would have to be used in conjunction with analytical distillation or chemical analysis since a high degree of separation is first required.

Gas-liquid partition chromatography has therefore been used in this work, since in addition to its use for qualitative analysis, the method gives more rapid and efficient separations than any other analytical technique. This makes infra-red spectroscopy a powerful supplementary tool.

2. ELECTRICALLY-HEATED GAS-LIQUID CHROMATOGRAPHY APPARATUS.

2.1. Introduction.

This section describes the construction and use of a gas-liquid chromatography apparatus in which temperature control is maintained by an electrically-heated air jacket.

A preliminary study is made of the rôle of the vapour detector in gas chromatography with a description of the various detectors.

The gas-liquid apparatus is first described as a working unit and then the essential features are dealt with in detail.

Preliminary experimental work determined the results obtainable with the apparatus at relatively low operating temperatures (ca.100°C). The adaptations necessary for high temperature work are discussed.

Optimum working conditions are enumerated for the examination of thirty tar acids ranging in boiling point from 180-250°C and a method of increasing the detector sensitivity is described as well as the application of additional flash heating at the column entry.

Retention time data is given for thirty tar acid control samples and chromatograms for two coal tar xylenol fractions.

2.2. Vapour Detectors.

Gas chromatographic apparatus is automatic in operation and separations are followed and recorded by some type of vapour detector placed in the effluent gas stream from the column. There are two distinct types, differential and integral detectors:-

(a) Differential Detector.

This detector measures some function of the vapour concentration and the resulting chromatogram from an elution analysis consists of a series of peaks. The position of a peak, retention volume or retention time, is characteristic of the vapour producing it. The area under the peak is a measure of the quantity of that vapour present.

(b) Integral Detector.

This detector measures some function of the total quantity of vapour which has passed through the column. The corresponding chromatogram from an elution analysis consists of a series of steps and is an integrated form of the trace given by the first detector. The positions of maximum slope correspond to the peak maxima (retention times), and step heights, measured between one step and the next, to peak areas giving the quantity of each vapour. The length of a step is of no significance apart from measuring the difference in retention times of two neighbouring components.

2.2.1. Essential Features of a Detector.

(a) Sensitivity.

The sensitivity should be as high as possible making trace components readily observed and enabling columns to be run with low sample quantities. The lower the sample load, the higher the performance. A detector should be sensitive to all vapours.

(b) Speed of Response.

Rapid changes of vapour concentrations are normally produced in a gas-liquid partition analysis. The detector must be correspondingly rapid in response to follow these changes accurately. Consequently it should have only a small internal volume.

(c) Linearity of Response.

The response should be linear to assist quantitative analysis and should preferably be some simple function of the number of vapour molecules, rather than of their kind, so that a fresh calibration is not required for each new vapour.

The detector should be simple and inexpensive to construct and should not react with or destroy any of the vapours which may have to be recovered after passage through the detector. The electric signal from the detector should be capable of operating an automatic recorder. The resulting base line should be stable both for short periods (noise) and for long periods (drift).

2.2.2. Differential Detectors.

Several differential detectors are available for gas chromatography:-

(a) Thermal Conductivity Cell.
(b) Gas Density Balance.
(c) The Hydrogen Flame Detector.
(d) Infra-Red Gas Analyser.
(e) The Beta Ray Detector.
(f) Surface Potential Detector.

These will now be studied in more detail.

(a) Thermal Conductivity Cell.

The thermal conductivity cell or katharometer has so far been the most widely used detector in gas chromatography. It consists of a hot wire suspended down the centre of a tube through which passes the gas from the column. An electric current heats the wire, its temperature rising until the stage is reached where input of electrical energy balances loss of heat energy. The hot wire serves as a resistance thermometer.

In most katharometer arrangements two thermal conductivity cells are used. Pure carrier gas passes through one (reference cell), and the effluent carrier gas containing the components to be identified passes through the other (analysis cell). The cells are generally incorporated in some type of Wheatstone Bridge arrangement. A battery or some other d.c. electrical source supplies the bridge current and heating for the wire. The out-of-balance from the bridge is a measure of the rate of loss of heat from the wire.

Nitrogen is the mobile phase normally employed. Since most gas-vapour mixtures have lower thermal conductivities than the gas alone, greater sensitivity to vapour concentration is obtained if hydrogen or helium, which have high thermal conductivities, is used instead of nitrogen. An increase in bridge current also produces a greater sensitivity since the temperature of the wire is increased.

Thermal conductivity cells are generally fitted within a metal block which must be maintained at constant temperature, since any change in the temperature of the tube walls will affect the rate of heat loss from the wire.

Metal block thermal-conductivity cells are in use in which the hot wires are replaced by thermistors.

(b) Gas-Density Balance.

This detector was developed for gas chromatography by James and Martin[25]. A system of gas channels is used like a Wheatstone Bridge to compensate pressure differences due to flow. The actual pressure difference set up and used in the measurement is then related to gas density only. The instrument consists of a copper block in which a number of tubes are bored. The unit is maintained at the column temperature. When a difference in density occurs between the gas from the outlet of the chromatographic column and

the pure nitrogen from a reference column, a flow of gas is caused in a cross-channel in the copper block. This flow is detected in the channel by a small electrically heated filament situated below and equidistant from two connected thermojunctions. The stream of hot convected gas from the filament is displaced towards one or other of the thermojunctions, heating one and cooling the other. A thermoelectric e.m.f. is produced which is amplified and recorded automatically. The recorder deflection has a linear relation to the difference in density of the two gas streams. The gas-density balance is rapid in response and extremely sensitive.

(c) The Hydrogen Flame Detector.

This microflare detector was designed by Scott[26]. Hydrogen is employed as carrier gas and is burnt at a small jet at the column exit. A thermocouple placed slightly above the flame is engulfed when the flame lengthens due to the presence of an organic vapour in the gas. The output from the thermocouple is fed through a suitable potentiometric network to a recorder.

The thermocouple may be made of platinum/platinum + 14% rhodium (high temperature work), Chromel/Alumel or iron/constantan. The last appears to give a higher overall sensitivity and a more constant zero than the others and has

proved most effective, although used outside its normal practical range.

The jet is made of pyrex glass capillary with a bore of approximately 0.2mm. A number of baffle plates are necessarily incorporated in the detector to reduce the effects of draughts.

The theory of the detector is, at the moment, rather uncertain but appears to depend on the heat of combustion and rate of burning of the substance present. A linear relation exists between peak area and weight of a hydrocarbon vapour producing the peak.

The only apparent disadvantage of the detector is that it destroys the vapour being analysed. It is, however, low in cost, simple to construct, and has a sensitivity as high as that of the vapour-density bridge.

A detector has been described by Grant[27], which employs a microflame similar to that of Scott, but the luminosity of the flame rather than its temperature is measured. The exit hydrogen from the column is carburetted and the detector produces a very much larger response for aromatic than for saturated hydrocarbons.

(d) Infra-Red Gas Analyser.

The infra-red gas analyser has been recommended by Martin (A.E.) and Smart[28] as a more uniform and more sensitive means of detecting components.

It was indicated that for infra-red absorbing gases, it would be sufficient to use a detector in the instrument which was sensitive to all the components present in the sample. Nevertheless the sensitivity to different vapours would still vary, and also adequate sensitivity might not be readily obtained. With organic vapours, these difficulties are overcome by passing each compound emerging from the column through a tube containing copper oxide heated to dull redness, or some other suitable oxidising agent, converting the carbon to carbon dioxide and any hydrogen to water vapour. These gases are then passed into an infra-red gas analyser sensitive to carbon dioxide.

The detector is capable of high sensitivity, 0.01 per cent carbon dioxide in nitrogen readily giving a full-scale deflection when using a 30cm. absorption cell. Once the gas analyser has been calibrated for carbon dioxide, the sensitivity to any other organic vapour is directly proportional to the number of carbon atoms in the molecule. Careful drying and special cooling of the gas after combustion are not required.

(c) Beta Ray Detector.

Measurements of the current passing between two electrodes at different potentials in a gas ionised by some type of radiation have been used for analytical purposes by a number of workers. A method based on this principle was

developed for detection in gas chromatography[29], using beta rays emitted from a radioactive source.

The detector described by Boer[30] employs two cells, one for the carrier gas and one for the column effluent. The gas in the cells is bombarded with beta rays from a radioactive source. The cells have a common central electrode and separate sources of stabilised voltage are connected between the walls of the cell and this electrode.

The two ionisation currents are arranged to be opposed and pass through a common high resistance (ca.10^{10}ohms). Any voltage developed across the latter by current variations is transferred to an electrometer-amplifier (impedance converter), and thence to the recorder. Radioactive strontium has been used as the source of radiation.

The detector is extremely sensitive and calibration is virtually unnecessary. The cell itself is simple to construct, and is adaptable for use at high temperatures, but the auxiliary apparatus required is more elaborate and costly than for, say, the katharometer. Care is also necessary in handling the radioactive source.

(f) Surface Potential Detector.

The work of Phillips (G.)[31] indicated the possibility of using changes in surface potential for the detection of small vapour concentrations. The method has been applied to gas chromatography.

The detector comprises two metal plates, one of which is coated with a suitable surface film (e.g. stearic acid or octadecanol). One plate is made to vibrate close to the other setting up an A.C. signal in a resistance connecting the two plates. This signal is proportional to the difference in the potentials at the two surfaces (metal and surface film on metal) and is amplified and recorded. In practice, when nitrogen alone passes between the plates, the signal produced is biased out by a potentiometer, so that only the changes in surface potential difference, from passage of nitrogen plus adsorbable vapour between the plates, are recorded.

Very high sensitivity is obtained with polar vapours, and since the adsorbability of vapours increases with molecular weight, so also does the instrument sensitivity. The detector is therefore particularly suitable for very low concentrations of relatively non-volatile materials. The instrument is somewhat sluggish and non-linear in response, so that its use has been mainly limited to displacement analysis.

Other Differential Detectors.

Gas interferometers[32,33] have been used in the field of gas-adsorption chromatography. Adsorption separations of krypton and xenon, produced as atomic fission

products, have been followed by measurements of radioactivity[34]. Griffiths[35] has investigated flow-impedance methods and carried out measurements on the specific heat of the effluent gas, the latent heat of vapour adsorption and on changes in the dielectric constant of the column during the chromatographic process.

2.2.3. Integral Detectors.

Detectors of this type which have been used include:-

(a) Automatic Recording Burette.
(b) Nitrometer.

These will now be discussed separately.

(a) Automatic Recording Burette.

The development of this detector was carried out by James and Martin[3] for the automatic analysis of volatile acids and bases in the first gas-liquid partition chromatography experiments.

The effluent gas from the column is bubbled up through a titration cell containing a suitable indicator. Phenol red is used for fatty acids and methyl red for volatile bases. The pH of the solution in the cell is altered by the acidic or basic vapours passing through and the indicator colour changes. This change is picked up by a photoelectric control circuit which then operates a burette and drives a recording pen across a revolving chart. Standard acid or alkali is added from the burette until the colour, and hence the pH, of the original solution is attained.

(b) Nitrometer.

The nitrometer was developed for gas chromatography

by Janak[36]. This integral detecting system is based on measurement of volume of the component over a concentrated potassium hydroxide solution in which the carrier gas, carbon dioxide, is absorbed. The increase of volume over the potassium hydroxide level, caused by the gaseous fraction, disturbs a set pressure system. The pressure change causes the movement of an equalizing liquid in a manometer. This switches on a motor which sets the recording mechanism in motion.

The detector can only be used with vapours which do not condense and which are unattacked by alkali. The method is therefore unsuitable for acid vapours and certain halogenated hydrocarbons which are prone to hydrolysis.

2.3. Apparatus.

The gas chromatography apparatus constructed was based on a design by Bradford[17] et al. (I.C.I., Billingham).

2.3.1. Essential Features.

1) Chromatographic Column.	:-	U-tube columns, 6 ft. in length.
2) Mobile Phase.	:-	Nitrogen.
3) Stationary Phases.	:-	Dinonyl phthalate, Apiezon L stopcock grease.
4) Inert Support.	:-	Kieselguhr (Celite 535).
5) Vapour Detection.	:-	Thermal conductivity.
6) Flow Measurement.	:-	Rotameter.
7) Introduction of Samples.	:-	Micropipette method.
8) Recorder.	:-	Honeywell-Brown (2.5m.v. full scale deflection).
9) Temperature Control.	:-	Electrically heated air jacket.

2.3.2. General Description.

The complete gas circuit is shown in Fig.1. Oxygen-free nitrogen from a cylinder is controlled first, by a reducing valve on the cylinder, and then by a fine pressure control device in the gas circuit. The nitrogen passes through two drying tubes containing silica gel, and then through a rotameter for flow rate measurement. An $\frac{1}{8}$ inch needle valve is used for flow rate control, and a mercury manometer records the inlet nitrogen pressure to the chromatographic column. The gas now passes through the reference cell of the thermal conductivity detector and into the U-tube column, which is maintained at the appropriate temperature by an electrically heated air jacket. The sample is introduced at the column entry and carried in the nitrogen stream through the column, the effluent gas then flowing through the analysis cell of the katharometer. The reduced outlet pressure is measured by a mercury barometer, and controlled by a second needle valve, on either side of which is a buffer vessel to maintain constant pressure. The gas finally passes through a trap which removes condensible compounds from the stream before it passes to atmosphere through the vacuum pump.

The apparatus will now be described in more detail.

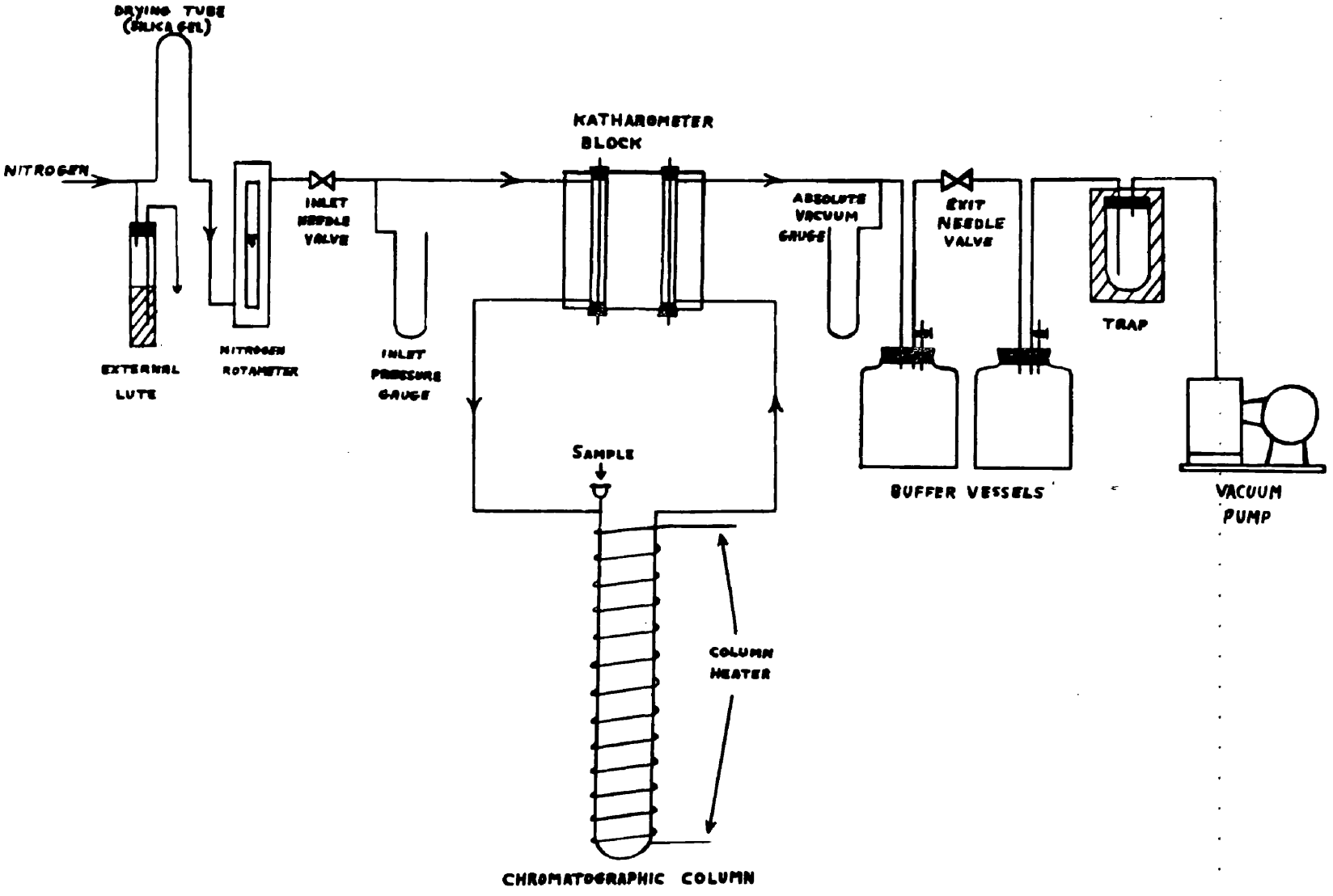


FIG. 1 GAS CIRCUIT

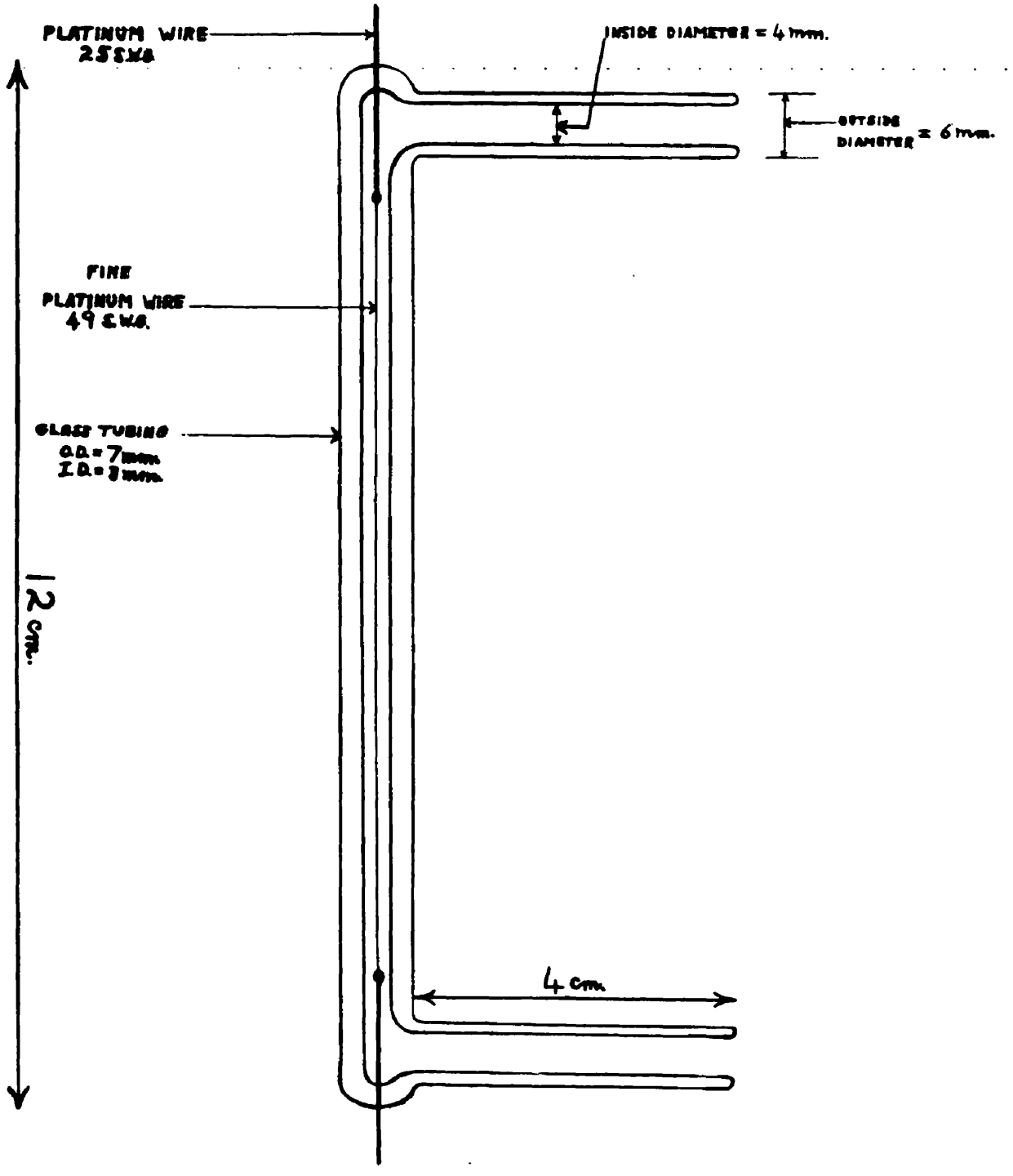
2.3.3. Katharometer.

Two thermal conductivity cells were used in the detector circuit. Fig.2 illustrates the type of cell employed. The two grades of platinum wire were connected by inserting the fine wire (49 s.w.g.) into a small hole drilled in the end of the heavier wire (25 s.w.g.) and "nipping" the two together with a small clamp.

Pyrex glass was used in the construction of the cells. Theoretically, platinum sealed into soda glass gives a more gas tight connection, since the respective coefficients of expansion are closer than those of pyrex and platinum. However, it was desired that the cells be temperature resistant, and, in practice, a pyrex/platinum seal could be made which was sufficiently gas tight.

A possible weakness exists at the junction of the heavy and fine wires. This is caused when the two wires are "nipped" together, since the sharp edge of the hole drilled in the 25 gauge platinum partially cuts into the fine wire. This is overcome if the edge of the hole is reamed using a slightly larger drill, before connection is made.

A simpler method of connection, which was latterly used, was to bend the heavier wire into a loop, round which several turns of the fine wire were wound. A pressure weld was then made by squeezing the loop tightly.



KATHAROMETER CELL (FIG. 2)

Soldering as a means of connection may be inadvisable because of possible corrosion of the solder by the gases passing through the cell.

The cell dimensions are shown in the diagram. The fine platinum wire is 8.25cm. in length and has a resistance of approximately 25 ohms.

2.3.3.1. Katharometer Block.

This is illustrated in Fig.3. The brass block can be split into halves to allow insertion of the thermal conductivity cells. Connected to each half is a heating element wound on a mica sheet. This is covered on either side by mica sheets of the same size for insulation and the whole is held against the block by a $5\frac{1}{4}$" x $3\frac{1}{4}$" x $\frac{1}{4}$" brass plate.

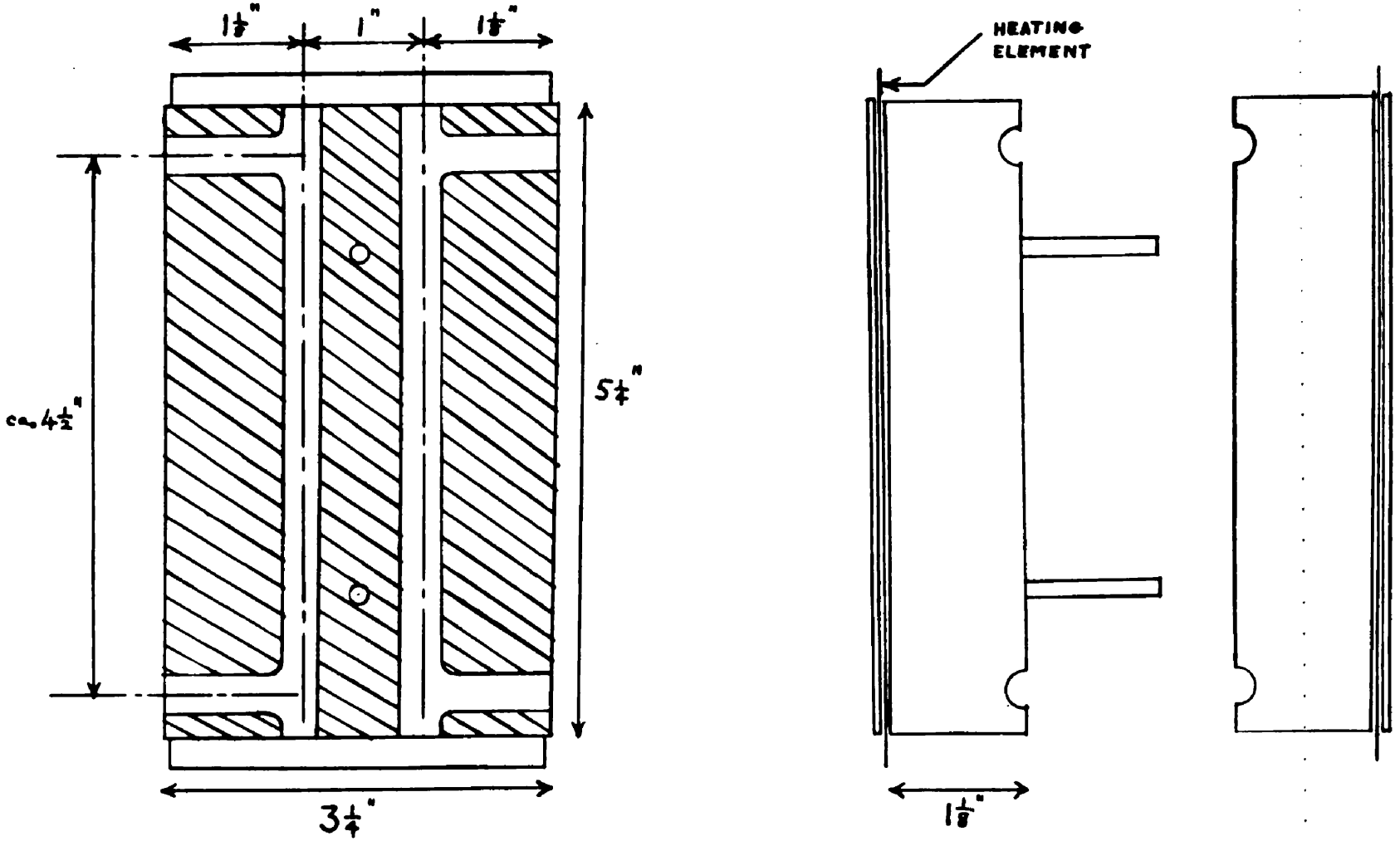
The entire block is encased in Syndanyo for insulation.

2.3.3.2. Katharometer Circuit.

The two thermal conductivity cells constitute two arms of a Wheatstone Bridge arrangement, the remainder of the circuit being made up by the bridge box.

Fig.4 shows the electrical arrangement within the box alone. Fig.5 includes the katharometer and recorder in the circuit, which is drawn as a bridge, and also indicates the connections from the katharometer cells and recorder to the terminals on the box.

KATHAROMETER BLOCK (FIG.3)



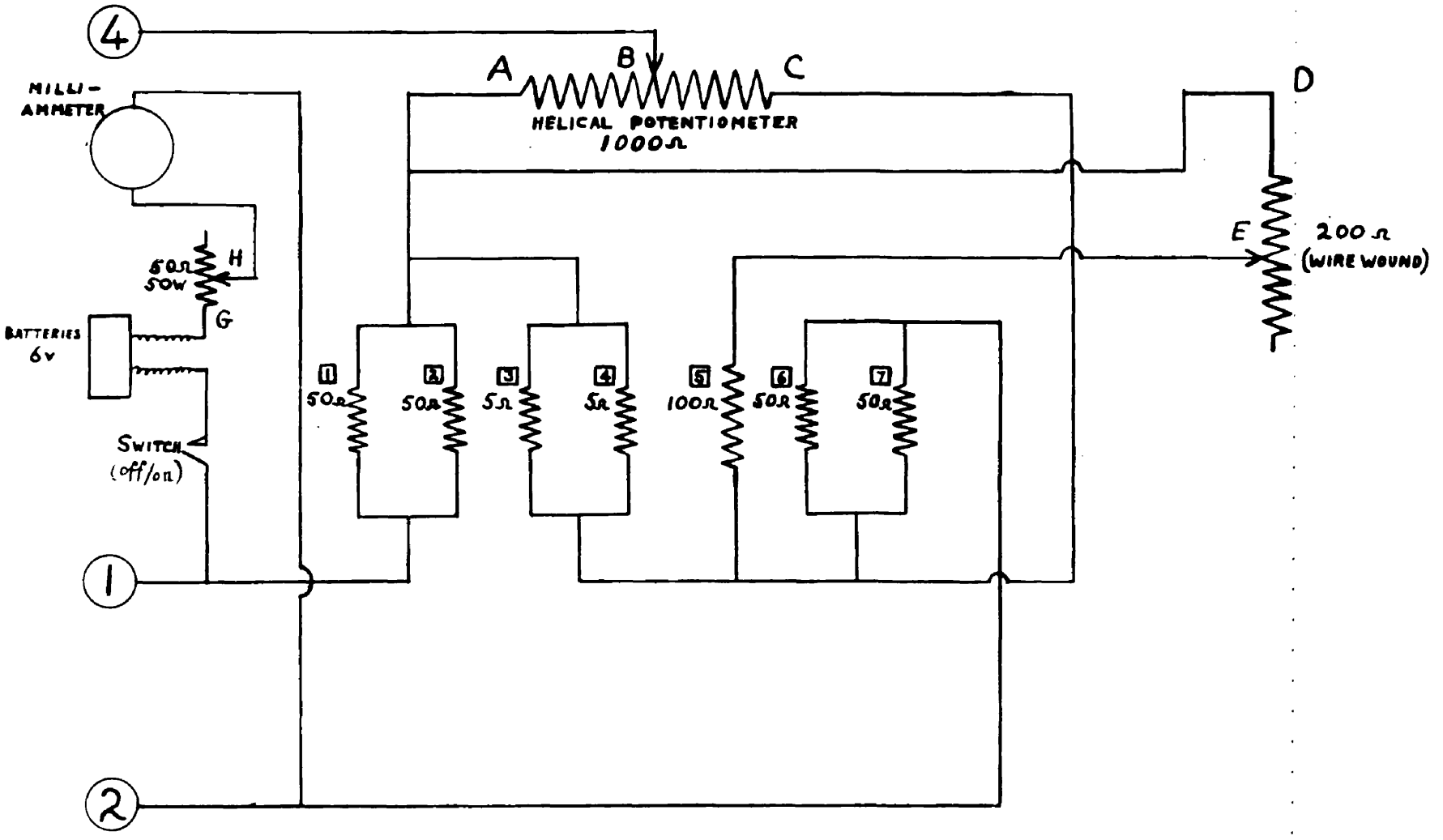

4
MILLI-
AMMETER
A
B
C
HELICAL POTENTIOMETER
1000Ω
D
E
200Ω
(WIRE WOUND)
50Ω
50W
H
G
BATTERIES
6v
SWITCH
(off/on)
1
50Ω
2
50Ω
3
5Ω
4
5Ω
5
100Ω
6
50Ω
7
50Ω
1
2

FIG. 4

KATHAROMETER BRIDGE CIRCUIT

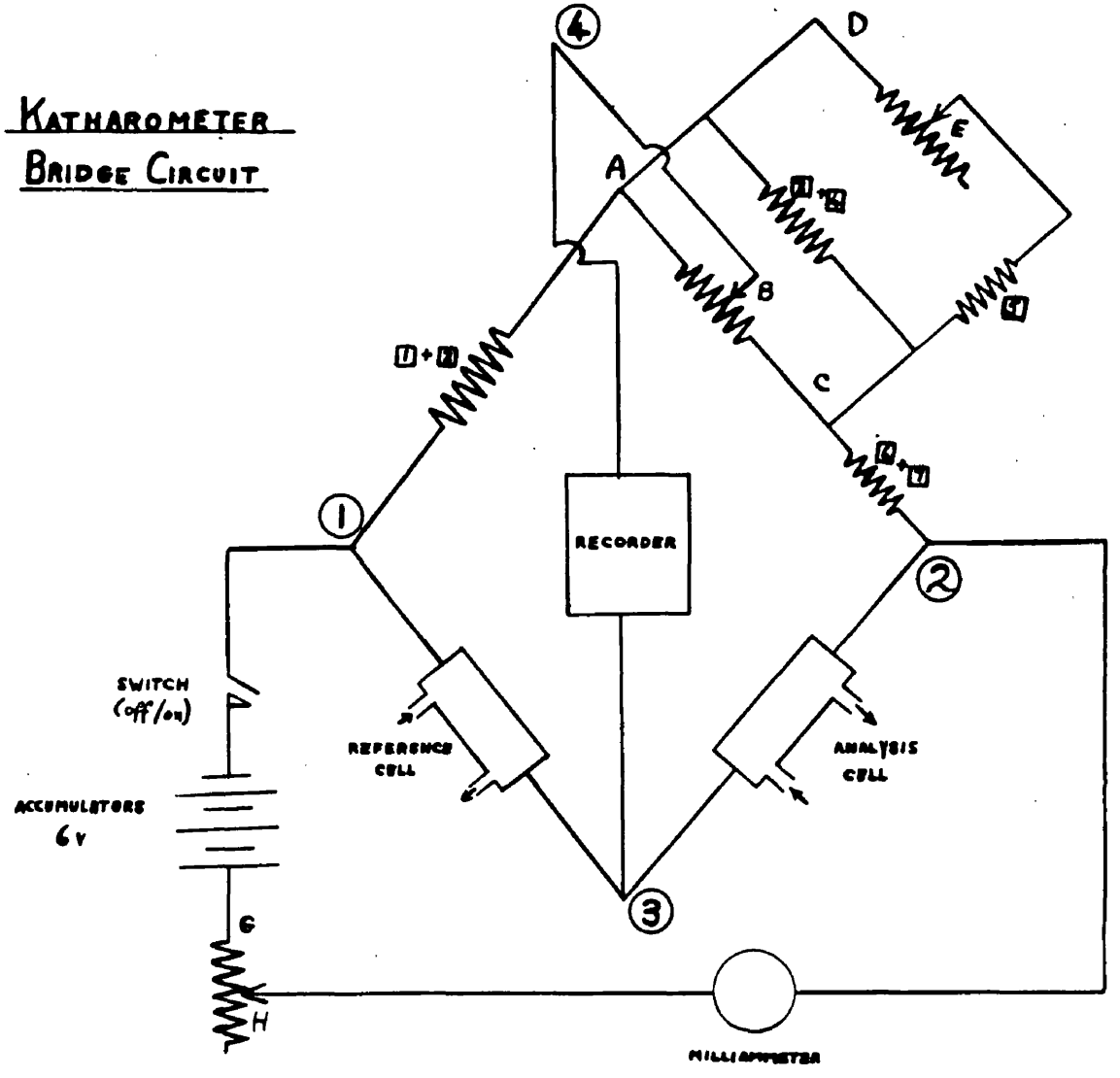


FIG. 5

Current to the bridge was supplied by a 6 volt accumulator, and the out-of-balance e.m.f. was measured on a Honeywell-Brown high speed potentiometric recorder with a 2.5 m.v. full scale deflection.

2.3.4. Chromatographic Column.

A U-tube column was used, 6 ft. in length and 4mm. internal diameter. If an "Agla" micrometer syringe is to be used for introduction of sample, the inlet end of the U-tube is enlarge to accommodate a rubber diaphragm through which injection is made, while at the base of the enlargement, a 4mm. internal diameter side-arm is attached through which carrier gas enters the tube. If introduction of samplo is effected by micropipette no enlargement is necessary and the gas circuit is broken while the sample is applied to the column.

The U-tube was housed within a pyrex glass tube of 2 inches diameter on which was wound the column heater; this, in turn, was contained in a 3 inch diameter pyrex glass jacket and the whole was well lagged to conserve heat. The heater consisted of 45 feet of 30 s.w.g. nichrome wire wound evenly on the inner tube and connected to a regulated supply of 240 v.

Connection from the outlet of the U-tube to the analysis cell of the katharometer was made by a short length of stainless steel capillary tubing 0.06 inch outside diameter and 0.03 inch internal diameter.

2.3.5. Column Packing and Stationary Phase.

Kieselguhr (Celite 535) was used as the inert supporting material for the stationary liquid phase. Pretreatment of the Celite consisted simply of oven-drying at 140°C under vacuum for 4 hours, no size-grading or acid-washing processes being carried out.

Thorough mixing of the Celite and liquid phase, in the proportion 3 gm. fixed phase to 7 gm. kieselguhr, was carried out until no globules of liquid remained visible in the packing. In the case of a highly viscous liquid phase like Apiezon L stopcock grease, or if the liquid phase is a solid, a satisfactory technique was to dissolve the phase in an appropriate solvent, which was preferably very low boiling, form this into a slurry with the Celite, and allow the solvent to evaporate with continuous stirring. Final traces of solvent were then removed under vacuum at a convenient temperature.

The mixture was poured into the column using a small funnel. Small quantities at a time were added to each limb of the U-tube alternately, and the column was vibrated by holding it against the shaft of an electric motor, the shaft having a flat machined on it. The packing was conveniently shaken down in this way, being further assisted

by gentle pressure from a close-fitting solid glass rod. Consequently gaps in the packing and "channelling" with resulting loss in efficiency were avoided. Small plugs of "Fibreglass" were pushed down on to the packing in both limbs.

The inlet limb of the U-tube was longer than the outlet, which was filled to the top with packing. The inlet limb was filled to the same level and this allowed part of the tube to project above the heated zone and facilitated the introduction of the sample, when the nitrogen supply was cut off.

2.3.6. Introduction of Samples.

The "Agla" Micrometer Syringe with which the sample may be injected on to the column through a serum bottle cap, has been widely used. It delivers an exact quantity of sample and would appear to be ideal for quantitative work. It has, however, a number of disadvantages:-

1) When working at very low outlet pressures there is the possibility that more than the requisite quantity of sample would be drawn into the column.

2) It is unsuitable for the introduction of solid samples, unless these are made up in a appropriate solvent. Where only small quantities of such samples are available, this is inconvenient.

3) The needle of the syringe should be touched against the top of the column, or against a small pad of glass wool placed at the column inlet, so that the whole of the sample is brought on to the column as rapidly as possible. Consequently more careful technique is required with the small syringe needle than is necessary with the larger contact area of the micropipette.

4) With high inlet pressures the serum bottle cap will begin to leak. If this is replaced by the more robust modification in which a piece of rubber is compressed by a butt-joint, more construction refinements have to be made at the entry of the U-tube column.

The Micropipette is preferred to the micrometer syringe and consists of approximately 1 ft. length of 2mm.

bore glass tubing, to the end of which is joined a short length of capillary tubing. After dipping into a solution, the pipette empties as far as the capillary, the remaining liquid being drained by touching the end of the tube on to the Fibreglass plug at the top of the Celite packing. Since the top of the packing is under full column temperature, volatilisation is immediate. To achieve the same speed of volatilisation with a micrometer syringe, a flash heater would be necessary. Also, there is no residual solution in the pipette to be drawn into the column. Micropipettes with different lengths of capillary can be used for the introduction of different amounts of sample, and for quantitative work, the pipettes can be calibrated.

The chromatographic column used with the micropipette method of sample introduction is simply a U-tube of the appropriate length and internal diameter. With the injection method, construction refinements are necessary at the U-tube entry.

2.3.7. Flow Control and Measurement.

The flow control device is illustrated in Fig.6 and provides a constant pressure at the column inlet. Any excess pressure depresses the mercury level and the gas escapes to atmosphere. The pressure at which this occurs can be varied by adjusting the level of the mercury reservoir.

Gas flow rate was measured by a rotameter situated at the column inlet and calibrated 0-25 ml/minute.

Additional flow control was given by two $\frac{1}{8}$ inch needle valves.

Buffer vessels of approximately 2 litres capacity ensured a constant reduced outlet pressure by accommodating any small fluctuations.

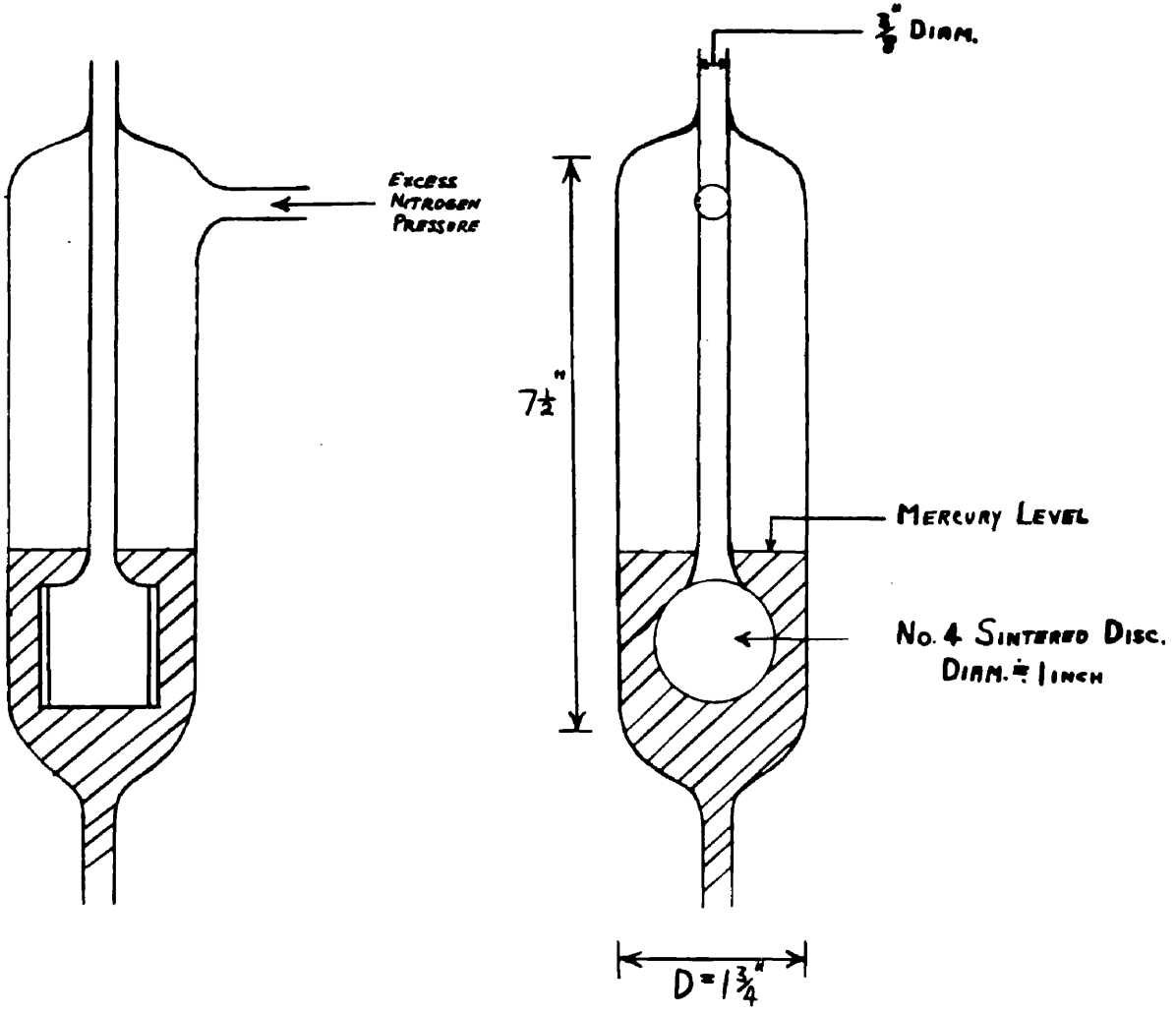


FIG. 6 EXTERNAL LUTE

2.3.8. Summary of General Technique.

In the apparatus described (Fig.1) a small sample of the mixture under examination (0.5-10 microlitres) is introduced into a stream of nitrogen where it is immediately vapourised by heat. The mixture is then carried through a chromatographic tube packed with a suitable support and liquid phase: provided the column is long enough, the various constituents emerge separately. They are then carried by the nitrogen stream through the analysis cell of a katharometer, the reference cell of which carries the inlet nitrogen stream to the chromatographic tube. The output from the katharometer circuit is fed to an electronic potentiometric recorder. The record obtained consists of a series of peaks rising from a base line corresponding to 100 per cent nitrogen in both the analysis cell and reference cell of the katharometer (Fig.2). For particular conditions of pressure, temperature, flow rate, etc. the retention time (effectively the time interval between the introduction of the sample and the occurrence of the appropriate peak on the record) enables the particular constituent to be identified.

2.4. Experimental Work.

2.4.1. Operation of the Apparatus.

The heating of the column to the required temperature must be gradual, otherwise there is danger of the hot wire spirals cutting through the inner glass cylinder while it is still cold.

The pressure control device was set to give the desired inlet nitrogen pressure and the gas turned on. Oscillation of the mercury level was damped by means of a screw clip and the outlet pressure reduced by the vacuum pump. The outlet needle valve was set to give the required reduced pressure and the inlet valve similarly adjusted to give a suitable flow rate of nitrogen. A short time was allowed for stabilisation of the gas circuit and then the detecting circuit was switched on. The bridge box controls were adjusted to give a current supply of 160 m.a. to the bridge and to bring the needle on scale.

2.4.2. Preliminary Low Temperature Work on Known Compounds.

In preliminary work low boiling compounds (b.p. $\leq$ 100°C) were introduced to the column at a temperature of approximately 100°C. The heater on the katharometer block was not required since there was little possibility that these compounds would condense in the thermal conductivity cells.

The retention times of methanol (2.5 min.), benzene (12.0 min.), and methyl ethyl ketone (8 min.) were found under typical experimental conditions:-

Column Temperature	(Tc) = 104°C
Inlet Nitrogen Pressure	(P1) = 1.2cm.Hg.(+ atmospheric).
Outlet Nitrogen Pressure	(P2) = 20.4cm. Hg.
Flow Rate	(F.R.)-15.0ml./min. at S.T.P.
Bridge Current	(I.) = 160 m.a.
Liquid Phase	:- "Dinonyl" phthalate.

Each elution trace showed a negative peak which appeared shortly after the sample introduction. This was caused by air which entered the column when the gas circuit was "broken" while applying the sample; it proved useful in subsequent work for measuring the "dead space" of the column (gas volume between point of sample introduction and detector).

The base line at this stage was rather erratic, causing some error in the measurement of peak heights.

The retention times for methanol, methyl ethyl ketone and benzene on the dinonyl phthalate column indicated that a mixture of the three compounds would be completely

resolved and that such a mixture was therefore suitable for quantitative analysis to determine the accuracy obtainable with the apparatus. Estimation of methanol in a synthetic mixture of the above compounds was carried out by the "Internal Standard Technique".

Procedure.

A "standard" solution of methanol (4 per cent), benzene (4 per cent), in methyl ethyl ketone (92 per cent) as carrier was made up. A sample was introduced by micropipette to the dinonyl phthalate column and a record obtained.

An "unknown" solution containing 8 per cent methanol in methyl ethyl ketone was then prepared. Benzene was chosen as the internal standard and sufficient quantity added such that the mixture then contained 8 per cent methanol, 4 per cent benzene in methyl ethyl ketone. A record was obtained for this solution under the same experimental conditions as before.

For the standard and "unknown" solutions the ratio $\frac{\text{height of methanol peak}}{\text{height of benzene peak}}$ was obtained.

$$\therefore \text{Percentage methanol in "unknown" solution.} = \frac{\text{Ratio of peak hts. for "unknown" solution}}{\text{Ratio of peak hts. for standard solution}} \times 4$$

Since the peak height is always referred to that of the internal standard, this method dispenses with the need to introduce exact sample quantities to the column.

Table I.

Ratio of Peak Hts. Standard Solution.	Ratio of Peak Hts. "Unknown" Solution.	Percentage Methanol by vol.		Error (per cent).
		Found	Present.	
1.35	2.36	7.0	8.0	12.5
1.31	2.55	7.78	8.0	2.75
1.50	2.7	7.2	8.0	10.0
1.58	2.8	7.1	8.0	11.3

Conclusions.

Table I. illustrates the considerable error in the analysis. The main reason for this was the uncertainty of the base line, which caused appreciable error in the measurement of peak heights. A variation of 5mm. in the base line can produce an error of 6-8 per cent in the value obtained for the constituent.

2.4.3. Modifications in Apparatus for High Temperature Work.

Since high boiling compounds are to be examined on the column, heating of the katharometer block will be necessary to prevent condensation of these compounds in the cells. Also, uniform heating of the block will probably eliminate any base line irregularity. The heater has been described (2.3.3.1.)

For high temperature work additional lagging will also be required on the connection from the U-tube outlet to the analysis cell of the katharometer. Since the stainless steel capillary tubing was connected to katharometer cell and U-tube through small rubber stoppers, this connection had to be altered so that it would be suitable for use at temperatures of approximately 250°C.

The modification used initially was a short length of stainless steel capillary tubing sealed at either end into B.7. stainless steel cones, which in turn were fitted into glass B.7. sockets at the column outlet and analysis cell inlet respectively, using silicone grease. It was difficult to make this connection completely vacuum tight, so a short length of glass capillary tubing, connected at either end with silicone rubber tubing was used.

2.4.4. High Temperature Work on Tar Acid Control Samples.

Nomenclature.

P_1 = Inlet nitrogen pressure to column (cm. of mercury).
= Manometer reading excluding barometric pressure.
P_2 = Column outlet pressure (cm. of mercury).
F.R.= Nitrogen flow rate (ml./min.)
R_T = Retention Time (min.)
T_C = Column Temperature (°C.)
T_B = Temperature of katharometer block (°C.)
I = Current supplied to thermal conductivity bridge (m.a.)
C.S.= Chart speed (inches per hour).

2.4.4.1. Determination of Optimum Working Conditions.

(a) Operating Temperatures and Nitrogen Pressure.

At a column temperature of 250°C great difficulty was found in maintaining a straight zero line on the recorder. This was due mainly to non-uniformity of temperature within the katharometer block, which was heated to 184°C. The introduction of a suitable resistance in series with one of the block heaters reduced the variation but did not eliminate it.

The object, at this stage, was to examine some 30 tar acids on the gas phase column to determine optimum conditions for satisfactory peak shapes and separation of mixtures, and to obtain retention times under standardised conditions.

Column efficiency is higher with the column outlet at atmospheric pressure rather than reduced pressure. Therefore, samples of phenol in acetone were introduced

to the column at

$P_1 = 35.5cm.$
$T_C = 240^oC.$
$T_B = 184^oC.$

without the use of vacuum. Broad, misshapen peaks were obtained except when the concentration of phenol was extremely low. This effect was even more pronounced with the cresols. Reduced pressure at the column outlet gave sharp, well-defined peaks for phenol, the cresols and the xylenols.

Table II shows retention times of certain tar acids obtained under different operating conditions. Apiezon L stopcock grease was now used as fixed phase because it was suitable for prolonged use at temperatures above 200°C. Reduced pressure was used in all cases as it was now considered necessary for satisfactory peak shape.

Table II.

Compound	R_T (min.)	P_1 (cm.)	P_2 (cm.)	T_C (°C.)	T_B (°C.)	Peak Ht. Inches
Phenol	6.0	34.5	18.5	204	194	
Phenol	5.5	30.6	8.2	204	194	
Phenol	3.7	30.4	7.6	233	233	0.5
Phenol	3.7	30.4	7.6	233	200	4.5
m-Cresol	10.5	34.0	19.6	204	194	
m-Cresol	10.3	34.0	19.6	204	194	
p-Cresol	10.2	32.0	18.5	204	194	
p-Cresol	10.2	32.0	18.5	204	194	
o-Cresol	8.6	32.0	19.3	204	194	
o-Cresol	8.3	32.0	19.3	204	194	
3:5-Xylenol	12.7	30.4	8.0	207	196	
3:5-Xylenol	13.2	30.2	8.0	206	196	
2:5-Xylenol	12.0	32.0	7.8	204	196	
2:5-Xylenol	12.0	31.0	8.0	204	196	
2:5-Xylenol	7.3	30.3	7.7	233	196	
2:5-Xylenol	7.4	30.3	7.6	233	196	
2:5-Xylenol	7.7	30.4	7.6	232	230	
2:5-Xylenol	7.6	30.4	7.6	232	230	

Stationary Phase:- Apiezon L grease
I = 160 m.a.
C.S. = 6 inches/hour

Conclusions.

From the table it was observed that temperature was the predominating factor influencing retention time. Changes in outlet and inlet pressure produce a change in the flow rate which consequently affects the retention time but not to the same extent as a temperature change.

Most of the compounds in Table II were separable from one another. Exceptions were m- and p-cresol. Although 2:5- and 3:5- xylenol differed by about 1 min. in retention time, the respective peaks were too broad to allow their resolution in a mixture. Resolution of these two compounds should be possible, however, under different experimental conditions.

The retention time was found to be unaffected by alteration in the temperature of the katharometer block.

For the same quantity of sample introduced to the column, the peak height decreased with increase in temperature of the katharometer block. This was in accordance with theory, since the thermal conductivities of all gases approach that of nitrogen as the temperature increases.

(b) Katharometer Sensitivity.

Although the sensitivity of katharometers decreases with temperature when using nitrogen as mobile phase, decrease in this case may also have been caused by increase in resistance of the katharometer wires with temperature. The standard resistances and the katharometer wires are all approximately 25ohms at room temperature, but at 230°C, although the standard resistances are still the same, the katharometer resistances have increased considerably. Therefore a smaller proportion of the 160 m.a. supplied is passing through the cell resistances than that passing through the smaller resistances in the bridge box. The temperature of the detection wire is therefore reduced.

Recommended bridge current for maximum sensitivity and minimum base line drift was 160 m.a. Although this is an optimum current at, say, 150°C, where decrease in sensitivity with temperature is not particularly pronounced, this may not be the case at 200°C or 230°C.

A series of experiments was carried out applying a constant volume of standard phenol solution to the column with different values of bridge current.

Operating conditions:- P_1 = 32.0cm. T_C = 230°C
P_2 = 9.1cm. T_B = 200°C

Increase in bridge current from 160-200 m.a. gave an increase in peak height. The sensitivity reached a maximum in the range 200-230 m.a. and the optimum current was established at 220 m.a.

This appeared to indicate that satisfactory sensitivity could be obtained with the katharometer block at the same temperature as the column, the bridge current then being increased until a new optimum value is found.

As the temperature of the block was increased from 200 to 236°C, the current fell from 220 m.a. to 215 m.a. The introduction of the same quantity of phenol/toluene solution gave a phenol signal of 0.04 full scale deflection, by comparison with a 0.4 f.s.d. when the block temperature was 200°C. Increasing the bridge current gave no improvement in sensitivity.

Conclusions.

Katharometer block temperatures higher than 200°C should be avoided and for increased sensitivity it would be desirable to work at temperatures lower than this value. Since the compounds under examination boil in the range 180-250°C, a block temperature of 200°C was used to prevent condensation in the katharometer cells, to which 220 m.a. current is supplied. The column temperature can be as high as is required to effect a suitable separation of tar acids. Independent heating of both block and

column has therefore proved an advantage in this respect.

Interim Optimum Conditions.

Optimum conditions at this stage were:-

Column Temperature	234°C
Katharometer Block Temperature	200°C
Inlet Nitrogen Pressure	30.0cm.of mercury
Outlet Nitrogen Pressure	6.3cm.
Flow Rate	12 ml./min.
Bridge Current	220 m.a.

The above katharometer block temperature and bridge current were employed as recommended (page 60).

An inlet nitrogen pressure of 30cm. was found suitable, while an outlet pressure of 6.3cm. improved the peak shape and sensitivity.

A column temperature of 234°C was necessary to obtain sharp, well-defined peaks but did not give satisfactory resolution (Table III). This temperature also appeared unnecessarily high compared to that generally employed in gas-liquid chromatography for the examination of compounds with boiling points of approximately 200°C.

Table III.

Stationary Phase:- Apiezon L stopcock grease.

Compound	R_T (min)	P_1 (cm.)	P_2 (cm.)	T_C (°C.)	T_B (°C.)	I (m.a.)	C.S. in/Hr
3:5-Xylenol	8.0	30.0	6.3	234	204	220	6
3:5-Xylenol	8.0	29.8	6.3	234	204	220	6
2:5-Xylenol	7.2	29.8	6.3	234	204	220	6
2:5-Xylenol	7.2	29.8	6.3	234	204	220	6
2:3-Xylenol	9.1	29.6	6.3	234	204	220	6
2:3-Xylenol	8.8	29.6	6.3	234	204	220	6

2.4.4.2. Use of Flash Heater to Improve Resolution.

A flash heater was now incorporated at the column entry. This served the purpose of "sharpening" broad, misshapen peaks. The column temperature could therefore be decreased making greater resolution possible.

The flash heater consisted of 14 turns of nichrome wire wound on a $\frac{3}{4}$ inch diameter glass former and totalling 30ohms. This was fed by a 38 volt transformer and was surrounded by a 3.5 inch length of 1 inch diameter pyrex glass tubing for draught exclusion.

It was found that with a flash heater temperature of 260°C and a column temperature of 210°C, the tar acids were eluted as rapidly as when a column temperature of 234°C was employed without the use of the flash heater. Satisfactory elution peaks were obtained at an operating temperature of 180°C and then the column temperature was decreased to 150°C with a flash heater temperature of 300°C. This column temperature appeared to be a lower limit for satisfactory peak shapes. The results obtained for phenol and the cresols at 150°C with a 4 ft. column are given in Table IV.

Table IV.

Stationary Phase:- Apiezon L.

Compound	R_T (min)	P_1 (cm.)	P_2 (cm.)	T_C (°C.)	T_B (°C.)	T_F (°C.)	I. (m.a.)	C.S. (in/Hr)
Phenol	7.9	32.7	7.9	150	147	310	220	6
Phenol	8.1	33.2	7.9	150	147	310	220	6
m-Cresol	15.2	33.0	8.0	150	147	310	220	6
m-Cresol	14.8	33.3	8.1	150	147	310	220	6
p-Cresol	14.0	33.3	8.1	150	147	311	220	6
p-Cresol	13.9	32.9	8.0	150	147	308	220	6
o-Cresol	11.6	32.7	8.0	150	147	308	220	6
o-Cresol	11.6	32.7	8.0	150	147	307	220	6

T_F = Flash Heater Temperature.

A sample of 2:4-xylenol introduced to the column under the same conditions as above resulted in a rather broad peak with an approximate retention time of 27 min. The flash heater temperature was therefore increased and under the conditions:-

P_1 = 33.8cm. T_C = 154°C T_F = 333°C
P_2 = 7.7cm. T_B = 146°C I = 200 m.a.

2:4-xylenol gave a retention time of 24.8 min. The peak was sharper but not sufficiently satisfactory. Since the flash heater temperature was now as high as was practicable, the column temperature had to be raised to give a satisfactory peak shape. A column temperature of 180°C was found to give satisfactory elution peaks for all the xylenols.

Effect of Slight Variations in Operating Conditions.

Some results for 2:4-xylenol under slightly varying conditions are shown in Table V.

Table V.

4 ft. column; Apiezon L.

	Compound	R_T (min)	P_1 (cm.)	P_2 (cm.)	T_C (°C.)	T_B (°C.)	T_F (°C.)	I. (m.a.)	C.S. (in/Hr
1	2:4-Xylenol	16.0	33.8	8.0	174	168	336	200	6
2	2:4-Xylenol	14.5	31.3	8.0	176	169	340	200	6
3	2:4-Xylenol	14.5	30.8	7.7	178	169	336	200	6
4	2:4-Xylenol	12.9	33.8	8.0	182	170	340	200	6
5	2:4-Xylenol	13.0	36.2	8.1	182	170	337	200	6

Mean Flow Rate = 21 ml./min.

Conclusions.

Cases (1) and (4) illustrate the expected decrease in retention time with increase in column temperature.

A fall in the inlet pressure would be expected to give an increase in retention time, but in cases (1) and (2) the increase in column temperature has more than offset this change and has produced a decreased retention time.

Cases (4) and (5) give retention times of reasonable agreement for the same column temperature in spite of the difference in inlet pressure.

Therefore, while it is desirable to maintain the inlet pressure constant, small differences do not affect the retention time as much as small changes in column temperature. Therefore for reproducibility the column temperature must be maintained exactly constant.

Base line drift is a noticeable result of any change in either the inlet or outlet pressure.

Further Improvements in Sensitivity.

A katharometer block temperature of 150°C can be employed for the examination of the lower boiling tar acids like phenol and the cresols. At this block temperature an increase in bridge current beyond 160 m.a. gives a more marked improvement in sensitivity than that obtained at a block temperature of 204°C (Table VI).

Table VI.

Compound	Concⁿ. in Toluene	P_1 (cm.)	P_2 (cm.)	T_C (°C.)	T_B (°C.)	T_F (°C.)	I. (m.a)	C.S. (in/Hr.)	Peak Ht f.s.d.
Phenol	5 per cent	33.4	7.8	150	148	330	160	6	0.04
Phenol	5 per cent	33.4	7.8	150	148	330	200	6	0.11
Phenol	2 per cent	33.4	7.8	150	148	330	200	6	0.04.

For the same sample quantity of the 5 per cent solution, the peak height was almost trebled by increase in bridge current from 160 to 200 m.a. The same response was given for the 2 per cent solution with 200 m.a. as that given for the 5 per cent solution with 160 m.a.

2.4.4.3. Retention Time Data for Tar Acid Control Samples.

Tests were carried out to determine the resolution possible of the available tar acids using the present apparatus. The operating conditions employed were based on the preliminary work just described (pages 55 to 65).

Solid samples were introduced to the column in toluene solution.

Table VII.

Compound	b.p. (°C.)	Retention Time (min.)
Toluene	111	1.9
Phenol	181.8	5.9
o-Cresol	191.0	8.0
p-Cresol	201.9	9.7
m-Cresol	202.2	9.6
2:6-Xylenol	203	9.9
2:5-Xylenol	210	12.2
2:4-Xylenol	210	12.3
2:3-Xylenol	218	14.2
3:5-Xylenol	221.5	14.0
3:4-Xylenol	227	14.5
3-Ethylphenol	218	14.7
2-Methyl-4-ethylphenol	225.5	19.5
2-Methyl-3-ethylphenol	227	19.6
3-isoPropylphenol	228	19.0
2-Methyl-5-ethylphenol	228	18.5
4-isoPropylphenol	229	18.2
3-n-Propylphenol	230.3	22.3
4-n-Propylphenol	232.6	22.6
3-Methyl-5-ethylphenol	235.5	20.7
2:3:5-Trimethylphenol	236	21.7
2-Methyl-5-isopropylphenol	-	24.3
4-Methyl-3-ethylphenol	ca.240	23.8
3-Methyl-4-ethylphenol	240	26.1

Table VII (Contd.)

Compound	b.p. (°C.)	Retention Time (min.)
4-Indanol	244	30.2
3:5-Diethylphenol	248-249	29.8
4-n-Butylphenol	248	31.2
2-Methyl-4-indanol	ca.250	35.5
1-Methyl-4-indanol	ca.250	35.8
5-Methyl-4-indanol	ca.250	36.2
6-Methyl-4-indanol	ca.250	44.7

Operating Conditions:-

Inlet Nitrogen Pressure	32.0cm.Hg.
Outlet Nitrogen Pressure	8.0cm.
Column Temperature	180 ± 2°C
Katharometer Block Temperature	168 ± 3°C
Flash Heater Temperature	320 ± 5°C
Bridge Current	185 m.a.
Nitrogen Flow Rate	21 ml/min.
Column Length	4 ft.
Stationary Phase	Apiezon L.

Table VIII.

Compound	b.p. (°C.)	RT (Main Peak)	RT (Impurities)
3-Ethylphenol	218	7.3	-
2-Methyl-4-ethylphenol	225.5	8.8	4.4
2-Methyl-3-ethylphenol	227	9.1	2.9
3-*iso*Propylphenol	228	8.7	5.2; 7.1
2-Methyl-5-ethylphenol	228	8.7	3
4-*iso*Propylphenol	229	8.5	
3-*n*-Propylphenol	230-232	10.0	4.1; 5.3; 17.7; 18.7
4-*n*-Propylphenol	232.6	10.2	3.6; 23.0; 28.4.
3-Methyl-5-ethylphenol	235.5	10.3	
2:3:5-Trimethylphenol	236	10.7	
2-Methyl-5-*iso*-propylphenol	-	11.1	
4-Methyl-3-ethylphenol	240	11.3	
3-Methyl-4-ethylphenol	240	11.8	4.2; 5.2
4-Indanol	244	14.4	
3:5-Diethylphenol	248	14.0	
3:4:5-Trimethylphenol	248-249	14.1	
4-*n*-Butylphenol	248	15.0	
2-Methyl-4-indanol	ca.250	15.3	
1-Methyl-4-indanol	ca.250	16.4	
5-Methyl-4-indanol	ca.250	16.6	
6-Methyl-4-indanol	ca.250	21.0	

Operating Conditions:-

Inlet Nitrogen Pressure	32 cm.of Hg.
Outlet Nitrogen Pressure	8.0cm.
Column Temperature	210 ± 2°C
Katharometer Block Temperature	168 ± 3°C
Flash Heater Temperature	320 ± 5°C
Bridge Current	185 m.a.
Nitrogen Flow Rate	21 ml/min.

Accuracy and Reproducibility of Results.

Since it was only possible to maintain the operating temperatures within certain limits, the consistency of results obtained for a series of runs on a single component was ± 1.5 per cent. It was also found that the retention times varied from day to day by ± 5 per cent. This was partly caused by the inconsistent operating conditions, but a variation has been experienced by other workers who now obtain reproducible figures by using relative retention volumes rather than absolute values. Using toluene as reference compound, relative retention times were consistent to ± 2 per cent.

Peak Shape and Resolution.

Peak heights and shapes varied with the operating conditions. The higher the column temperature, the sharper and better defined were the peaks produced. Compounds with boiling points only slightly above the column temperature gave better peak shapes than those with higher boiling points. An increase in column temperature for a group of compounds gives a decrease in retention times and consequently a decrease in resolution. For 3-methyl-4-ethylphenol and 3-ethylphenol, which differ in boiling point by 22°C, the difference in retention time at 180°C was 11.4 min., decreasing to 4.8 min. at 210°C and 4.1 min. at 220°C (Tables VII, VIII and IX).

If the column temperature is too low, broad misshapen peaks are produced, making retention time measurements inaccurate. Also resolution is not necessarily improved by decrease in temperature since the broader component peaks of a mixture may overlap. If the column temperature is too high, the difference in retention times will be too small to give satisfactory resolution.

Conclusions.

1) In Table VII, peak shapes were well defined for retention times less than 15 min.(b.p.= approx.220°C). Above this value peak shapes began to deteriorate, this deterioration increasing with the boiling point of the components, making retention time measurements very difficult.

2) In Table VIII, satisfactory peaks were obtained in all cases.

3) Trace impurities in several of the liquid samples were not all detected at 180°C, but were clearly discernible at 210°C.

4) In Tables VII and VIII resolution was possible of only certain groups of compounds. Greater separation of components should have been possible and it is probably the limitations of this apparatus which have prevented this being attained.

Further Variation of Operating Conditions.

An operating temperature of 210°C was more satisfactory than 180°C for the majority of the tar acids, but only certain groups of compounds could be resolved. Table IX represents tests carried out to determine whether better separations might be achieved by further variation of the operating conditions. Compounds representing those in Table VIII were introduced to the column under different operating conditions. The given retention times are mean values from two runs on each compound.

Table IX.

Run No.	Compound	R_T (min.)	T_C (°C.)	T_B (°C.)	T_F (°C.)	P_1 (cm.)	P_2 (cm.)
1	3-Ethylphenol	8.7	200	165	305	32.1	8.0
	3-Methyl-4-ethylphenol	15.1					
	4-Butylphenol	19.8					
2	3-Ethylphenol	10.4	200	168	312	13.5	8.0
	3-Methyl-4-ethylphenol	18.0					
	4-Butyphenol	25.8					
3	3-Ethylphenol	6.5	220	166	310	31.8	8.0
	3-Methyl-4-ethylphenol	10.6					
	4-Butylphenol	13.7					
4	3-Ethylphenol	6.9	220	167	318	13.2	8.0
	3-Methyl-4-ethylphenol	11.3					
	4-Butylphenol	14.7					
5	3-Ethylphenol	7.2	210	167	310	31.9	8.0
	3-Methyl-4-ethylphenol	12.0					
	4-Butylphenol	15.2					

The retention times in Runs 1 and 2 appear to indicate good resolution of the three components. The peak shape for each compound, however, was so broad that a mixture of the three compounds would be unresolved under either set of conditions, and would produce instead one single broad peak over a range of approximately 15 minutes.

Run 5 gives the results obtained under the same conditions as Table VIII.

The only advantage in using a higher temperature (Runs 3 and 4) is to improve the peak shapes. Retention times are decreased and resolution is poorer.

Summary.

For phenol, the cresols and the xylenols, 180°C is a satisfactory operating temperature. For the remaining tar acids, 210°C combines good peak shapes with the maximum resolution possible with the present apparatus, unless longer columns are used. For all the tar acids, an inlet pressure of 32.0cm. and outlet pressure of 8.0cm. producing a flow rate of 21 ml./min. is satisfactory. A flash heater temperature of 320°C is necessary in all cases and a katharometer block temperature of 168°C is sufficient to prevent condensation of components. A bridge current of 185 m.a. gives suitable detector sensitivity.

2.4.4.4. Separation of Mixtures.

The following mixtures were introduced to the chromatographic column at an operating temperature of 180°C.

(a) o-, m-, and p-Cresols in toluene.
(b) Phenol, m-cresol, 3:5-xylenol in toluene.
(c) The six xylenols.
(d) A low-boiling coal tar xylenol fraction (209-219.5°C.)
(e) A high-boiling coal tar xylenol fraction (220-236.1°C.)

Results and Conclusions.

From (a) it was observed that m- and p-cresol were separable from o-cresol but not from each other.

Mixture (b) was resolved completely (Fig.7).

Three peaks were produced by mixture (c):-

Peak 1	..	2:6-xylenol
Peak 2	..	2:5-xylenol
		2:4-xylenol
Peak 3	..	3:5-xylenol
		2:3-xylenol
		3:4-xylenol

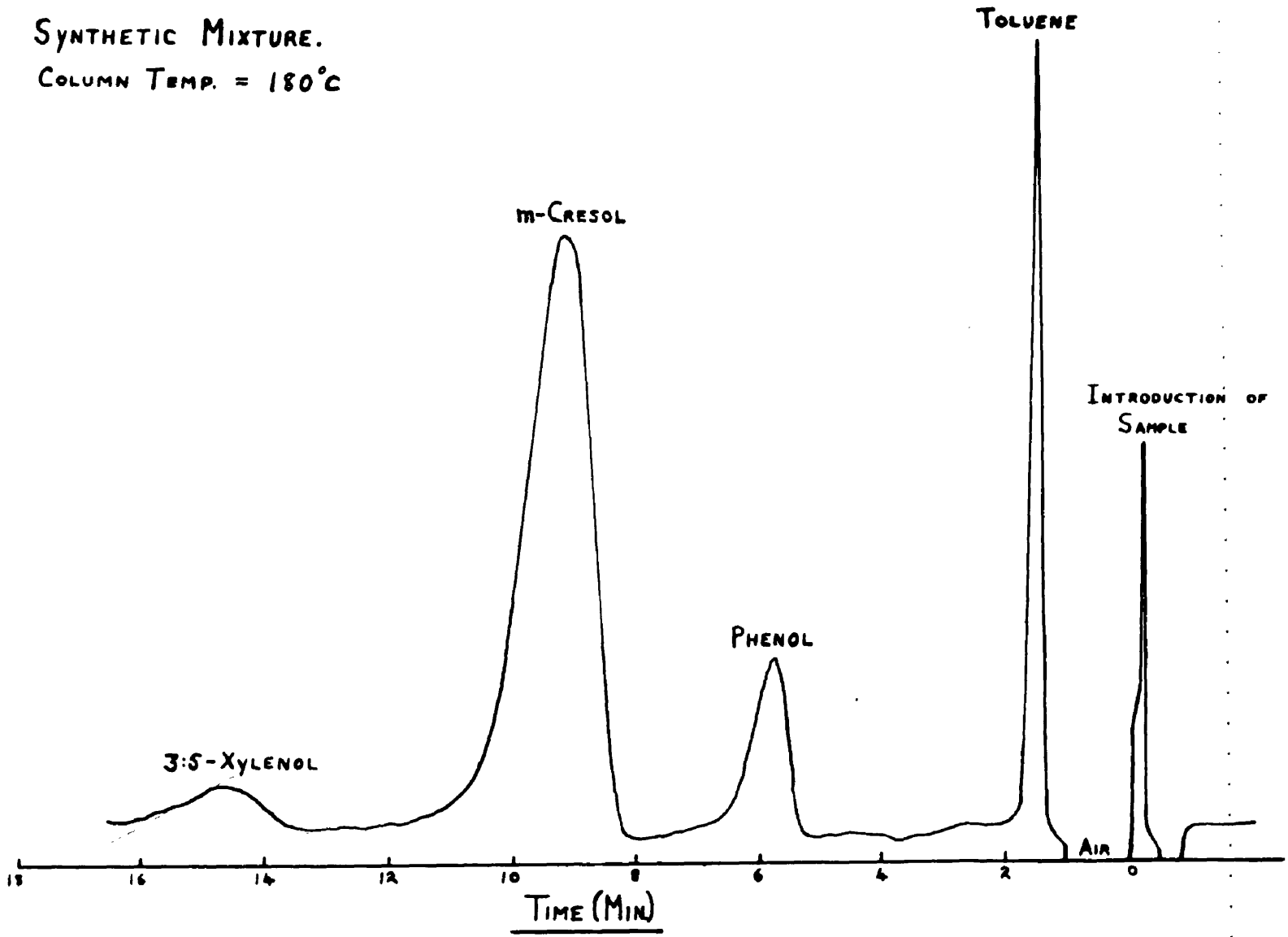
The compounds 2:4- and 2:5-xylenol have the same boiling point (210°C.) and the same chemical characteristics. Therefore their lack of resolution is expected.

The components 2:3-xylenol (b.p.218°C.), 3:5-xylenol (b.p.221.5°C.) and 3:4-xylenol (b.p.227°C.) should be capable of resolution and it must therefore be the limitations of this apparatus which have prevented their separation.

FIG. 7

SYNTHETIC MIXTURE.

COLUMN TEMP. = 180°C



Chromatograms of the two coal tar fractions were obtained at a column temperature of 180°C.

For the low boiling fraction three peaks were obtained but complete separation did not take place (Fig.8).

The high boiling fraction produced five peaks and again separation was incomplete (Fig.9).

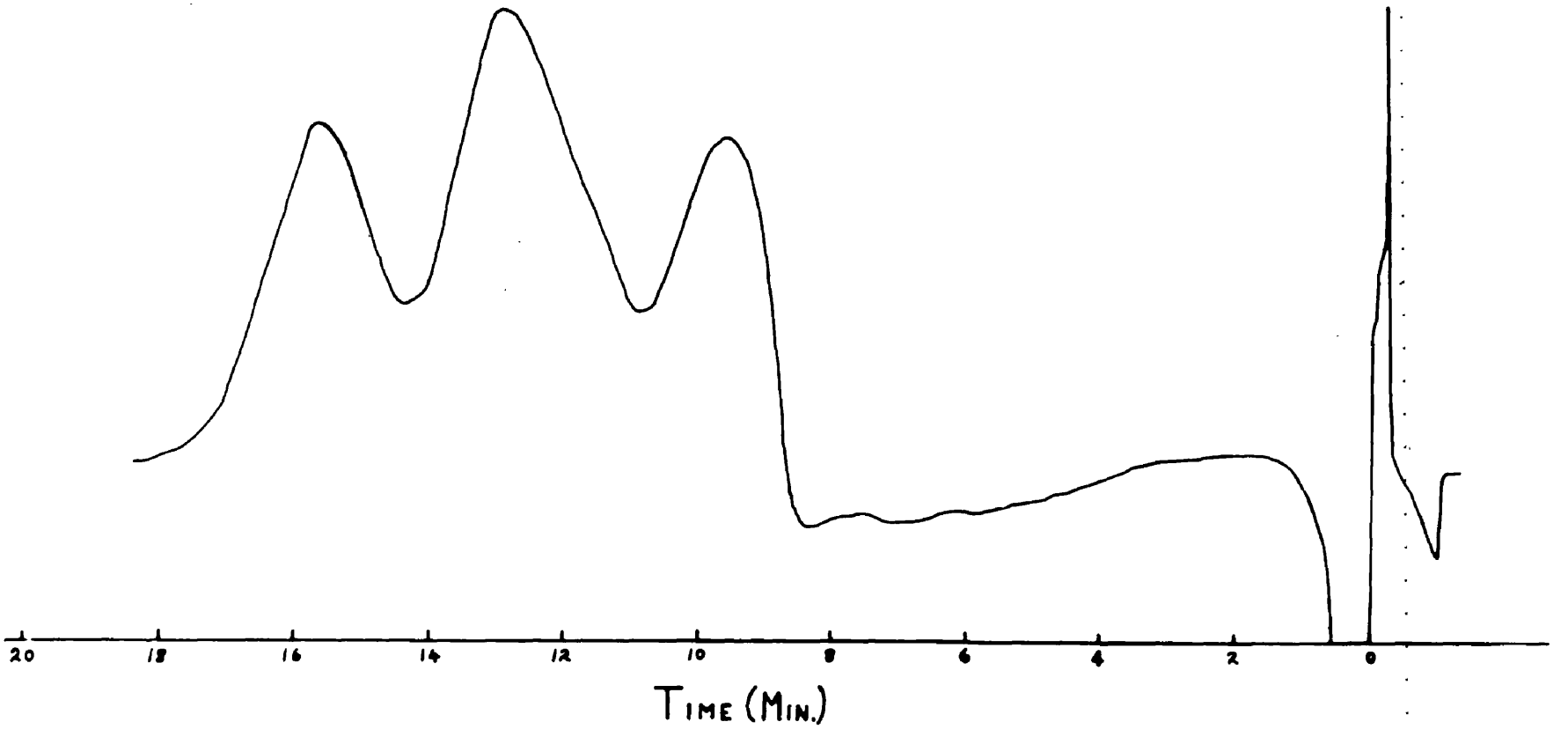
Table X compares the known retention times of the cresols and the xylenols at 180°C with the retention times of the peaks given by the fractions.

Table X.

Retention Times (min.)

	Pk.1	Pk.2	Pk.3	Pk.4	Pk.5
Low Boiling Fraction	9.7	12.9	15.6	-	-
High Boiling Fraction	8.9	11.2	13.8	16.8	20.6
o-Cresol	8.0				
m-Cresol	9.6				
p-Cresol	9.7				
2:6-Xylenol	9.2				
2:5-Xylenol		12.2			
2:4-Xylenol		12.2			
3:5-Xylenol			14.0		
2:3-Xylenol			14.2		
3:4-Xylenol			14.5		

FIG. 8
CHROMATOGRAM OF LOW BOILING
XYLENOL FRACTION.
COLUMN TEMP. = 180°C



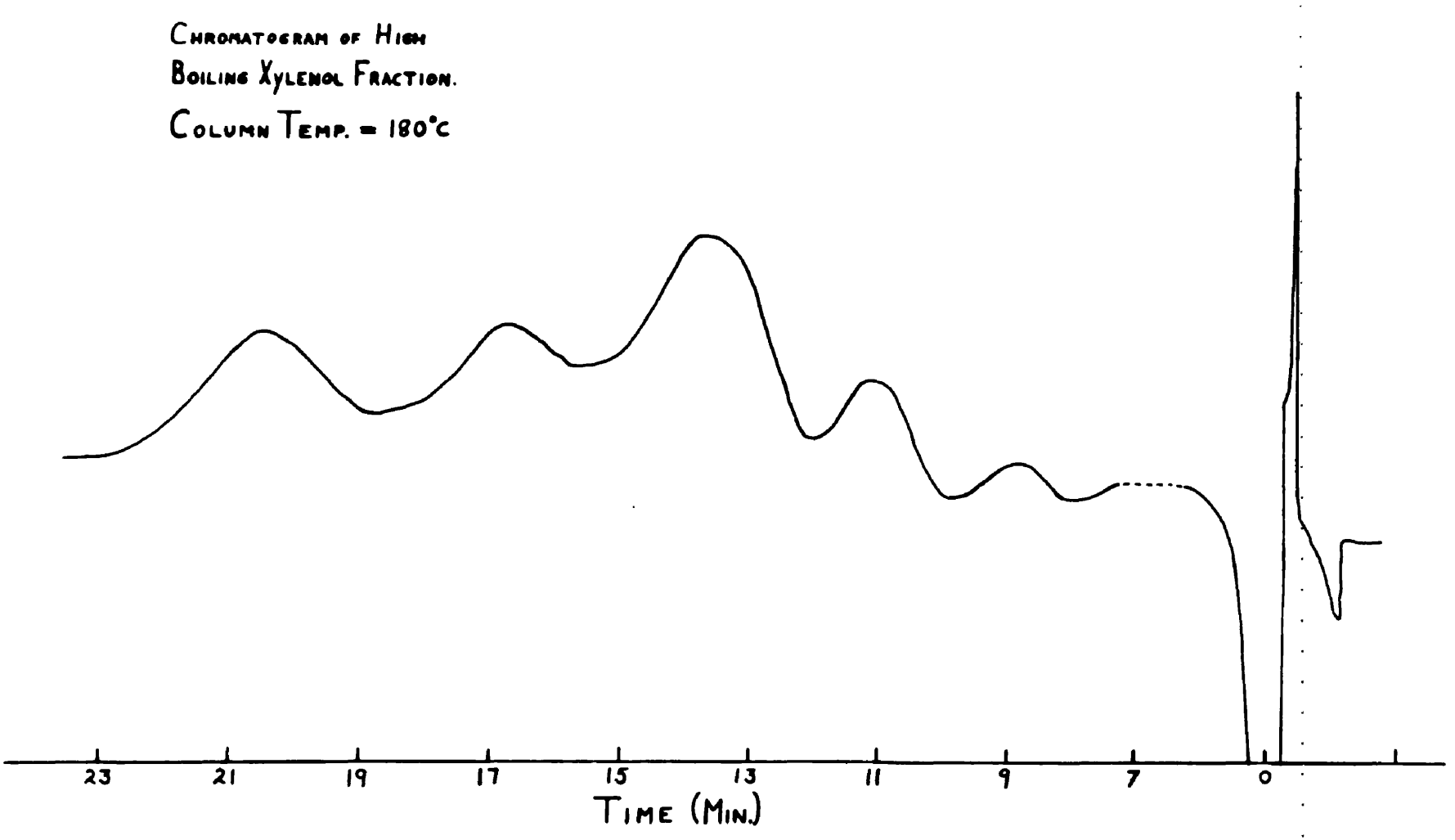

Chromatogram of High
Boiling Xylenol Fraction.
Column Temp. = 180°C
23
21
19
17
15
13
11
9
7
0
Time (Min.)

Fig. 9

In Figs.8 and 9 each peak does not represent one single compound; there are several possibilities for each. Compounds possibly present are indicated in Table X against the appropriate peak. The occurrence of several compounds under each peak accounts for the discrepancy in retention time.

Separation of the two coal tar fractions has not been sufficiently sharp to prevent the same compounds occurring in each. Possibilities for peaks 4 and 5 are numerous.

No further analysis of either fraction was attempted since this electrically-heated apparatus did not have a sufficiently high separating efficiency. (see pages 79 and 80).

Compounds having a difference of two minutes in retention time were capable of resolution while those with a difference of less than 1.25 minutes could not be resolved. These conclusions are specific for the column used and for the working conditions of temperature and pressure. By using a longer column or a more efficient apparatus, compounds with a difference of 1.25 minutes in retention time on the present unit could probably be resolved.

2.4.5. General Conclusions.

1) Gas chromatography apparatus is simple to operate and analyses can be carried out very rapidly.

2) The estimation of methanol in a synthetic mixture gave an error of almost 10 per cent. The main reason for this was irregularity of the recorder base line, which caused appreciable error in the measurement of peak heights.

3) Reduced pressure was considered necessary at the column outlet since the elution peaks broadened and deteriorated in shape when atmospheric outlet pressure was employed. Also detector sensitivity is greater when working at low outlet pressures since there is an increase in the partial vapour pressure of the vapour in the mobile phase.

4) The operating temperature is the predominating factor influencing retention time. Changes in outlet and inlet pressure produced a change in the flow rate which consequently affected the retention time, but small pressure variations did not alter the elution time as appreciably as small temperature changes, tending rather to produce base line drift.

5) Decrease in katharometer sensitivity was observed with rise in temperature. This could be offset by increase in the bridge current, but at katharometer block temperatures above 200°C the sensitivity was so low that

such current increases no longer produced any improvement.

6) Change in the temperature of the katharometer block did not affect retention time values. In practice, the temperature of the block should be as low as possible to give maximum detector sensitivity, at the same time being sufficiently high to prevent condensation in the analysis cell.

7) A column temperature of 234°C was necessary to give satisfactory elution peaks, but retention times were too close together to give satisfactory separation of the compounds under examination.

8) The incorporation of a flash heater allowed the column temperature to be decreased without causing misshapen peaks. Elution was as rapid at an operating temperature of 210°C with a flash heater temperature of 260°C as that given formerly at 234°C.

9) Retention time data obtained for thirty tar acids showed that a column temperature of 180°C gave the maximum resolution that was possible for phenol, the cresols and the xylenols using a 4 ft. column. For the remaining compounds, an operating temperature of 210°C gave the most satisfactory peak shapes and the best separation obtainable with this electrically-heated apparatus, unless longer columns were used.

Complete resolution of all thirty compounds was not found possible; only certain groups of compounds were separable.

10) A low-boiling and high-boiling xylenol fraction were examined on the gas-chromatography unit. By comparing the unknown peaks with known retention times, evidence was obtained for the presence of certain tar acids in each fraction.

2.5. Comments on the Electrically-heated Apparatus.

Inconsistency of the recorder base line was experienced throughout. This instability was neither "noise" nor a steady drift in one direction, but simply an irregular meandering with no fixed pattern.

Doubt has been expressed by some workers about the suitability of electrical heating of the packed column and especially of the katharometer block, on the basis that in both cases the distribution of heat is not sufficiently uniform to obtain reproducible results. In the present work the temperature of the column, although possibly consistent for a series of runs could vary throughout the day by 2°C. Therefore more accurately controlled heating of the chromatographic column would have given more reproducible retention times. Also more efficient heating of the column would probably have given satisfactory elution peaks at column temperatures lower than those which were actually required. This would have resulted in greater resolution of components and higher sensitivity.

The heating on the katharometer block is even more critical, since this directly affects the base line stability. In the present apparatus the temperature of the katharometer block could vary throughout a day by as much as 3°C. Although thermometers inserted at suitable positions in the block may register a constant temperature during an

individual run, they are not sufficiently sensitive to indicate a slight temperature variation, which on amplification is shown as irregularity of the base line. The uncertainty of the zero line therefore made the presence of a trace component difficult to establish, thereby losing the main advantage of gas chromatography over other forms of analysis. For the same reason, quantitative work involving the accurate measurement of peak heights could not be attempted.

Changes in design, particularly for the heater on the katharometer block, would be necessary to overcome this difficulty, as well as to give an improvement in overall performance, since the present apparatus appears to be suitable for the separation of only a limited group of components, unless columns are used that are too long to be practicable.

Since this meant extensive alterations of the apparatus, it was decided at this stage to change to a vapour heated unit. Vapour jacketed columns give more uniform heating conditions, and lower temperatures can be employed giving a higher degree of separation.

3. VAPOUR-HEATED GAS-LIQUID CHROMATOGRAPHY APPARATUS.

3.1. Introduction.

This section describes the use of a gas-liquid chromatography apparatus in which temperature control is maintained by a vapour-heated air jacket. Details are given of the apparatus and its component parts.

Retention time data is given for thirty tar acids at 183°C., 155°C., and 135°C. Graphs of corrected retention volumes per gram of stationary phase (Vg) are shown against reciprocal of temperature for each compound.

Examination of the tar acid extract from a low temperature coal tar has been made. The separation of the total tar acids was attempted and then examination was confined to the fraction 230-250°C. distilled from the extract. This fraction was further subdivided by the gas-liquid partition technique into six fractions, in each of which the presence of probable compounds was indicated by retention time data. The identity of these tar phenols was confirmed by infra-red spectroscopy.

Investigation and discussion of stationary phases was carried out.

3.2. Apparatus.

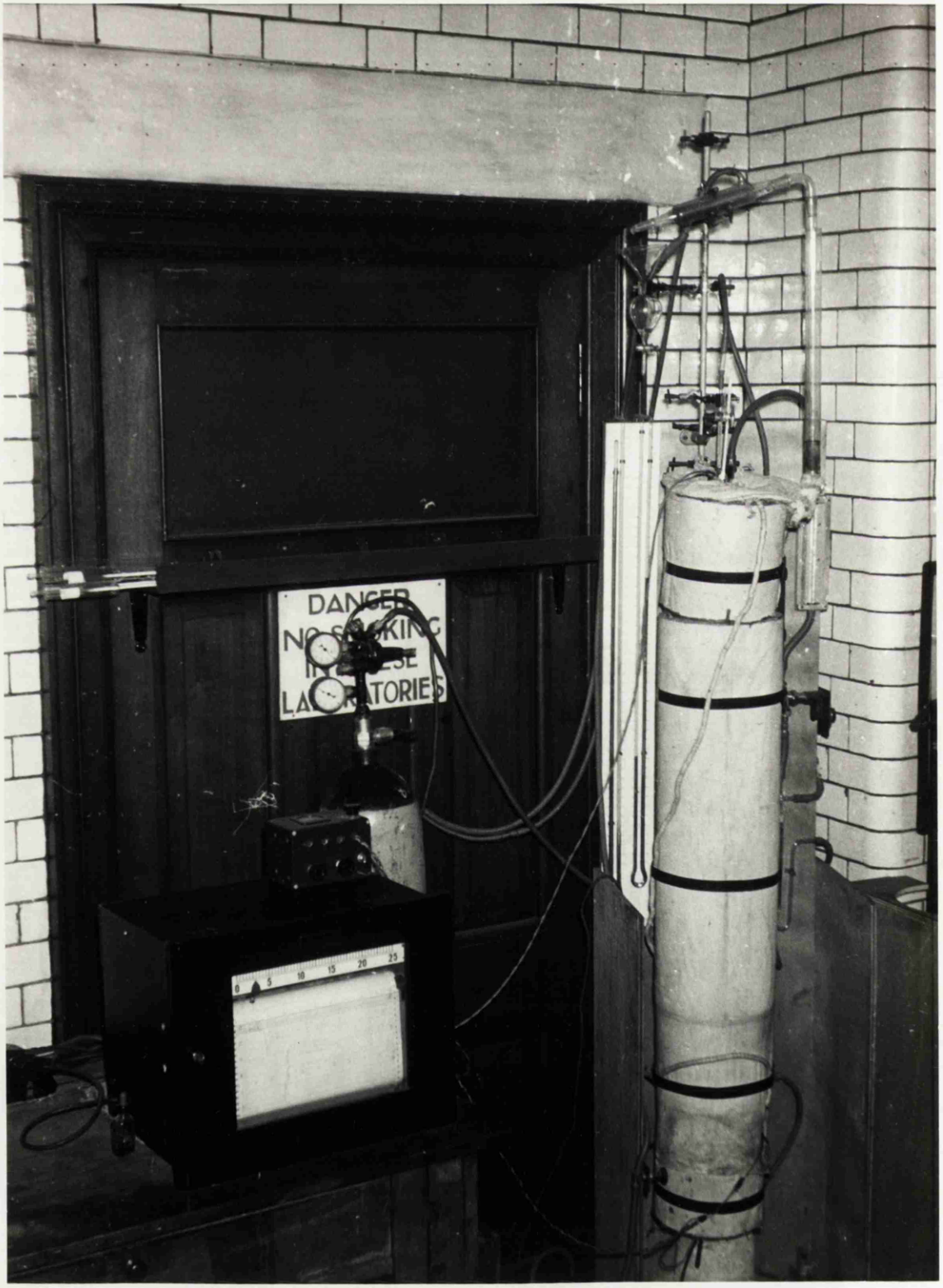
The vapour heated apparatus used was designed by Williams[6] *et al* and supplied by I.C.I., Nobel Division.

3.2.1. Essential Features.

1) Chromatographic Column	:-	Two straight columns, 4 ft. in length. One analytical column, one reference column.
2) Mobile Phase	:-	Nitrogen.
3) Stationary Phase	:-	Apiezon L stopcock grease.
4) Inert Support	:-	Kiesolguhr (Celite 535).
5) Vapour Detection	:-	Thermal conductivity.
6) Introduction of Samples	:-	Micropipette method. Flash heater.
7) Temperature Control	:-	Vapour heated air jacket.

Pressure controls, flowmeters, recorder and all other accessories were the same as used with the electrically-heated apparatus.

The chromatographic columns and katharometer were incorporated within a single unit (Fig.10) and heated to the same temperature by the vapour from a boiling solvent.



VAPOUR-HEATED GAS-LIQUID CHROMATOGRAPHY APPARATUS.

3.2.2. Column and Katharometer Assembly.

The apparatus is shown in Fig.10. It consisted of a copper vapour jacket, length 4 ft., surrounding the chromatographic columns and connected by a flange joint to a shorter jacket which surrounded a brass block containing the working and reference arms of the katharometer. Only one arm is shown in Fig.10. The analysis column was connected to the working cell of the katharometer and a "blank" column to the reference cell. Narrow silicone rubber valve tubing which withstands temperatures higher than 250°C. was used for the connections between the columns and thermal conductivity cells. Such a joint could be readily made and broken so facilitating a change of column. The test column and reference column have separate nitrogen streams and rotameters measured the flow rates in each column. At the column outlet reduced pressure was used with the analysis column and atmospheric pressure with the reference column.

The base of the vapour jacket surrounding the katharometer block was connected to a two litre copper boiler containing an appropriate solvent which heated the column by boiling under reflux.

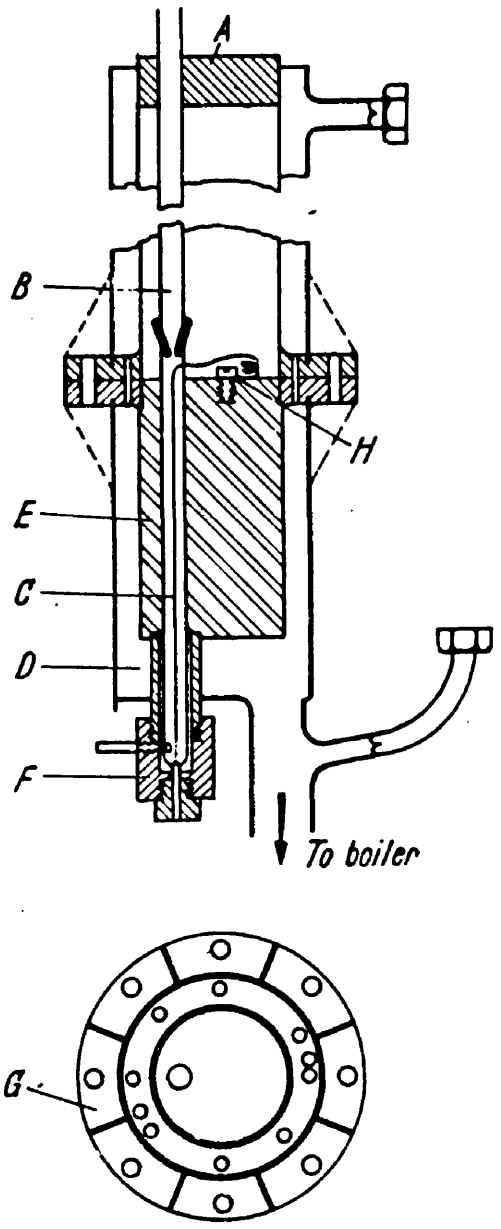


Fig. 10 *Column and katharometer unit*

A Tufnol plug
B Analysis arm
C Katharometer
D Vapour jacket
E Metal block
F Metal seal and 'take-off' (see Fig. 12)
G Top and bottom flanges
H Earthing screw

3.2.3. Katharometer.

A thermal conductivity cell is shown in Fig.11. It consisted of a fine platinum wire of length 10 cm. suspended down the centre of a glass tube 2.8mm. in diameter. The fine wire was 49 s.w.g. (approx. 0.025mm.diameter) and was joined to thicker platinum wires (0.5mm. diameter) leading to the connections to the bridge box and recorder.

The joints were made by inserting the fine wire into concentric holes drilled in the thick wires, good electrical contact being made by squeezing the wires together. Glass thermal conductivity cells were used because the vapours being analysed might be corrosive to metals. The upper and lower glass seals were made to the thick platinum. A 5g. weight was attached to the lower thick wire and the corresponding seal made sufficiently molten to allow the weight to pull the wire taut. To minimise vibrational effects, a small glass bead was sealed on to the inner wall of the lower end of the cell, as near as practicable to the thin wire without blocking the tube to the flow of gas. The thin wire was maintained in a reasonably central position by a spiral in the thick platinum wire just below the glass bead. A small hole in the base of the cell supplied the outlet for the nitrogen stream which then entered a gas-tight

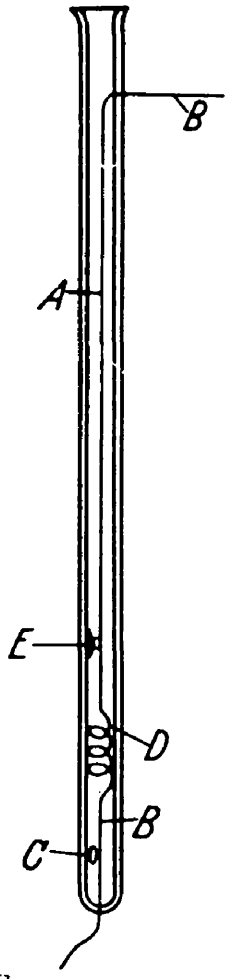


Fig. 11 *Glass katharometer*

A 49 s.w.g. *platinum wire* 4 in. *long*
B 22 s.w.g. *platinum leads*
C *Gas exit*
D 22 s.w.g. *platinum spiral*
E *Glass 'pip' sealed to wall*

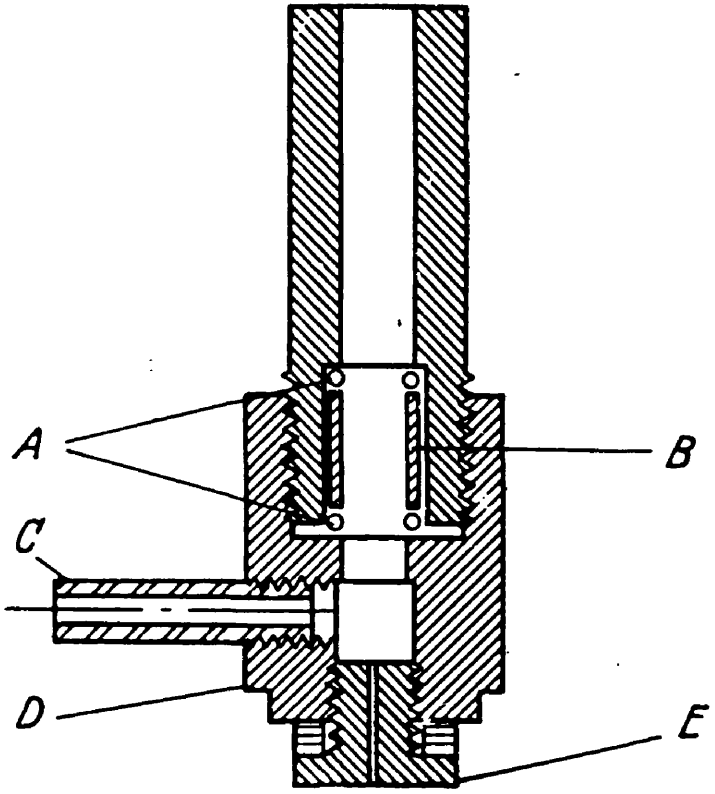


Fig 12 *Metal seal*

A *O-ring washers*
B *Brass ferrule*
C *Gas outlet*
D *Brass cap*
E *Tufnol plug*

metal seal (Fig.12). This metal seal ensured that the delicate katharometer cells were robust and rigid.

The two platinum wires from the inlets of the thermal conductivity cells were connected to an insulated terminal block screwed to the top of the brass block. Two wires from this, in turn, led to another terminal screwed to the outside of the heating jacket and enabled the leads to the bridge to be readily attached. The cell outlet leads were joined to a terminal fixed to the base of the jacket of the block and one lead from this formed the common connection to the Wheatstone bridge. This replaced a previous method (Fig.10) where the cell inlet leads were made the common connection to the Wheatstone bridge through an earthing screw, any part of the column then being used as the common lead.

The Wheatstone bridge circuit was the same as that shown in Figs.4 and 5 except that resistances 2 and 7 were omitted. This change ensured that the standard resistances (50ohms) would be approximately the same as the resistances of the katharometer wires at the operating temperatures employed.

3.2.4. Chromatographic Column.

Straight glass tubes, 4mm. in diameter and 4 ft. in length, were packed with Celite containing 30 per cent stationary phase in the same way as before. The open end of the tube through which nitrogen passed was inserted through a Tufnol plug at the top of the inner metal jacket (Fig.10). The top 3 inches of the tube were surrounded by a jacket which contained a "flash" heater and the tube filling was extended into this zone so that the sample could be introduced at or above its boiling point.

The lower end of the column was drawn out to a taper round which a piece of silicone rubber valve tubing was fitted. This was then inserted in the top of the thermal conductivity cell thereby making a gas-tight seal. A similar seal was used at the column entry for the nitrogen supply.

3.2.5. Heating Liquids.

A heating liquid is chosen for its appropriate boiling point, but it is of primary importance that it should be stable against decomposition or oxidation under continuous reflux conditions for long periods of time.

Before use, heating liquids were distilled and a cut of constant boiling point taken.

Reflux from the top of the heating jacket was returned directly down the column to the boiler and at the same time was reduced to the minimum reflux rate to maintain homogeneous temperature conditions in the column. A long air condenser was used to cool the solvent, with a water condenser in series as an additional safety device. The heat input to the boiler was controlled to give the minimum reflux rate.

Heating liquids used:-

Ethylene glycol monoethyl ether	B.Pt. 135°C
cycloHexanone	B.Pt. 155°C
cycloHexanol	B.Pt. 158°C
2-Ethylhexanol	B.Pt. 183°C
Ethylene glycol	B.Pt. 197°C

The boiler was heated by a 2-litre capacity Isomantle with an unheated upper cover. The Isomantle comprised two heating circuits totalling 750 watts. Both heaters were used when putting the apparatus into operation. When the solvent began to reflux in the air condenser, the smaller heater was switched off and the larger one reduced using a rheostat or Variac transformer, until the minimum reflux rate was attained.

A steady electrical supply was necessary otherwise irregularity of the recorder base line occurred. For this reason on-off controls (e.g. "Simmerstats") were unsuitable.

3.3. Experimental Work.

3.3.1. Retention Time Data for Tar Acid Control Samples.

The inlet nitrogen pressure and reduced outlet pressure were adjusted to give a flow rate of approximately 12ml./min. in the analysis column. The flow rate in the reference arm was 2 ml./min., the outlet being at atmospheric pressure.

Operating conditions:-

Column Temperature	(T_C.)	= 183°C
Flash Heater Temperature	(T_F.)	= 258°C
Inlet Nitrogen Pressure	(P_1.)	= 21.8cm.of Hg.
Outlet Nitrogen Pressure	(P_2.)	= 5.6cm.
Flow Rate, Analysis Column	(F.R.)	= 11.5ml./min.
Flow Rate, Reference Column	(f.r.)	= 2.0ml./min.
Bridge Current	(I.)	= 160 m.a.
Chart Speed	(C.S.)	= 12 inches/Hr.
Column Length	(L.)	= 4 ft.

Stationary Phase:- Apiezon L.

Initial work with the vapour jacketed column has given greatly improved results from those obtained with the electrically heated apparatus. Marked improvement was observed in the zero stability, a straight and steady base line now being obtained.

Tar acid samples were run individually through the column at 183°C, 155°C and 135°C, and their mean retention times obtained. Retention times were corrected for dead space, and for this measurement use was made of the negative air peak eluted immediately after the introduction

of the sample. Delay was anticipated in future introduction of tar samples to the column and this would result in a broad off-scale air peak. The centre of this peak would be difficult to determine and so retention time measurements were taken from the intercept of the tangent to the rear of the air peak with the base line.

Experimental conditions for inlet and outlet nitrogen pressures, flow rate and flash heater temperature were maintained constant during individual runs but varied slightly over a complete set of results at one temperature. The range of these variations is shown in Table XI.

Table XI.

T_C		P_1 cm.	P_2 cm.	F.R. ml./min.	T_F °C.
183°C	Range of conditions	20.2-22.0	5.3-6.0	10.5-11.5	246-268
	Typical conditions	21.7	5.8	11.0	258
155°C	Range of conditions	20.7-21.6	5.3-5.7	11.5-12.5	230-242
	Typical conditions	21.4	5.6	12.0	239
135°C	Range of conditions	21.6-21.9	4.8-5.0	6.0-6.75	244-252
	Typical conditions	21.8	5.0	6.25	248

Bridge current = 160 m.a.
Load (liquid samples) = 5 µl.

Wt. of Apiezon L grease on 4 ft. column.	135°C	155°C	183°C
	2.27gm.	2.46gm.	2.46gm.

Results.

Tables XII, XIII and XIV show the retention times (R_T), limiting retention volumes (V_R^0) and corrected retention volumes per gram of stationary phase (Vg) for the given tar acids at 183°C, 155°C and 135°C. Figs.13, 14 and 15 show graphs of Vg against reciprocal of temperature ($10^4/T$).

Since the flow rate was measured at inlet nitrogen pressure and room temperature, a correction was made in the calculation of the retention volume (V_R) to obtain the flow rate at reduced outlet pressure and column temperature[11,37]. To obtain the limiting retention volume (V_R^0), the usual correction for pressure drop was made[3].

Specimen Calculation.

Compound:- 3-Methyl-5-ethylphenol

Column Temperature	:-	155°C
Flash Heater Temperature	:-	240°C
Inlet Nitrogen Pressure	:-	21.6cm. of Hg.
Outlet Nitrogen Pressure	:-	5.7cm.
Barometric Pressure	:-	75.8cm.
Flow Rate	:-	11.5 ml./min.
Bridge Current	:-	160 m.a.
Chart Speed	:-	12 inches/Hr.
Retention Time	:-	14.5 min.

$$\text{Retention Volume } (V_R) = 14.5 \times 11.5 \times \frac{97.4}{5.7} \times \frac{428}{293}$$

= 4162ml. of nitrogen at 5.7cm. of Hg. and 155°C.

$$V_R^0 = V_R \cdot \frac{3}{2} \left[\frac{(p_1/p_2)^2 - 1}{(p_1/p_2)^3 - 1} \right]$$

$$= 4162 \times 1.5 \; \frac{(97.4/5.7)^2 - 1}{(97.4/5.7)^3 - 1}$$

$$= 364.2 \text{ ml. of nitrogen at } 5.7\text{cm. of Hg. and } 155^\circ\text{C.}$$

$$\therefore \quad V_g = \frac{364.2}{2.46}$$

$$= 148\text{ml.}$$

Table XII.

Column Temperature = 183°C.

Compound	b.p. °C.	R_T min.	V_R^0	Vg.
Phenol	181.8	1.0	26.0	11
o-Cresol	191.0	1.95	50	20
p-Cresol	201.9	2.1	54	22
m-Cresol	202.2	1.9	49	20
2:6-Xylenol	203	2.9	73	30
2:5-Xylenol	210	3.5	88	36
2:4-Xylenol	210	3.6	88	36
2:3-Xylenol	218	4.2	107	44
3:5-Xylenol	221.5	3.8	96	39
3:4-Xylenol	227	4.5	114	46
3-Ethylphenol	218	3.5	89	36
2-Methyl-4-ethylphenol	225.5	5.6	144	59
2-Methyl-3-ethylphenol	227	6.7	158	64
3-isoPropylphenol	228	5.2	122	50
2-Methyl-5-ethylphenol	228	6.0	139	57
4-isoPropylphenol	229	5.2	123	50
3-n-Propylphenol	230-232	6.1	142	58
4-n-Propylphenol	232.6	5.8	142	58
3-Methyl-5-ethylphenol	235.6	6.3	159	65
2:3:5-Trimethylphenol	236	7.0	178	72
2-Methyl-5-isopropyl-phenol	-	7.4	189	77
4-Methyl-3-ethylphenol	ca.240	7.4	180	73
4-Indanol	244	9.4	239	97
3:5-Diethylphenol	248	9.1	212	86
4-n-Butylphenol	248	9.6	250	102
3:4:5-Trimethylphenol	249	9.6	223	91
2-Methyl-4-indanol	ca.250	11.8	279	113
1-Methyl-4-indanol	ca.250	12.4	294	120
5-Methyl-4-indanol	ca.250	14.2	334	136
6-Methyl-4-indanol	ca.250	16.0	388	158

Table XIII.

Column Temperature = 155°C.

Compound	b.p. °C.	R_T min.	V_R^0	Vg.
Phenol	181.8	2.7	70	29
o-Cresol	191.0	4.3	105	43
p-Cresol	201.9	5.2	130	53
m-Cresol	202.2	5.1	130	53
2:6-Xylenol	203	6.8	169	69
2:5-Xylenol	210	8.0	199	81
2:4-Xylenol	210	7.9	197	80
2:3-Xylenol	218	9.4	232	94
3:5-Xylenol	221.5	9.1	232	94
3:4-Xylenol	227	10.6	264	107
3-Ethylphenol	218	9.0	223	91
2-Methyl-4-ethylphenol	225.5	13.6	338	137
2-Methyl-3-ethylphenol	227	14.9	354	144
3-isoPropylphenol	228	12.0	297	121
2-Methyl-5-ethylphenol	228	13.6	339	138
4-isoPropylphenol	229	11.8	280	114
3-n-Propylphenol	230-232	14.0	340	138
4-n-Propylphenol	232.6	14.2	352	143
3-Methyl-5-ethylphenol	235.6	14.5	364	148
2:3:5-Trimethylphenol	236	16.6	413	168
2-Methyl-5-isopropylphenol	-	19.2	455	185
4-Methyl-3-ethylphenol	ca.240	17.4	416	169
4-Indanol	244	23.0	578	235
3:5-Diethylphenol	248	22.0	529	215
4-n-Butylphenol	248	25.4	609	248
3:4:5-Trimethylphenol	249	22.5	539	219
2-Methyl-4-indanol	ca.250	27.8	668	272
1-Methyl-4-indanol	ca.250	27.7	660	268
5-Methyl-4-indanol	ca.250	34.2	820	333
6-Methyl-4-indanol	ca.250	39.0	927	377

Table XIV.

Column Temperature = 135°C.

Compound	b.p. °C.	R_T min.	V_R^0	Vg.
Phenol	181.8	8.2	107	47
o-Cresol	191.0	15.3	202	89
p-Cresol	201.9	16.9	218	96
m-Cresol	202.2	17.2	229	101
2:6-Xylenol	203	26.0	345	152
2:5-Xylenol	210	28.8	380	167
2:4-Xylenol	210	28.2	375	165
2:3-Xylenol	218	33.8	440	194
3:5-Xylenol	221.5	31.8	422	186
3:4-Xylenol	227	36.3	478	211
3-Ethylphenol	218	28.5	360	159
2-Methyl-4-ethylphenol	225.5	48.2	601	265
2-Methyl-3-ethylphenol	227	57.8	706	311
3-isoPropylphenol	228	40.3	509	224
2-Methyl-5-ethylphenol	228	50.8	636	280
4-isoPropylphenol	229	41.0	505	223
3-n-Propylphenol	230-232	48.6	613	270
4-n-Propylphenol	232.6	49.2	620	273
3-Methyl-5-ethylphenol	235.6	51.8	675	297
2:3:5-Trimethylphenol	236	63.8	799	352
2-Methyl-5-isopropylphenol	-	70.0	881	388
4-Methyl-3-ethylphenol	ca.240	60.0	755	333
4-Indanol	244	87.0	1090	480
3:5-Diethylphenol	248	83.7	1053	464
4-n-Butylphenol	248	93.2	1168	515
3:4:5-Trimethylphenol	249	83.6	1021	450
2-Methyl-4-indanol	ca.250	102.1	1252	552
1-Methyl-4-indanol	ca.250	114.9	1443	636
5-Methyl-4-indanol	ca.250	139.0	1741	767
6-Methyl-4-indanol	ca.250	-	-	-

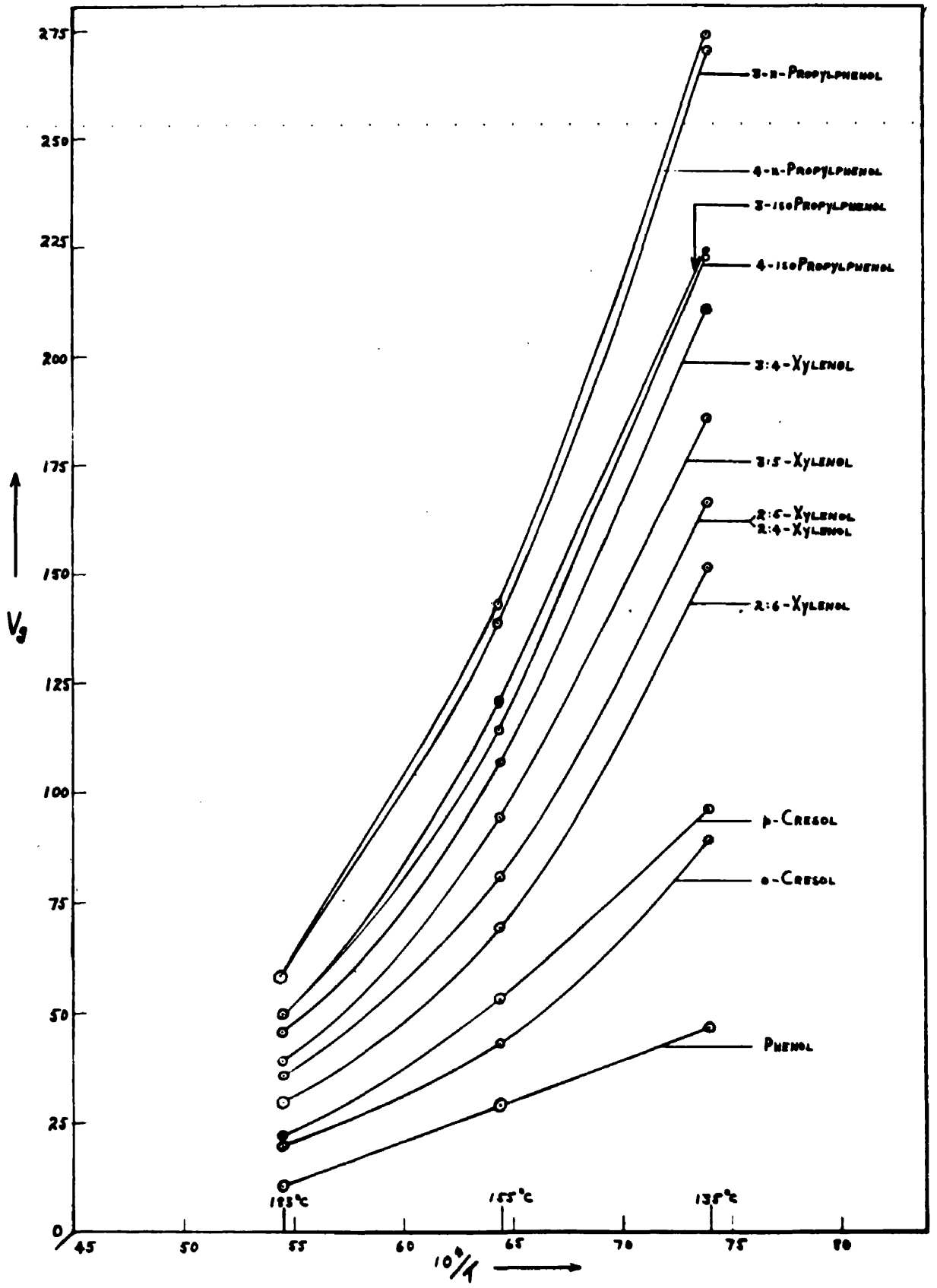
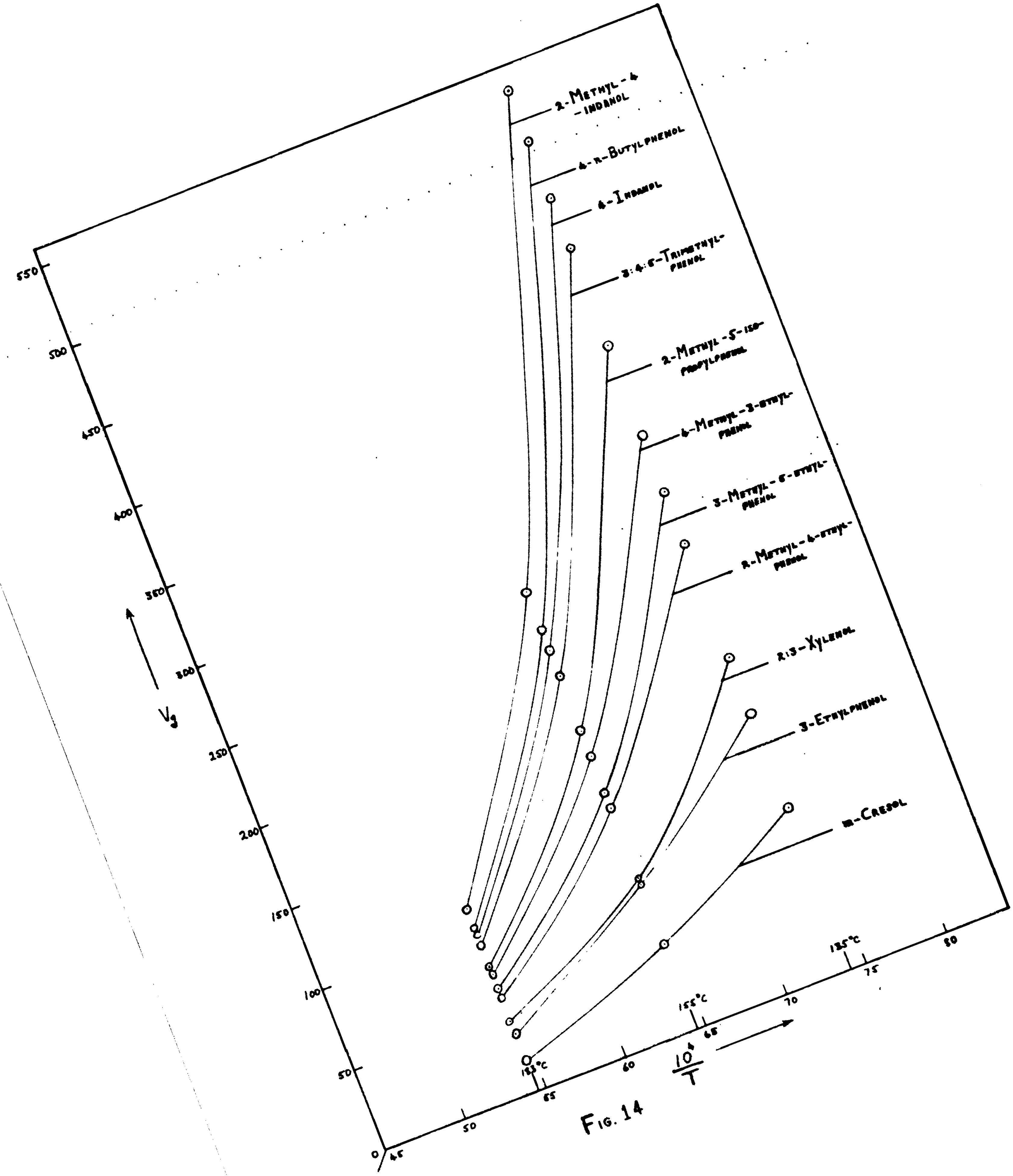

275
250
225
200
175
150
125
100
75
50
25
0
V_g
45
50
55
60
65
70
75
80
$10^4/T$
193°C
155°C
135°C
3-n-Propylphenol
4-n-Propylphenol
3-iso Propylphenol
4-iso Propylphenol
3:4-Xylenol
3:5-Xylenol
2:5-Xylenol
2:4-Xylenol
2:6-Xylenol
p-Cresol
o-Cresol
Phenol

Fig. 13



2-Methyl-4-indanol
4-n-Butylphenol
4-Indanol
3:4:5-Trimethylphenol
2-Methyl-5-isopropylphenol
4-Methyl-3-ethylphenol
3-Methyl-5-ethylphenol
2-Methyl-4-ethylphenol
2:3-Xylenol
3-Ethylphenol
m-Cresol
V_g
$\frac{10^4}{T}$
550
500
450
400
350
300
250
200
150
100
50
0
45
50
55
60
65
70
75
80
125°C
155°C

Fig. 14

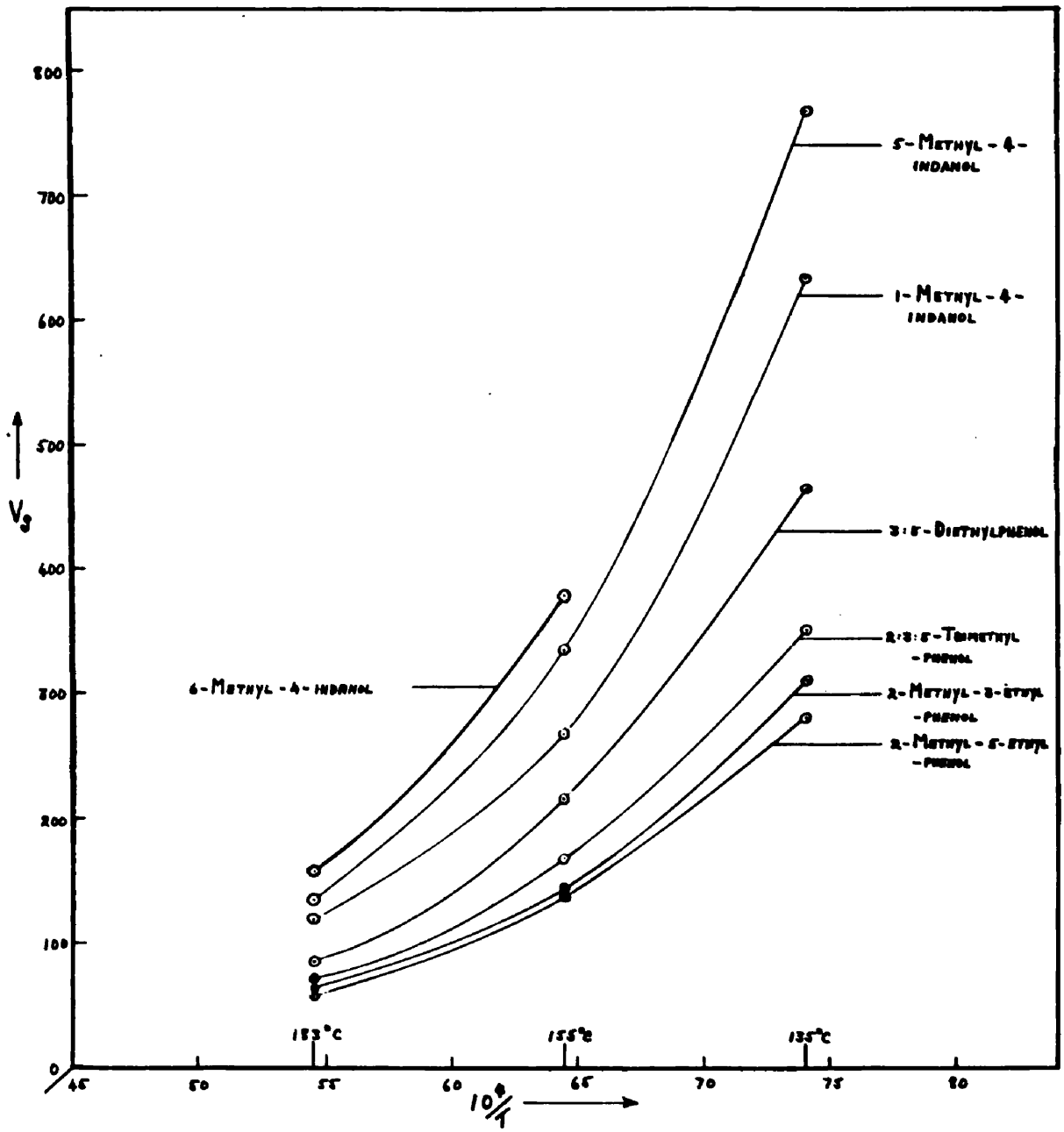

800
700
600
500
400
300
200
100
0
V_g
5-Methyl-4-Indanol
1-Methyl-4-Indanol
3:5-Diethylphenol
2:3:5-Trimethyl-Phenol
2-Methyl-3-Ethyl-Phenol
2-Methyl-5-Ethyl-Phenol
6-Methyl-4-Indanol
183°C
155°C
135°C
45
50
55
60
65
70
75
80
$10^4/T$

Fig. 15

Discussion of Results.

(a) Comparison with Electrically-Heated Apparatus.

1) More rapid elution was obtained at 183°C with the vapour-heated apparatus than at 210°C with the electrically-heated unit.

2) Operating temperatures lower than 180°C could be employed with the vapour-jacketed column but not with the former apparatus because of deterioration of peak shape.

3) Peak shapes at 183°C and 155°C were much sharper and better defined than those obtained at 210°C with the original unit.

4) Peak shapes at 135°C were similar to those at 210°C with the electrically-heated apparatus but resolution was at least five times greater.

Therefore in addition to a steadier base line better overall performance has been obtained with the vapour-heated apparatus at much lower operating temperatures than those required by the electrically-heated unit.

(b) General.

At 183°C separation is only possible of some specific groups of components: in most cases Vg values are too close together. At 155°C a more extensive range of compounds can be separated than at 183°C. Resolution, increasing with decreasing temperature, is greater at 135°C than at either of the higher temperatures.

The difference in Vg values at 135°C between m- and p-cresol, and 2:4- and 2:5-xylenol is due to experimental error. The Vg values for 2:4- and 2:5-xylenol are so close together that they have been represented by one curve in Fig.13. It has not been found possible to separate the members of these groups. Figs.16 and 17 show the separation between 3-ethylphenol (B.Pt.218°C.) and 2:3-xylenol (B.Pt.218°C.) at 135°C and 155°C.respectively.

The most satisfactory peak shapes are obtained at 183°C, peak heights decreasing with diminishing temperature while the peak becomes broader. At 135°C, increase in resolution is offset by broadening of the peaks so that overlapping may occur, particularly with the higher boiling compounds in the latter half of the table. This, coupled with the decrease in peak height makes 135°C less satisfactory for the detection of traces of components having retention times greater than 70 minutes.

Figs. 18 and 19 represent runs carried out on a sample of 3-isopropylphenol while Fig.20 is the record of a synthetic mixture of 3-ethylphenol, 3-isopropylphenol and 4-n-propylphenol. The three diagrams illustrate the increase in resolution and the decrease in peak height with diminishing temperature. Impurities A, B and C are clearly seen at 183°C. At 155°C, A is now barely discernible while the 3-isopropylphenol peak has decreased

FIG 16

T = 135°C
F.R. = 9·5 ml./min.
P_1 = 24·7 cm.
P_2 = 4·3 cm.

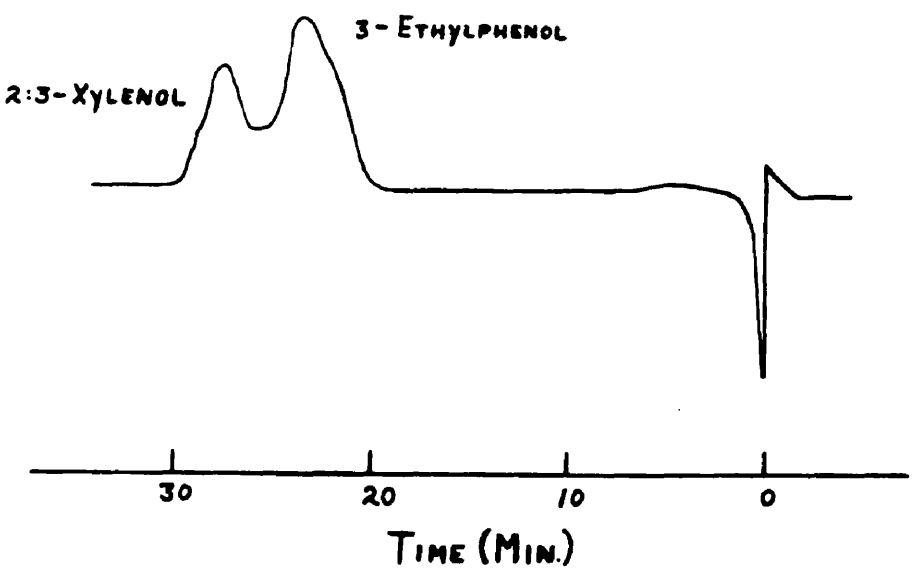


FIG 17

T = 155°C
F.R. = 8·5 ml./min.
P_1 = 24·1 cm.
P_2 = 4·4 cm.

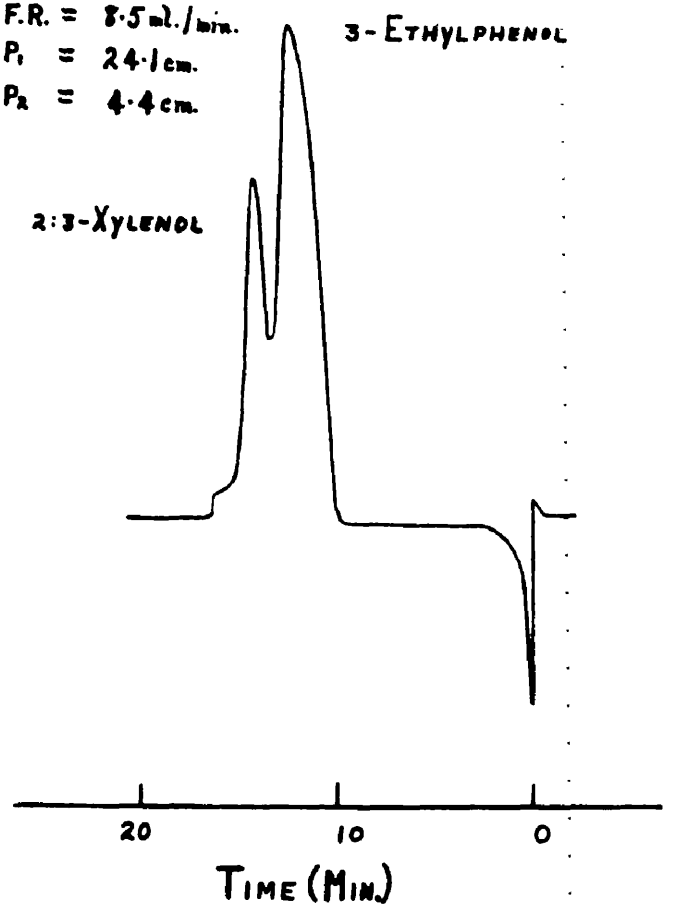


Fig. 18

T = 183°C

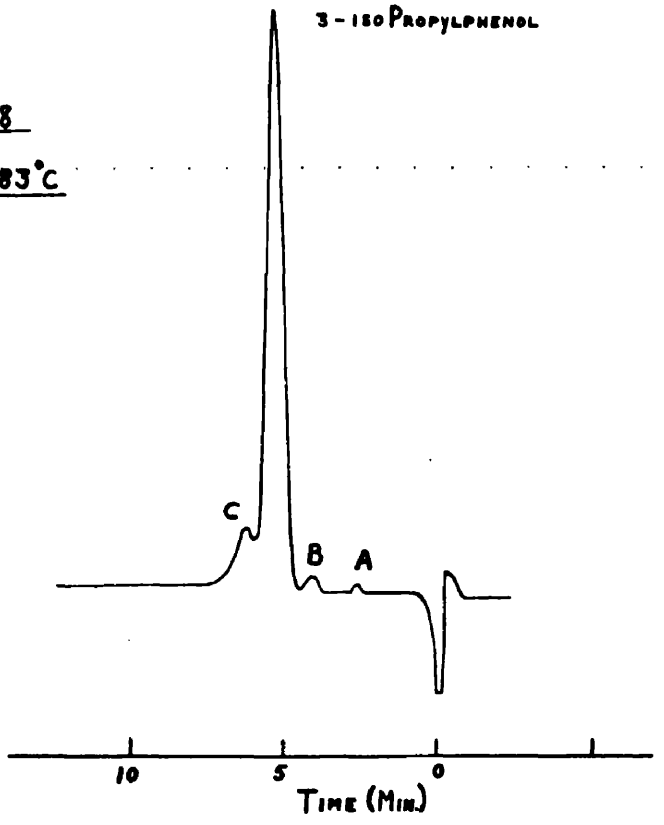


Fig. 19

T = 155°C

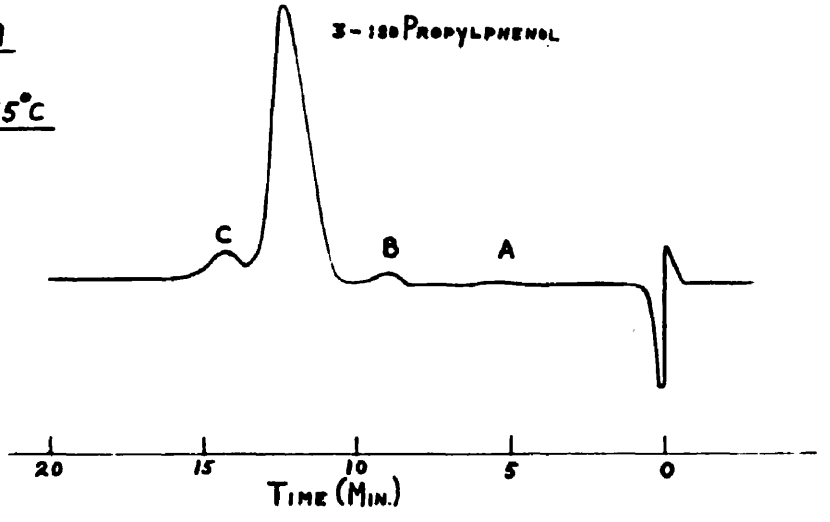
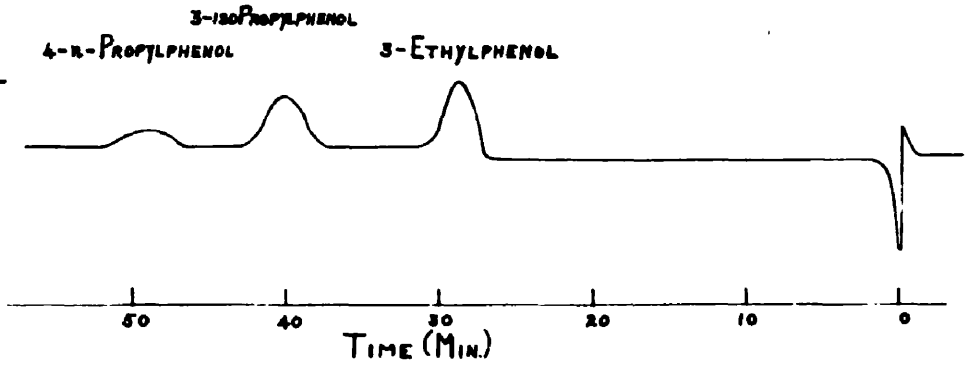


Fig. 20

T = 135°C



in height and become broader. At 135°C, 3-isopropylphenol itself now shows a small, broad peak in the three component mixture, while the peaks for 3-ethylphenol and 4-n-propylphenol are representative of the general deterioration in response at this temperature. Resolution between the components in Fig.20 is considerably greater at 135°C than it is at the higher temperatures, despite the broadening of the peaks. Therefore, even better resolution is possible at temperatures lower than 135°C, provided a more sensitive detector is used to offset the corresponding decrease in response.

3.3.2. Analysis of Tar Acid Extract.

3.3.2.1. Introduction.

(a) History of Tar Examined.

(1) Coal Carbonised.

Codo Rank	902
B.S. Swelling No.	1
Agg. Value	1
Grey King type	B

Proximate Analysis.

Moisture	12-15	per cent.
Ash (dry)	5.9	per cent.
Volatile Matter (d.a.f)	44.3	per cent.

Ultimate Analysis (dry, mineral matter-free):-

C	79.1	per cent.
H	5.3	per cent.
O	14.9	per cent.

(2) Carbonising Conditions.

The coal was carbonised in an 8 inch diameter fluid bed carboniser, with air as fluidising medium, at 600°C.

(3) Method of Obtaining Tar Acid Fraction.

The crude tar was distilled (Engler) at reduced pressure in an atmosphere of nitrogen, until a temperature of 250°C/5mm.Hg. was reached. The phenols were extracted from the distillate with alkali, regenerated with mineral acid, extracted with benzene and distilled. Phenols boiling up to 230°C (normal b.p.) were removed and the residual high boiling tar acids

constitute the extract under examination. In this latter distillation, highly efficient fractionation was not used so that in the sample under examination small quantities of phenols of boiling point below 230°C may be present.

(b) Proposed Experimental Procedure.

Complete resolution of all thirty tar acids was not found possible at any of the three operating temperatures, but a mixture of the thirty compounds could be resolved into fractions containing six or less components. These, in turn, could be further subdivided by using suitable operating conditions or a different stationary phase. Where a particular fraction is not capable of further resolution, infra-red spectroscopy can be used to aid identification of the constituents.

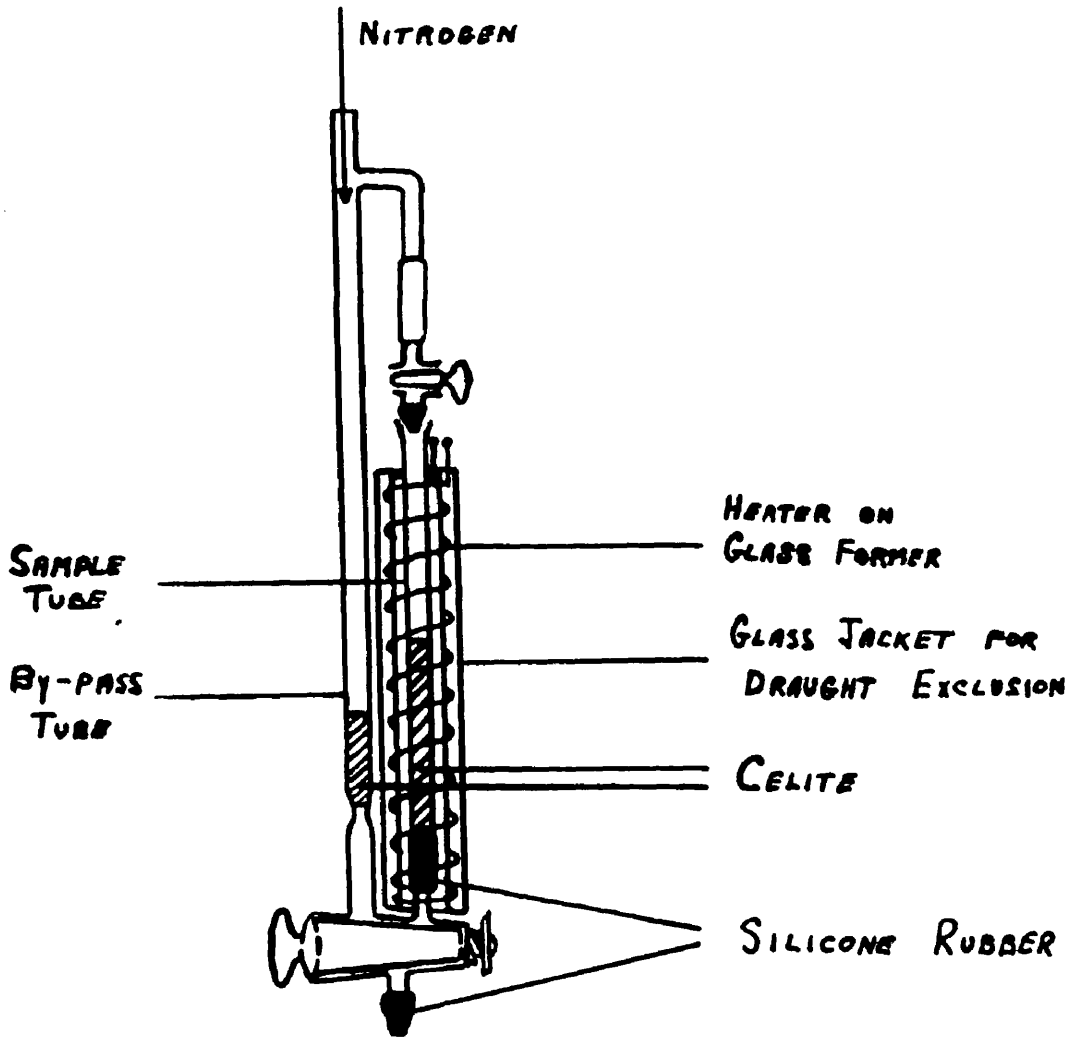
Future experimental procedure therefore involves obtaining a preliminary record for a sample of the phenolic extract on the 4mm. bore column. The peaks given then determine the number of fractions to be separated. A wider bore column, which can accommodate larger samples, is then employed for separation of the appropriate fractions. Further subdivision is carried out where possible.

3.3.2.2. Preliminary Examination of Extract using Analytical Column (4mm. diam.)

(a) Auxiliary Attachments for Introduction of Samples.

Direct application of the tar acid extract to the column was considered unsuitable, because of the formation of a residue after elution of the tar acids. An introductory tube was required in which the sample could be added, and in which a residue would not interfere with the subsequent analysis. The ancillary unit described by Williams[6] *et al* was used (Fig.21). This attachment has two tubes, namely a by-pass tube and a sample tube (lengths 10cm., diameters 4mm.), both of which are partially filled with vacuum-dried Celite 535. By a suitable arrangement of taps the nitrogen stream can be made to pass through the by-pass tube or easily changed to the sample tube prior to passing through the column. The sample is placed on the Celite in the side arm which is heated under standard conditions and volatile components are then displaced from the sample on to the column. The nitrogen stream is then switched to the by-pass tube and the chromatographic separation made in the usual way. The attachment is connected to the inlet of the chromatographic column with silicone rubber valve tubing.

FIG. 21



ANCILLARY ATTACHMENT

(MODIFIED).

This apparatus is suitable for the elution of highly volatile compounds, but had to be adapted for the elution of higher boiling compounds since the lowest boiling tar acid, phenol, condensed in the stopcock during elution from the side-arm. A heater wound on the stopcock prevented this, and fairly well-shaped peaks were obtained for phenol, the cresols and the xylenols with a side-arm temperature of 268°C. As the boiling point of the compound increased beyond 230°C, the peak shape deteriorated considerably, since there was always a cooling effect at the stopcock and a tendency for compounds to condense before they entered the chromatographic column. Therefore rapid vaporization of the sample, which is essential for maximum column efficiency, no longer took place. Consequently the apparatus appears to be unsuitable for the elution of compounds with boiling points greater than 230°C. The alternative is a heater which could surround the entire unit while still allowing access to the stopcock.

Use of Single-Limb Introductory Tube.

The fault in the ancillary attachment is the presence of the stopcock. If the residue left by the extract does not interfere with the carrier gas flow rate, then an auxiliary side-arm in which the sample is applied is no longer necessary. Therefore a single-limb introductory

tube was used with the 4mm. bore column. This consisted of a 6.5cm. length of 1cm. bore glass tubing tapered at one end to enter the 4mm. diameter tube, the gas-tight connection being made with silicone rubber tubing. The outlet of the tapered end practically touched the column packing, the introductory tube being packed with Celite and plugged at both ends with glass wool (Fig.22). Flash heaters enclosed both the normal entry to the chromatographic column and the introductory tube.

Pure phenols were applied to the column using this tube and a retention time "lag" was observed (Table XV).

Table XV.

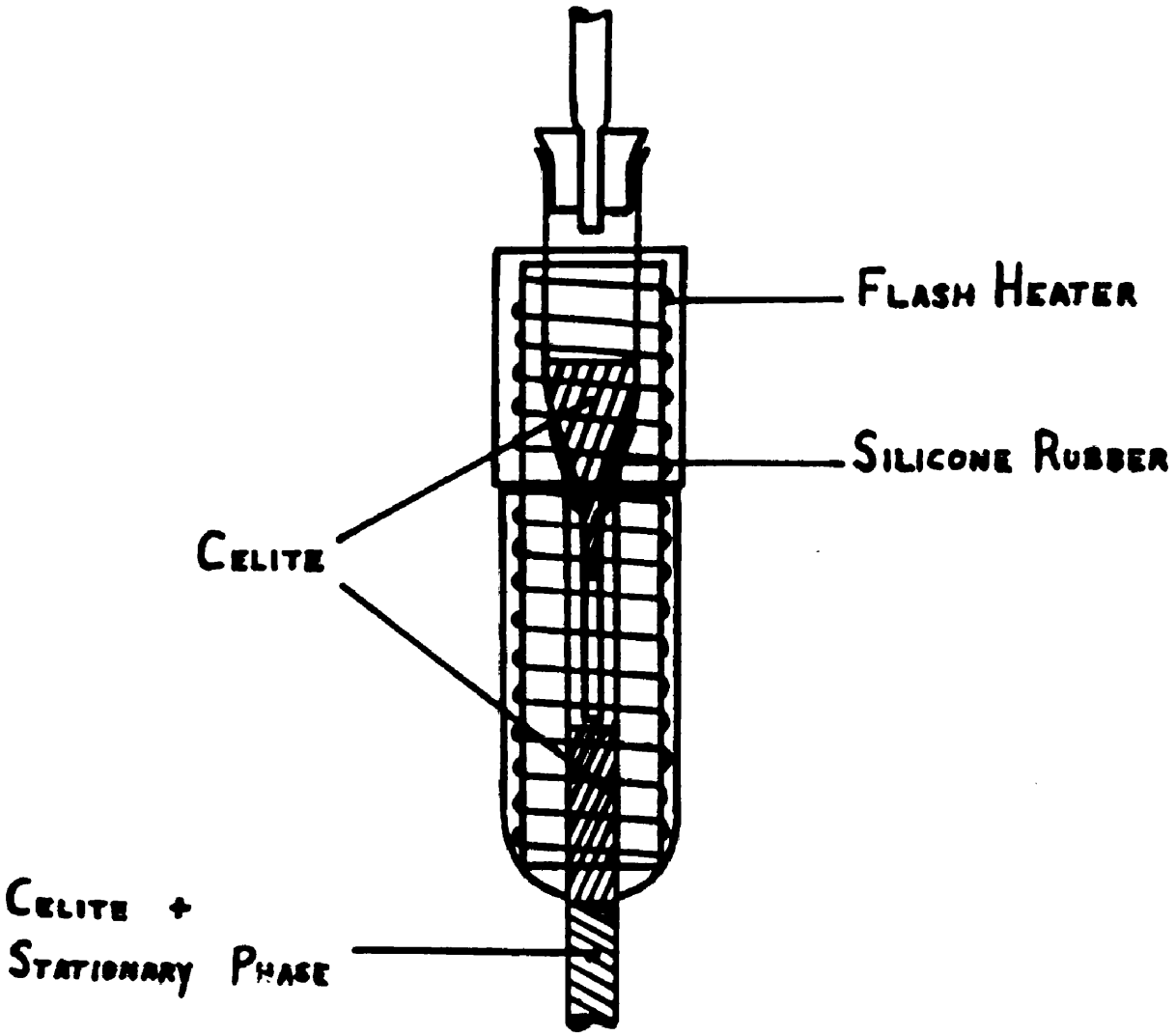
Compound	R_T (normal) min.	R_T (Intry.tube attached) min.
Phenol	2.0	2.5
m-Cresol	3.9	4.9
2:6-Xylenol	6.0	8.4
3:5-Xylenol	6.8	9.5
3:4-Xylenol	8.4	11.0

P_1 = 31.6cm. T_C = 183°C I = 160 m.a.
P_2 = 4.3cm. T_F = 237°C C.S.= 6 in./Hr.

F.R. = 2.50ml./min.
Load (liquid samples) = 5 µl.

Tar acids with boiling points up to 250°C gave sharp well-defined peaks, and the introductory attachment was therefore considered suitable for the application of a sample of the tar acid extract.

FIG. 22



INTRODUCTORY TUBE

(b) Addition of Tar Acid Extract Sample to Column.

A sample of the phenolic extract was added to the 4mm. column at 183°C. The material was heated to make it mobile and sufficient quantity for a sample "dripped" from a solid glass rod into the introductory tube. The record is shown in Fig.23. The flow of nitrogen was unaffected by the residue deposited.

Examination is confined to the retention time range shown in the figure, since comparison samples are available for this range alone. The removed xylenol cut corresponds to retention times lower than 13 minutes and traces still present are observed. Each peak does not represent only a single component: there are several known possibilities for each.

It is therefore necessary to separate into fractions the peaks shown in Fig.23, and to obtain sufficient quantity of these fractions for further examination. For this, a wide bore "separating" column is required which can accommodate larger samples, ca.0.1g., as distinct from ca.5mgm. on the 4mm. column.

Column Temperature	=	183°C
Flash Heater Temperature	=	237°C
Inlet Nitrogen Pressure	=	31·6 cm.
Outlet Nitrogen Pressure	=	4·3 cm.
Flow Rate	=	2·5 ml/min.
Bridge Current	=	160 m.a.
Column Bore	=	4 mm.

Sample:- Tar Extract.

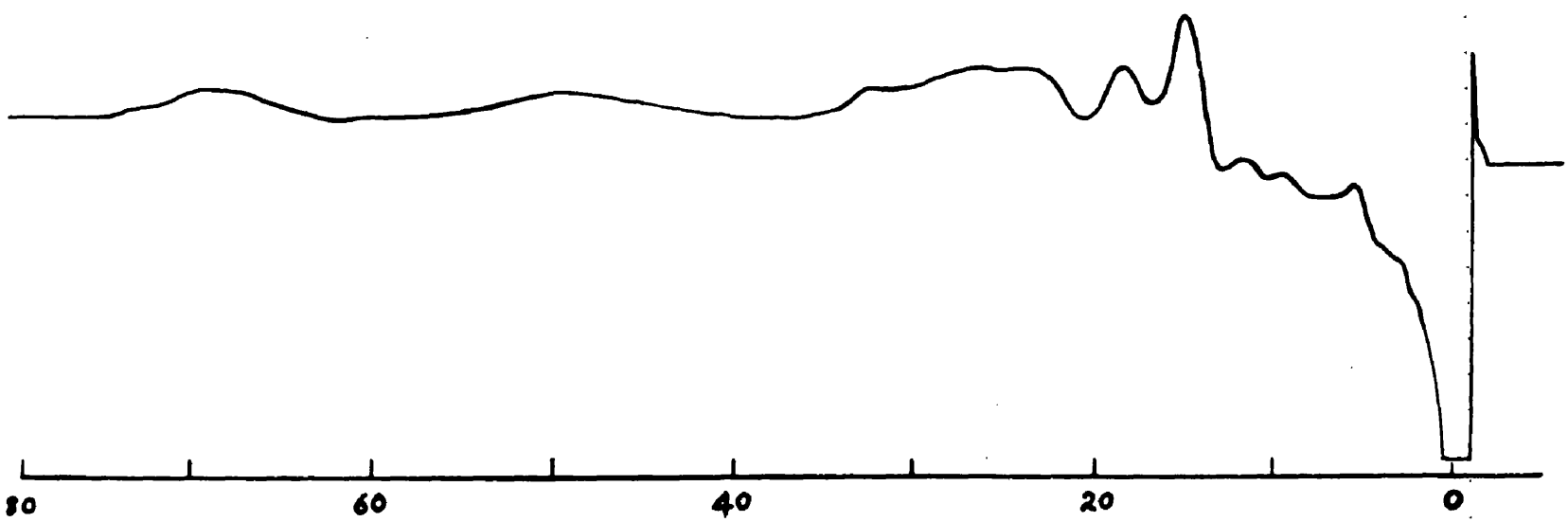


Fig.23

3.3.2.3. Preliminary Work with Separating Column (1cm.diam.)

The "separating" column was 1cm. bore and 4 ft. in length. This was packed in the usual way with Celite 535 containing 30% Apiezon L stopcock grease.

Table XVI shows the retention times obtained for some tar acids, an introductory tube not yet being attached. Atmospheric outlet pressure was employed to facilitate collection of fractions and so the peaks were broader, but still well-shaped. Elution times were higher than those obtained on the 4mm. column.

Table XVI.

Compound	R_T (min.)
Phenol	7.9
m-Cresol	13.4
2:6-Xylenol	20.3
3:5-Xylenol	23.9

P_1 = 31.5cm. T_C = 183°C I = 160 m.a.
P_2 = atmospheric T_F = 250°C C.S. = 6 in./Hr.
F.R. = 28 ml./min.

Introductory Tube Incorporated.

The tube was 14cm. in length and 1cm. bore. The outlet was not tapered but was connected to the chromatographic column by a normal Quickfit joint using retaining springs. Connection of the nitrogen supply to the inlet of the introductory tube was made in the same way.

Silicone grease, which can withstand temperatures of 250°C, ensured gas tight joints. The tube was surrounded by a flash heater and packed with Celite in the same way as before.

Freezing Trap.

This consisted of a straight length of glass tubing from the column outlet leading to a U-tube immersed in acetone/Drikold in a Dewar flask. The outlet was maintained at atmospheric pressure, making it simple to exchange one trap for another without the inconvenience of a vacuum line. In addition, use is made of the high boiling characteristics of the tar acids to facilitate their condensation.

More than 90% of a phenol sample (0.3g.) was recovered in the glass tube before the trap, owing to room-temperature cooling alone. Any "mist" not condensed in this tube also passed through the freezing trap, even when a spiral was substituted for the U-tube. A short zig-zag of glass tubing attached to the column outlet was sufficient to collect phenol and higher boiling compounds as a pool of liquid in the first bend of the tube. More than 85% of the sample could readily be recovered in this way, a small amount still passing on as "mist".

A mixture of phenol (0.5g.), p-cresol (0.5g.) and 3:5-xylenol (0.5g.) was introduced to the 1cm. bore column and the three components frozen out. The purity and identity of each was established by reapplication to the column (Table XVI).

3.3.2.4. Separation and Purification of Fractions:-

(a) from total tar acid extract,
(b) from distillate from tar acid extract.

(a) Direct Introduction of Tar Acid Extract to Separating Column.

A sample of the tar acid extract was applied to the 1cm. bore column at 183°C using the introductory tube. The resulting trace gave one large unresolved shallow peak which was separated and on the 4mm. column gave the same record as in Fig.23. After this peak appeared, elution of vapour continued for over 6 hours.

The highest boiling control sample is 6-methyl-4-indanol (ca.250°C), and so the fraction with the boiling range 230-250°C is required in sufficient quantity for further examination. Therefore a sample was applied to a 2cm. bore 4ft. column containing Celite but no stationary phase, sacrificing resolution to obtain rapid elution of the lowest boiling fraction present.

A cut was obtained which gave the same record on the analysis column as before (Fig.23), but elution of higher boiling compounds, outwith the range of interest, again continued for an excessive length of time.

Elution of this extraneous vapour was prolonging each run unnecessarily and the shape of the elution curves indicated that little fractionation was obtained. The separation of the total tar acids was therefore abandoned.

(b) Introduction of Distillate from Tar Acid Extract to Separating Column.

Engler distillation was carried out on 150ml. of tar acid extract at 3mm. pressure. The fraction corresponding to the boiling range 230-250°C was separated for further examination. This fraction gave the same record as before on the 4mm. column at 183°C (Fig.24). Closer fractionation would have been obtained with, say, a 10 plate column, but the shortest distillation time possible was desired to minimise change in composition of the fraction.

A sample of the distillate (1.4g.) was applied to the 1cm. column at 183°C, the introductory tube no longer being necessary, and fractions were collected (Fig.25).

Although the significant range of compounds was separated in 165 min., elution of higher boiling compounds again continued for some time afterwards. In addition, tarry material appeared at the column outlet just after elution of fraction 4, and was also present in fraction 5. The final fraction was uncontaminated.

A second sample was applied to the column and fractions were collected over the same ranges. Tarry material appeared at the same position as before. Fraction 1 was retained for future infra-red study. The same cuts from both runs were combined, the tarry cuts being combined separately.

T_c = 183°C F.R. = 4·3 ml./min.
T_r = 260°C I = 160 m.a.
P_1 = 15·8 cm. C.S. = 6 inches/hr.
P_2 = 8·0 cm.

SAMPLE:- DISTILLATE FROM TAR EXTRACT.

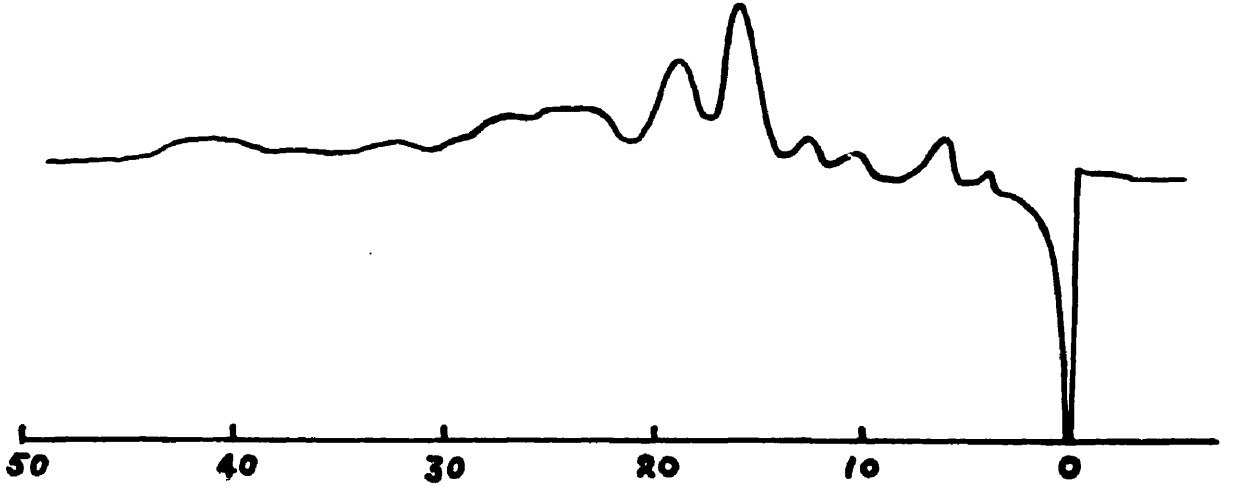


FIG. 24

Column Temperature	=	183°C
Flash Heater Temperature	=	260°C
Inlet Nitrogen Pressure	=	28·0 cm.
Outlet Nitrogen Pressure	=	Atmospheric
Flow Rate	=	26 ml./min.
Column Bore	=	1 cm.
Wt of Sample	=	1·4 g.

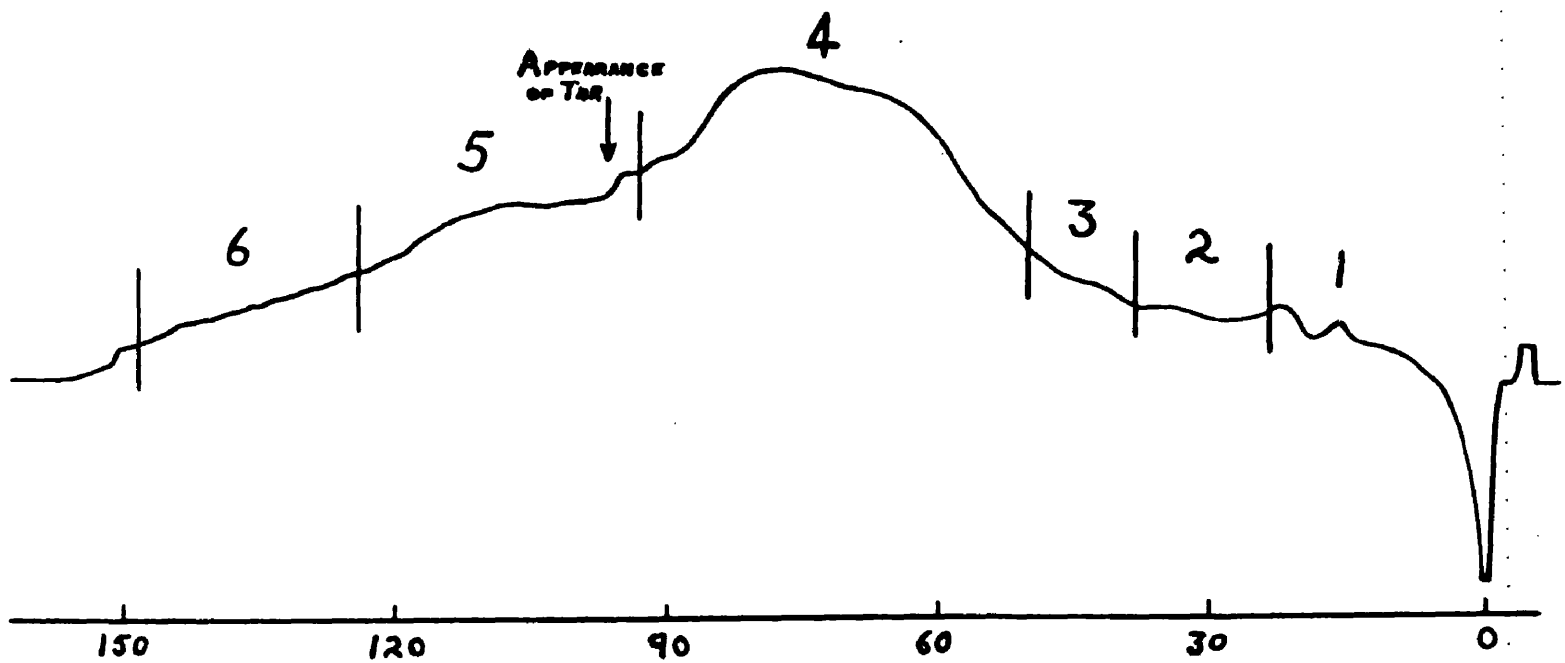


Fig. 25

Since the 1cm. bore column may have been contaminated by previous direct applications of tar acid extract, a distillate sample was introduced to a 2cm. bore 4 ft. column, which was packed with fresh Celite but contained no stationary phase. The eluant was clear initially (Cut A) then tarry matter appeared (Cut B). The final residue was clear again (Cut C). Re-application of the tarry fraction to the 1cm. column gave the elution of a clear cut, the tar being left behind on the Celite at the column entry.

If the tar acids had decomposed during elution because of the column temperature, any tar formed would have been left on the packing.

Since there was no stationary phase in the 2cm. bore column, there was no possibility of tar being produced by decomposition of the Apiezon L, and similarly the use of a fresh packing eliminated the possibility of residual tar elution from previous runs.

It therefore appears that decomposition had been caused by the hot wire of the thermal conductivity cell, the tarry material then being eluted at the same time as the fractions being collected.

Since a number of separate samples, both clear and tarry, had been collected from the various sources, those which were similar had to be combined, and all were therefore subjected to examination on the 4mm. column. This also served to show whether there was any appreciable difference between tarry and clear samples of the same fraction.

Examination of Separated Fractions on Analytical Column.

Chromatograms were obtained for the following samples:-

Fig.26 Clear No.4 fraction from distillate, obtained from 1cm. bore column.

Fig.27 Tarry No.4 fraction from distillate, obtained from 1cm. bore column.

Fig.28 Tarry No.5 fraction from distillate, obtained from 1cm. bore column.

Fig.29 Clear fraction (A) from distillate, obtained from 2cm. bore column containing no stationary phase.

Fig.30 Tarry fraction (B) from distillate, obtained from 2cm. bore column.

It required several runs to obtain sufficient quantity of fractions 2 and 3 (Fig.25) for possible infra-red study in the event that resolution could not be improved, and so these fractions were not examined on the analytical column.

FIG. 26
CLEAR NO. 4 FRACTION

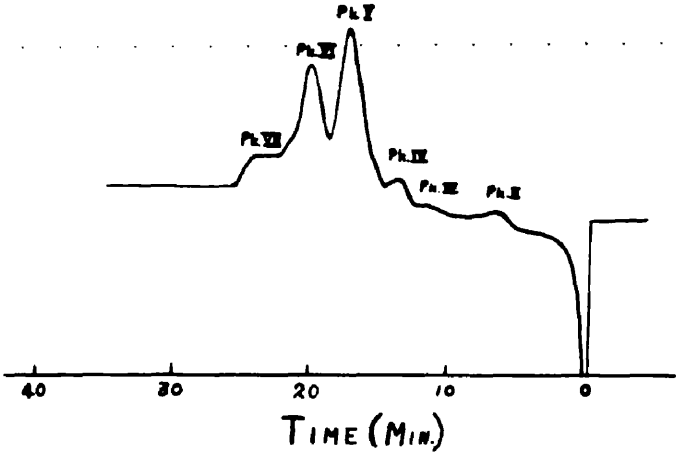


FIG. 27
TARRY NO. 4 FRACTION

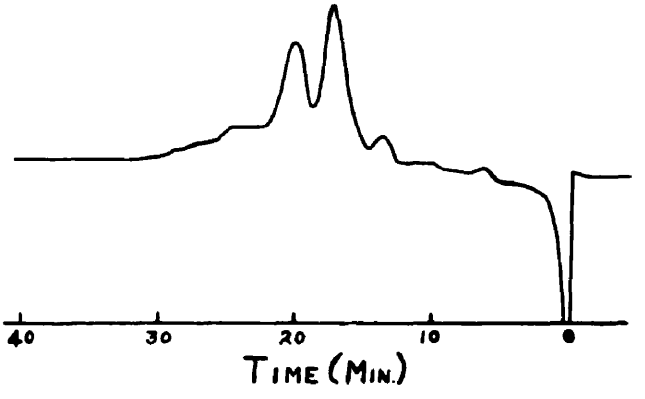


FIG. 28
TARRY NO. 5 FRACTION

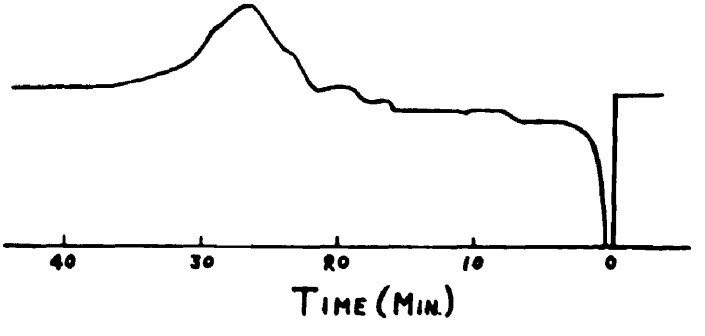


FIG. 29
CLEAR FRACTION (A)

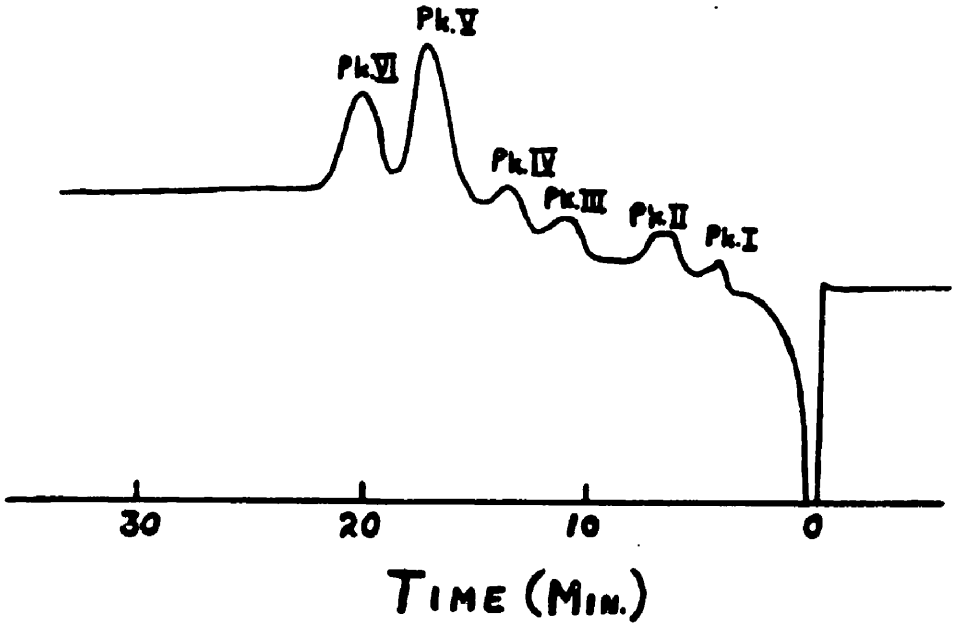
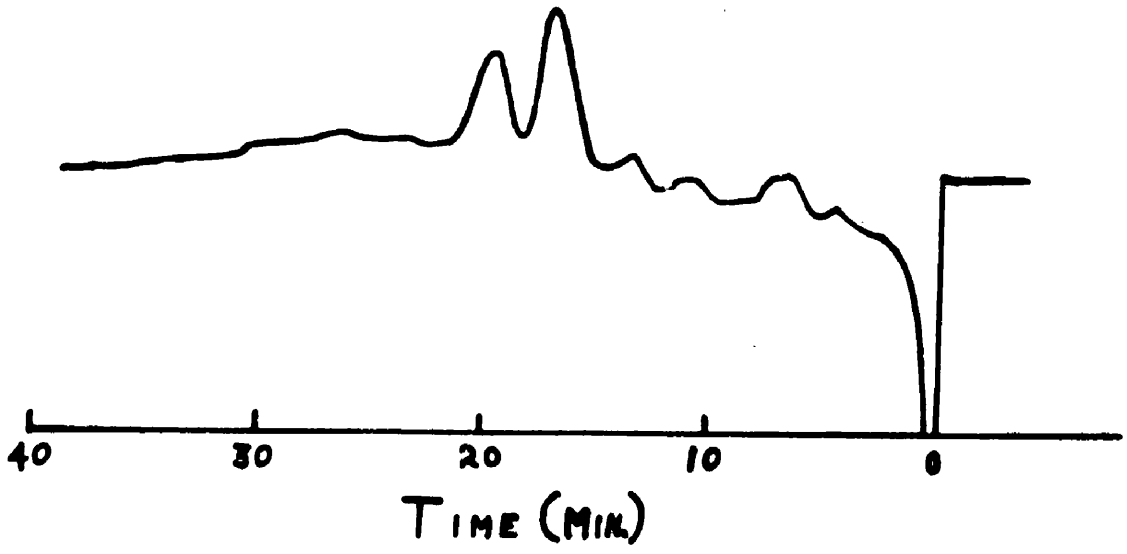


FIG. 30
TARRY FRACTION (B)



Comments on Records obtained.

Fig.26 and Fig.27.

Clear No.4 fraction was separated before contamination by the tar and therefore the cut at an approximate retention time of 25 mins. in Fig.26 is sharper than that in Fig.27. Both chromatograms are otherwise identical. Although the required peaks (V and VI) predominate, resolution has been poor, and small amounts of the xylenol cut as well as peak VII have overlapped.

Fig.28.

Small amounts of peaks V and VI overlapping and xylenol traces still present. This fraction was expected to consist mainly of peak VI, but because of poor resolution at 183°C (Fig.25), peak VII and the higher boiling compounds expected in fraction 6 predominated.

Fig.29.

Peaks I-VI all present in their original proportions. Sharp cut after peak VI.

Fig.30.

Identical with Fig.29 but cut after peak VI is not sharp since this was the later fraction.

Combination of Fractions.

The tarry No.4 fraction was added to the 1cm. column and any clear eluant combined with the clear No.4 fraction sample. With heavy loads tarry material was still eluted. Such fractions were recycled. Tarry fractions obtained from the 2cm. bore column were similarly recycled on the 1cm. Apiezon L column and the clear eluants combined with fraction (A).

Summary.

By application of distillate samples to the 2cm. bore column, the whole of the significant zone, although unresolved, was separated rapidly from the higher boiling compounds, which were themselves eluted in a suitable time. By reapplication of any tarry fractions formed to the 1cm. bore column (Celite, 30% Apiezon L), suitable quantities of clear cuts were gradually built up.

3.3.2.5. Attainment of Maximum Peak Resolution.

Suitable operating conditions are now required for separation of the two main peaks (V and VI) in No.4 fraction and this would also give an overall improvement in resolution. By comparison of retention times, 3-methyl-5-ethylphenol and 2:3:5-trimethylphenol were found to be possible constituents of peaks V and VI. A mixture of the two can therefore be considered representative of these two major peaks and avoids waste of the accumulated fraction. This mixture was applied to the 1cm. column under different conditions of inlet pressure and flow rate. Decrease in flow rate increased the difference in retention times, since these were measured to the top of the peak, but separation was unimproved since the peaks were correspondingly broader and overlapped.

Resolution at 183°C, although affected by overloading of the column (Fig.25) could not therefore be improved by alterations in flow rate and inlet pressure.

The temperature was decreased to 158°C and a sample of the distillate from the tar acid extract introduced to the 4mm. bore column. The same peaks were given as at 183°C but were now shorter and broader.

Resolution of the major peaks was improved but was not yet complete. However, good separation of peaks III and IV now appeared possible and a mixture of the clear No.4 fraction and clear fraction (A) was introduced to the 1cm. bore column (0.11gm.) at 158°C (Fig.31). Fractions 2-6 were collected for infra-red analysis, three runs being required to obtain sufficient quantity of fractions 2 and 3. Fraction 5 in this case should consist almost entirely of peak VI whereas, because of poor resolution, peak VII was shown to predominate (Fig.28) in the fraction 5 obtained at 183°C (Fig.25). A further reduction in temperature to 135°C gave the record shown in Fig.32. Resolution being greater than at 158°C, fractions 2-6 were re-collected from runs at 135°C for infra-red study and were preferred to those previously obtained at the higher temperature.

Column Temperature	=	158°C
Flash Heater Temperature	=	250°C
Inlet Nitrogen Pressure	=	38·0 cm.
Outlet Nitrogen Pressure	=	Atmospheric
Column Bore	=	1 cm.
Wt. of Sample	=	0·11g.

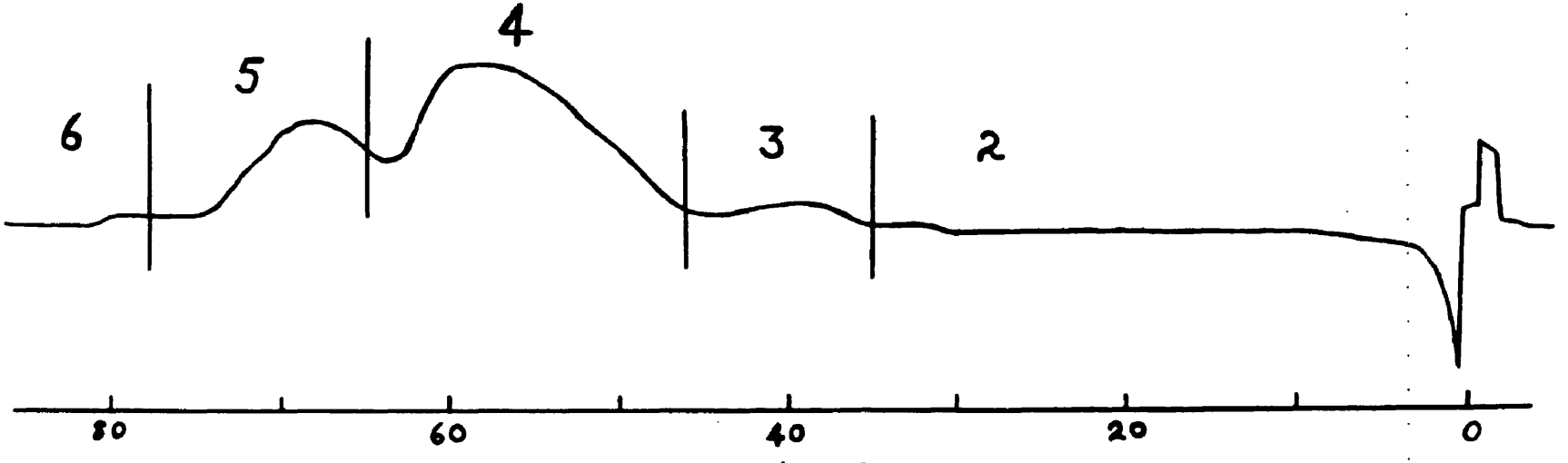
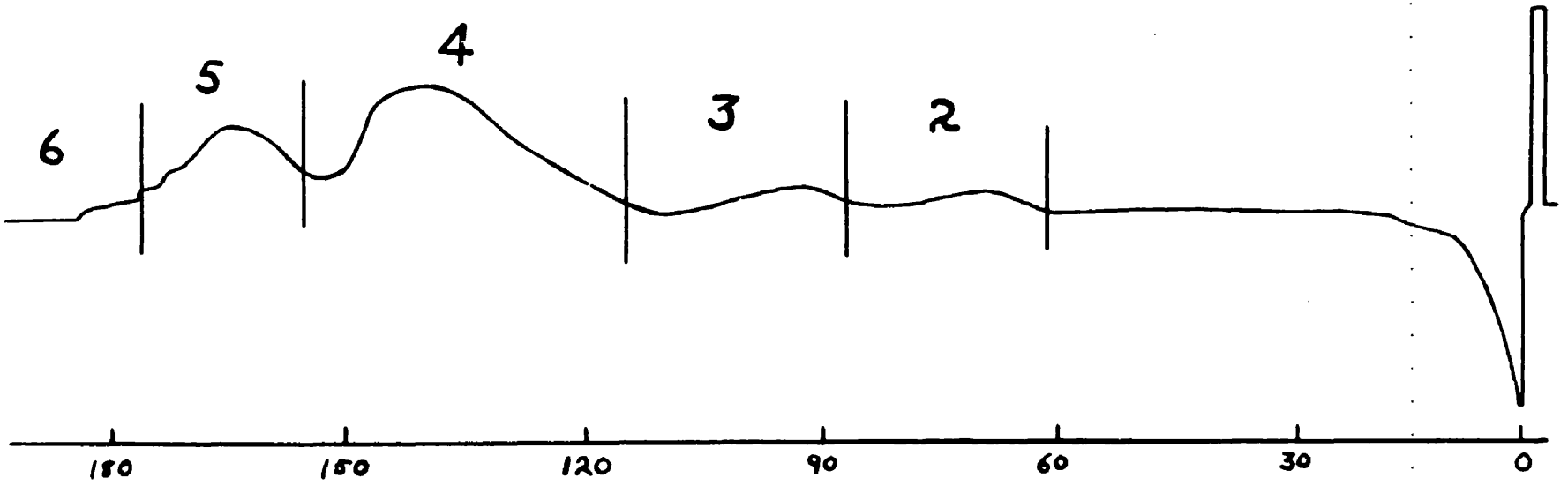


Fig. 3!

Column Temperature = 135°C
Flash Heater Temperature = 237°C
Inlet Nitrogen Pressure = 39·7 cm.
Outlet Nitrogen Pressure = Atmospheric
Column Bore = 1 cm.



Time (Min.)

Fig. 32

3.3.2.6. Identification of Tar Acids.

(a) Preliminary Identification from Retention Time Data.

Duplicate runs were carried out on a sample of the original distillate from the tar acid extract using the 4mm. column at 158°C. The retention times of the peaks obtained are shown in Table XVII, and also the separated fractions to which these retention times correspond. The same information obtained under the same operating conditions is given for the pure tar acid control samples. This table shows how retention times from the peaks given by the original distillate and those obtained for the reference samples made it possible to indicate the presence of probable compounds in each fraction.

In the chromatogram of the original distillate (Fig.24), each peak may contain a number of components. If there is a slight difference in the retention times of each component, the peak is broader than that given by any one compound. The top of the peak, to which the retention time is measured, is therefore displaced according to the relative concentrations of each constituent under the peak. For this reason, the retention times of suspected compounds and "unknown" peaks in Table XVII do not compare exactly and the "range" of retention time of the unknown peak is also given.

Each fraction was now subjected to infra-red spectroscopy.

Table XVII.

Compound	R_T (min.) (range)	R_T (min.) (Pk. centre)	Fraction
Original Distillate Pk.I	—	6.0	1
Phenol		6.5	1
Original Distillate Pk.II	—	10.0	1
o-Cresol		11.5	1
m-Cresol		11.9	1
p-Cresol		11.8	1
Original Distillate Pk.III	—	18.5	2
2:6-Xylenol		16.5	2
2:4-Xylenol		18.8	2
2:5-Xylenol		18.2	2
3:5-Xylenol		22.0	2
3-Ethylphenol		20.8	2
Original Distillate Pk.IV	22-26	23.5	3
2:3-Xylenol		23.4	3
3:4-Xylenol		26.0	3
3-isoPropylphenol		27.9	3
4-isoPropylphenol		28.5	3
Original Distillate Pk.V	29-34	31.5	4
2-Methyl-4-ethylphenol		32.8	4
3-n-Propylphenol		32.8	4
4-n-Propylphenol		33.6	4
2-Methyl-5-ethylphenol		32.4	4
3-Methyl-5-ethylphenol		32.9	4
2-Methyl-3-ethylphenol		33.2	4
Original Distillate Pk.VI	34-39	36.5	5
2:3:5-Trimethylphenol		39.4	5
4-Methyl-3-ethylphenol		37.8	5
2-Methyl-5-isopropylphenol		39.4	5
Original Distillate Pk.VII	48-55	51.0	6
3:5-Diethylphenol		50.2	6
4-Indanol		52.3	6
3:4:5-Trimethylphenol		53.1	6
4-n-Butylphenol		56.6	6

(b) Identification by Infra-Red Spectroscopy.

Introduction.

Infra-red radiation is selectively absorbed by an organic molecule because of the vibrational frequencies of the atoms in the molecule. This, in turn, depends on the bond strength between any two atoms in the molecule, the atomic masses and the molecular structure. All compounds, except optical isomers may then be expected to have some difference in their frequencies of vibration, though related compounds will have some identical frequencies. Therefore, the series of absorption bands in the infra-red spectrum are specific for a given compound and are usually unaffected by the presence of other compounds. This is the basis of infra-red analysis.

A double beam infra-red spectrometer was used, with a Nernst lamp as the source of radiation and a rock salt prism as dispersing medium. The wavelength of the band centre was determined by the rotational setting of a Littrow mirror. The transmitted radiation passed through the substance between the prisms and was detected by a thermopile. The output was amplified and fed to a pen recorder which gave a continuous record of the deflections produced by the absorption bands of the substance. Rotational

settings of the Littrow mirror were indicated on the chart by a second pen as equally spaced marks or "break" numbers.

Procedure.

Daily calibration of the instrument was carried out by obtaining a spectrum for "Analar" benzene and noting the "break" numbers for each absorption peak. The wavelengths of these peaks were known from the literature. It is, however, more usual in infra-red analysis to use "wave numbers" rather than wavelengths, where

$$\text{Wave number} = \frac{10^4}{\text{Wavelength (Microns)}} = \text{cm}^{-1}$$

Therefore a curve of wave number against "break" number was drawn and used to calibrate the spectra of other compounds run on the instrument.

The fractions separated by gas chromatography were all liquid and their spectra were obtained by the "capillary" method, in which a drop of liquid was sandwiched between two salt prisms to give a thin film. The prisms were placed in the radiation beam and the corresponding spectrum obtained.

The spectra of pure liquid control samples, not available in the literature, were obtained by the above method. Those of pure solid samples were obtained by sandwiching a suspension of the material in "Nujol" (liquid paraffin) between two salt prisms. Nujol has few absorption bands in the infra-red region.

Results.

Tables XVIII-XXIII compare the wave numbers of the absorption peaks for each fraction with those of the control samples believed to be present. The absorption ranges used for identification are limited to those shown in the tables. Outwith these ranges a large number of coincident peaks occur.

For identification an error of 11 wave numbers has been allowed. In a few cases, where a very broad peak in the spectrum of the unknown fraction has occurred, an error of 19 wave numbers has been allowed.

Absorption maxima are denoted as strong (s), medium (m) or weak (w). It is important to note, however, that a weak absorption peak in the spectrum of the unknown fraction may well have been a medium or even strong peak in the spectrum of the pure compound causing it. Medium peaks in the unknown spectrum have then an even greater significance for the same reason.

The results for each fraction will be considered in turn.

Table XVIII.

Wave Nos. ($cm.^{-1}$) for Fraction 1 and Control Samples.

Absorption peaks for Fraction 1.	Phenol	o-Cresol	m-Cresol	p-Cresol	2:6-Xylenol	2:4-Xylenol	2:5-Xylenol
1106 m	-	1102 s	-	1100 m	1100 m	1100 s	1110 s
1070 m	1068 w	-	1080 w	-	1082 m	-	-
1037 m	-	1042 m	1035 w	1042 w	-	1040 w	1036 m
1018 s	1020 w	-	-	1018 w	1019 m	1010 w	-
1000 m	1000 w	-	1000 w	-	-	-	-
986 w	-	985 w	-	-	985 m	990 w	994 s
952 w	-	-	-	-	950 w ∠	-	-
928 m	-	928 w	928 s	925 w	-	926 w	930 m
914 w	-	-	-	-	909 m ∠	-	-
877 w	882 w	-	873 w	-	-	872 m	870 m
844 m	-	847 s	851 w	844 m	-	-	847 m
828 w	825 w	-	-	-	828 m	-	-
815 s	813 m	-	-	821 s	-	815 s	801 s
775 s	-	-	775 s	-	768 s	769 s	-
752 s	751 s	752 s	-	742 s	-	-	750 w
733 w	-	-	730 m	-	729 m	-	725 m
712 m	-	714 m ∠	-	-	-	720 w	-
690 s	687 s	-	687 s	700 w	-	-	-

Fraction 1.

From retention time data this fraction was believed to contain phenol and the cresols and the cut was taken before the cresol elution peak returned to the base line in order to prevent overlapping of compounds from fraction 2. From Table XVIII it is observed that this has not been successful. The compound 2:6-xylenol is the only one for which specific absorption maxima are indicated (✓).

A weak absorption peak for 2:4-xylenol at 720cm^{-1} is not sufficient to explain a medium (or perhaps strong) absorption peak at 712cm^{-1} in the spectrum of the "unknown" fraction. Therefore the medium peak given by o-cresol at 714cm^{-1} confirms the presence of this latter compound. Peaks which can be used in this way for confirmation will henceforth be indicated by (x).

Although there are no specific absorption maxima to confirm the presence of phenol and the two remaining cresols, previous retention time data alone practically assured their presence and the fact that satisfactory agreement has been obtained between the absorption maxima for fraction 1 and these control samples is sufficient evidence for their presence.

Of the "overlapping" compounds, 2:6-xylenol has been shown to be present, while the table provides strong evidence for the presence of 2:4- and 2:5-xylenol.

Table XIX.

Wave numbers ($cm.^{-1}$) for Fraction 2 and Control Samples.

Absorption peaks for Fraction 2	2:6-Xylenol	2:4-Xylenol	2:5-Xylenol	3:5-Xylenol	2-Ethylphenol	3-Ethylphenol	4-Ethylphenol	2.3-Xylenol	3:4-Xylenol
1109 m	1100 m	1100 s	1110 s	-	1108 s	1095 w	1110 m	1090 s	1118 s
1070 m	1082 m	-	-	-	1054 w	-	1063 w	1060 s	-
1038 m	-	1040 w	1036 m	-	1033 w	1045 w	1045 w	-	-
1019 s	1019 m	1010 w	-	1026 s	-	1000 w	1020 w	1020 w	1020 m
994 m	985 m	990 w	994 s	-	-	985 w	-	990 m	1000 s
966 w	-	-	-	-	966 w	-	-	-	-
945 w	950 w	-	-	943 s	-	-	-	950 w	943 m
929 m	-	926 w	930 m	-	926 w	-	-	-	-
905 m	909 m	-	-	-	-	905 s	-	900 m	-
870 m	-	872 m	870 m	870 m	-	862 m	-	-	865 s
834 s	828 m	-	847 m	834 s	840 s	-	828 s	-	842 m
816 s	-	815 s	801 s	-	-	-	810 m	820 m	811 s
775 s	768 s	769 s	-	-	787 w	780 s	-	768 s	-
752 s	-	-	750 w	-	749 sx	-	-	-	747 w
730 w	729 m	-	725 m	-	730 m	725 m	730 m	-	728 m
714 m	-	720 w	-	-	-	-	710 w	-	-
692 s	-	-	-	-	699 w	692 s	-	702 m	699 m
685 w	-	-	-	685 s	-	-	-	-	-

Fraction 2.

Specific absorption peaks for 3:5-xylenol and 2-ethylphenol are indicated (✓). The maximum at 749cm^{-1} in the spectrum of 2-ethylphenol is used for confirmation in the same way as with o-cresol in the previous fraction.

All the absorption peaks for the remaining control samples are present in the spectrum of fraction 2 but coincide with one another.

Neither of the weak absorption maxima given by 2:4-xylenol at 720cm^{-1} and 4-ethylphenol at 710cm^{-1} is alone sufficient to cause a medium peak at 714cm^{-1} in the spectrum given by fraction 2. This evidence indicates the presence of both compounds, one absorption peak reinforcing the other.

There are no specific absorption maxima to establish definitely the presence of the remaining compounds in this fraction, but the satisfactory agreement that has been obtained between the absorption peaks of each control sample and those given by fraction 2, in addition to the previous retention time data, gives strong evidence for their presence.

The compounds 2:3- and 3:4-xylenol are observed to be present in both fraction 2 and fraction 3. This overlap is expected because of the arbitrary cut taken.

Table XX.

Wave Nos. for Fraction 3 and Control Samples.

Absorption peaks for Fraction 3	2:3-Xylenol	3:4-Xylenol	3-iso-Propyl-phenol	4-iso-Propyl-phenol	2-Methyl-4-ethyl-phenol.
1290 s	1278 s	1295 s	1272 s	1291 m	1295 w
1260 s	-	1264 s	-	-	1260 s
1235 s	-	-	1242 s	1240 s	1225 m
1210 s	1210 m	1210 m	-	-	-
1198 m	-	1192 m/	-	-	-
1175 m	1180 m	-	1184 s	1181 s	1175 s
1157 s	1160 m	1152 s	1168 m	1156 m	1150 m
1111 m	-	1118 s	1120 w	1110 s	1110 s
1094 w	1090 s/	-	-	-	-
1070 w	1060 s	-	-	1065 m	-
1048 w	-	-	1050 w	-	1056 w
1016 s	1015 w	1020 m	-	1019 m	1035 w
1000 s	990 m	1000 s	1000 w	-	995 w
-	-	-	-	-	970 w
943 m	950 w	943 m	-	955 w	-
930 m	-	-	930 s	930 w	-
-	-	-	-	-	910 w
883 m	898 m	-	-	892 w	881 m
859 s	-	865 s	860 s	-	-
831 s	-	842 m	-	830 s	822 s
811 s	815 m	811 s	811 w	-	810 s
781 m	-	-	780 sx	-	785 w
762 w	768 s	-	-	-	765 m
747 m	-	747 w/	-	-	-
728 s	-	728 s/	-	-	-
712 w	-	-	-	710 mx	706 w
699 s	702 m	699 m	-	-	-
690 w	-	-	680 s/	-	-

Fraction 3.

Specific absorption maxima are given by 2:3- and 3:4-xylenol, and 3-isopropylphenol. The weak absorption peak at 712cm^{-1} in the spectrum of fraction 3 may well be a medium or even a strong peak in the spectrum of the pure compound causing it. The corresponding medium peak given by 4-isopropylphenol at this position therefore confirms the presence of this compound.

The sharpest of the cuts taken was between fractions 3 and 4 (Fig.32), and 2-methyl-4-ethylphenol, the next compound in the elution sequence, is the only constituent of fraction 4 which may also be present in fraction 3. There are no corresponding absorption peaks for 2-methyl-4-ethylphenol at 970cm^{-1} and 910cm^{-1} but since these are weak maxima in the control sample, it is quite possible that they may not be observed in the spectrum of a mixture like fraction 3.

Table XXI.

Wave Nos. (cm^{-1}) for Fraction 4 and Control Samples.

Absorption peaks for Fraction 4.	2-Methyl-4-ethyl-phenol.	3-n-Propyl-phenol	4-n-Propyl-phenol	2-Methyl-5-ethyl-phenol.	3-Methyl-5-ethyl-phenol.	4-Methyl-3-ethyl-phenol.	2:3:5-Tri-methyl-phenol.
1375 m	1370 w	1369 s	1364 m	1370 s	1375 w	1380 m	1380 m
1330 s	1320 m	-	1344 m	1334 s	1332 m	1330 m	-
1295 s	1295 w	1280 s	1288 s	1300 s	1290 s	1298 s	1308 s
1252 s	1260 s	-	-	1267 m	1250 w	1258 s	1265 s
1225 s	1225 m	1228 m	1231 s	1232 m	1214 w	1234 s	1220 m
1202 m	-	-	1207 s	-	-	1204 s	-
1180 m	1175 s	1175 s	1175 m	-	1180 m	-	1180 w
1161 m	-	-	-	-	1160 m	1162 s	1160 m
1154 s	1150 m	-	-	1140 s	1148 s	-	1140 m
1133 w	-	1135 m	1130 m	-	-	-	-
1119 m	1110 s	1122 m	1114 m	-	-	1122 m	-
1095 w	-	1090 m$\swarrow$	-	-	-	-	-
1076 w	-	-	-	1069 m	-	-	1075 s
1059 m	1056 w	-	-	-	1065 m	1060 m	-
1041 w	1035 w	-	-	1031 m	-	1041 w	-
1020 s	-	1015 m	-	-	1025 m	1015 m	-
999 w	995 w	-	-	-	1000 w	990 w	-
985 w	-	-	-	-	-	-	-
958 s	970 w	960 s	953 w	970 m	958 s	-	965 m
916 w	910 w	-	-	910 m	-	925 s	909 w
901 m	-	-	-	-	900 m$\swarrow$	-	-
878 w	881 m	888 s	-	-	-	870 s	-
865 m	-	866 m	-	-	855 m	-	-
844 s	-	-	850 w	840 s	845 s	-	838 s
819 m	822 s	825 m	820 s	-	830 m	-	825 s
805 w	810 s	805 m	-	-	-	805 s	-
785 m	785 w	782 sx	-	-	-	-	-
770 w	765 m$\swarrow$	-	-	-	-	-	-
745 w	-	750 m	-	-	-	-	743 w
727 m	-	-	-	-	-	-	-
717 w	706 w	-	-	-	-	-	708 w
693 s	-	690 m	-	-	693 s	-	-

Fraction 4.

Specific absorption peaks establish the presence of 2-methyl-4-ethylphenol, 3-n-propylphenol and 3-methyl-5-ethylphenol.

The absorption maxima given by 4-n-propylphenol and 4-methyl-3-ethylphenol, corresponding to 1202cm^{-1} in the fraction 4 spectrum, show that one or other of these compounds is present. Similarly the peaks for 2-methyl-5-ethylphenol and 2:3:5-trimethylphenol corresponding to wave number 1076cm^{-1} establish the presence of one or other of these compounds. This evidence in addition to previous retention time data gives a strong indication that all four compounds are present.

Overlapping compounds from fraction 5 are 4-methyl-3-ethylphenol and 2:3:5-trimethylphenol.

Table XXII.

Wave Nos. (cm^{-1}) for Fraction 5 and Control Samples.

Absorption peaks for Fraction 5.	2-Methyl-3-ethyl-phenol.	4-Methyl-3-ethyl-phenol.	2:3:5-Tri-methyl-phenol	2-Methyl-5-iso-propyl-phenol.	3:5-Diethyl-phenol	3:4:5-Tri-methyl-phenol	4 Indanol	4-n-Butyl-phenol.
1380 m	1380 m	1380 m	1380 m	1370 m	1370 m	1380 s	-	1375 s
1350 w	1355 s	1355 m	-	-	-	-	1350 w	-
1324 w	-	1330 m	-	-	1333 s	1318 s	-	-
1305 m	1295 s	1298 s	1308 s	1308 m	1296 s	-	1310 m	-
1278 s	1274 s	-	1265 s	1272 s	1270 m	1280 w	1275 s	-
1250 m	-	1258 s	-	-	-	-	-	1249 s
1230 w	1235 m	1234 s	-	-	1228 m	-	-	-
1221 m	-	-	1220 mx	-	-	1215 w	-	-
1198 s	-	1204 s	-	1197 s	-	-	1200 s	1190 s
1180 w	1187 s	-	1180 w	1170 m	-	-	-	-
1156 m	1169 s	1162 s	1160 m	-	1156 s	1150 s	1159 s	-
1139 m	-	-	1140 m	1129 s	-	-	-	-
1118 m	-	1122 m/	-	-	-	-	-	-
1110 w	1107 s	-	-	1100 m	-	-	-	1110 m
1080 s	1089 s	-	1075 s	-	-	-	-	1082 w
1060 w	1069 s	1060 m	-	1069 m	1061 m	-	1050 w	-
1030 w	1030 s	1041 w	-	1040 w	-	1030 m	-	-
1018 s	-	1015 m	-	-	1018 m	-	-	1018 w
1000 m	-	-	-	1000 s	-	-	1000 m	-
985 w	-	990 w	-	-	992 m	978 m	987 s	-
966 w	967 m	-	965 m	-	966 w	-	-	-
946 w	-	-	-	945 s/	-	-	-	-
921 w	-	925 s	-	-	932 s	-	-	930 w
912 w	-	-	909 w	-	-	-	910 w	-
889 w	892 s	-	-	-	886 w	-	-	885 w
873 m	881 s	870 s	-	-	-	-	-	-
864 m	-	-	-	867 s	-	865 m	-	-
845 w	-	-	-	-	855 s	850 m	-	850 m
837 m	-	-	838 s	-	-	-	-	829 s
816 m	819 w	-	825 s	820 s	-	-	818 w	-
796 w	790 s	805 s	-	-	-	-	-	-
772 w	775 s	-	-	-	-	-	775 s	765 m
746 w	-	-	743 w/	-	-	-	-	-
711 w	710 s	-	708 w	-	700 s	710 m	700 m	-

Fraction 5.

The compounds 4-methyl-3-ethylphenol, 2:3:5-trimethylphenol and 2-methyl-5-isopropylphenol are shown to be present by the specific absorption peaks indicated.

The weak absorption peak at wave number 912 cm^{-1} in the spectrum of fraction 5 may very possibly be a medium peak caused by the combined effects of the two weak absorption maxima given by 2:3:5-trimethylphenol and 4-indanol, thus giving evidence for the presence of the latter compound.

The compounds 3:5-diethylphenol, 3:4:5-trimethylphenol and 4-n-butylphenol each have an absorption peak which corresponds to 845cm^{-1} in the spectrum of fraction 5. At least one of these tar acids must therefore be present, and since these are three of the four compounds overlapping from fraction 6, the presence of all three is very probable.

The presence of 2-methyl-3-ethylphenol is strongly indicated by retention time data and the agreement shown in Table XXII between infra-red absorption peaks, but no specific absorption maxima are given.

Compounds overlapping from fraction 6 are 3:5-diethylphenol, 3:4:5-trimethylphenol, 4-indanol and 4-n-butylphenol.

Table XXIII.

Wave Nos. (cm^{-1}) for Fraction 6 and Control Samples.

Absorption peaks for Fraction 6.	3:5-Dimethylphenol.	3:4:5-Trimethylphenol.	4-Indanol	4-n-Butylphenol.
1155 m	1156 s	1150 s	1159 s	-
1138 s	-	-	-	-
1114 w	-	-	-	1110 m/
1083 s	-	-	-	1082 w/
1057 w	1061 mx	-	1050 w	-
1030 m	-	1030 m/	-	-
1022 m	1018 mx	-	-	1018 w
996 m	-	-	1000 m/	-
990 m	992 m	-	987 s	-
980 w	-	978 m/	-	-
966 m	966 w/	-	-	-
936 s	932 sx	-	-	930 w
919 w	-	-	910 w/	-
878 m	886 w	-	-	885 w
860 w	-	865 m/	-	-
856 s	855 s	850 m	-	850 m
828 w	-	-	-	829 s/
813 s	-	-	818 w/	-
771 s	-	-	775 s	765 m
732 s	-	-	-	-
700 s	700 s	710 m	700 m	

Fraction 6.

The range 1155-1380 (cm^{-1}) has been omitted since it consists of one broad absorption maximum in which any of the appropriate peaks given by the control samples may be present.

The presence of all four tar acids in this fraction is established by the specific absorption maxima indicated.

Compounds Identified.

Fraction 1.

Phenol
o-Cresol
m-Cresol
p-Cresol
2:6-Xylenol
2:4-Xylenol
2:5-Xylenol

Fraction 2.

2:6-Xylenol
2:4-Xylenol
2:5-Xylenol
3:5-Xylenol
2-Ethylphenol
3-Ethylphenol
4-Ethylphenol
2:3-Xylenol
3:4-Xylenol

Fraction 3.

2:3-Xylenol
3:4-Xylenol
3-isoPropylphenol
4-isoPropylphenol
2-Methyl-4-ethylphenol

Fraction 4.

2-Methyl-4-ethylphenol
3-n-Propylphenol
4-n-Propylphenol
2-Methyl-5-ethylphenol
3-Methyl-5-ethylphenol
4-Methyl-3-ethylphenol
2:3:5-Trimethylphenol

Fraction 5.

2-Methyl-3-ethylphenol
4-Methyl-3-ethylphenol
2:3:5-Trimethylphenol
2-Methyl-5-isopropylphenol
3:5-Diethylphenol
3:4:5-Trimethylphenol
4-Indanol
4-n-Butylphenol

Fraction 6.

3:5-Diethylphenol
3:4:5-Trimethylphenol
4-Indanol
4-n-Butylphenol

3.3.3. Study of Further Stationary Phases.

Using Apiezon L grease it was not possible to resolve the compounds present in fractions 4 and 5 respectively, because of their similar retention times. It is therefore desirable to obtain a stationary phase in which these compounds have widely differing elution times and which would therefore produce satisfactory resolution.

The study of a large number of fixed phases has not been possible and the retention times of the tar acid control samples have been obtained using only silicone grease (W.Edwards and Co.,Ltd.) and polythene. Both packings were made up by dissolving the fixed phase in solvent, mixing with the Celite in the same proportion as before and removing the solvent under vacuum. Solvents used were benzene for the silicone grease and trichlorethylene for the polythene.

These stationary phases were chosen because of their expected stability at high column temperatures over prolonged periods. The results obtained are shown in Tables XXIV and XXV, corrected retention volumes per gram of stationary phase again being given.

Table XXIV.

Stationary Phase:- Silicone Grease.

Fraction No.	Compound	R_T (min.)	V_R^0	Vg.
1	Phenol	5.9	57.1	28.3
1	o-Cresol	9.8	82.9	41
1	p-Cresol	10.5	95	47
1	m-Cresol	10.0	96	48
2	2:6-Xylenol	13.1	113	56
2	2:5-Xylenol	15.2	132	66
2	2:4-Xylenol	15.2	131	65
2	3:5-Xylenol	17.0	144	72
3	2:3-Xylenol	17.4	150	74
3	3:4-Xylenol	19.7	170	84
2	3-Ethylphenol	16.6	136	68
3	3-isoPropylphenol	22.7	196	97
3	4-isoPropylphenol	22.5	192	95
4	2-Methyl-4-ethylphenol	23.8	208	103
4	3-n-Propylphenol	26.2	227	112
4	4-n-Propylphenol	26.0	222	110
4	2-Methyl-5-ethylphenol	24.5	214	106
4	3-Methyl-5-ethylphenol	26.2	221	109
5	2-Methyl-3-ethylphenol	26.0	212	105
5	2:3:5-Trimethylphenol	29.2	229	113
5	4-Methyl-3-ethylphenol	30.0	246	122
5	2-Methyl-5-isopropylphenol	30.2	250	124
6	3:4:5-Trimethylphenol	36.0	267	132
6	3:5-Diethylphenol	38.6	282	140
6	4-n-Butylphenol	43.1	354	175

Column :- 4mm.
Column Temperature :- 158°C
Flash Heater Temperature :- 240°C
Inlet Nitrogen Pressure :- 37.5cm.
Outlet Pressure :- atmospheric
Flow Rate :- 5.0ml./min.

Table XXV.

Stationary Phase:- Polythene.

Fraction No.	Compound	R_T (min.)	V_R^0	Vg.
3	3-isoPropylphenol	37.8	427	177
3	4-isoPropylphenol	37.6	425	176
4	2-Methyl-4-ethylphenol	43.8	485	200
4	3-n-Propylphenol	46.0	519	214
4	4-n-Propylphenol	44.5	503	208
4	2-Methyl-5-ethylphenol	46.0	519	214
4	3-Methyl-5-ethylphenol	47.0	535	221
5	2-Methyl-3-ethylphenol	52.0	589	244
5	2:3:5-Trimethylphenol	52.2	593	245
5	4-Methyl-3-ethylphenol	54.0	611	252
5	2-Methyl-5-isopropylphenol	60.0	656	272
6	3:4:5-Trimethylphenol	66.0	806	333
6	3:5-Diethylphenol	66.5	800	330
6	4-n-Butylphenol	74.0	875	362

Column :- 4mm.
Column Temperature :- 158°C
Flash Heater Temperature :- 230°C
Inlet Nitrogen Pressure :- 37.5cm.
Outlet Prossure :- atmospheric
Flow Rate :- 6.5ml./min.

Discussion of Results.

In Tables XXIV and XXV atmospheric outlet pressure was employed with the 4mm. column to give the maximum resolution possible with these stationary phases. The fractions in which the various compounds were found to be present are indicated. In Table XXV retention times are given only for the compounds present in the later fractions. Inlet pressure and flow rate conditions were constant while obtaining each result but, in a few cases, varied slightly from run to run.

With silicone grease as stationary phase the order of elution of the tar acids is practically unaltered. Also, the compounds present in fraction 4 and fraction 5 of the tar acid extract again have elution times which are too close together for their resolution to be possible.

With polythene little alteration in the order of elution is observed. Slightly increased resolution of the compounds in fraction 4 appears possible while resolution of those in fraction 5 seems to be more pronounced. The corresponding elution peaks given by the actual tar acid fraction, however, are broader than those given by the pure tar acids since a larger sample quantity is added in order to show up trace components as sizeable elution peaks. Therefore in the chromatogram of the tar acid distillate the peaks will tend to merge into one

another, and it is doubtful if the slight increases in resolution that have been obtained will be of any practical value in the separation of these compounds. A difference of at least 5 minutes in retention time is desired between adjacent phenols present in fractions 4 and 5.

For further resolution of the components in fractions 4 and 5 of the tar acid cut, the most suitable stationary phase can only be found by experiment, since the relatively high operating temperatures preclude the use of a number of fixed phases suitable for their chemical characteristics.

A satisfactory fixed phase may be obtained by distillation of the original tar acid extract from which the 230-250°C fraction was taken. Continual distillation of this extract will produce a high boiling tar acid residue which would be an ideal fixed phase from the chemical standpoint and which may be suitable for use at 183°C.

The use of polyethylene glycols should also be worth investigation.

Column Efficiencies.

The efficiency of the silicone grease column varied from 400-850 plates (phenol to 4-n-butylphenol) and from 570-810 with the polythene column. The efficiency of the previous Apiezon L column at 158°C varied from 580-1100 plates. Direct comparison of the efficiencies of

the first two columns with the Apiezon L column cannot be made, however, since

(a) The same sample quantities were not necessarily used in obtaining the peaks used for calculation of the plate numbers.

(b) Different operating conditions were used with the Apiezon L column.

Nevertheless, since atmospheric outlet pressure was used with the silicone grease and polythene columns, it was expected that these columns would have had higher plate efficiencies than the Apiezon L column. This has not occurred, probably because of the difficulty in completely dissolving silicone grease and polythene in a suitable solvent, with the result that these stationary phases were not dispersed on the Celite as uniformly as the Apiezon L grease.

3.3.4. General Conclusions.

The examination of some 30 tar acid control samples, ranging in boiling point from 180-250°C, on Apiezon L grease, silicone grease and polythene as fixed phases, showed that separation was only possible of certain groups of compounds. Retention time data obtained at three different temperatures with Apiezon L indicated the improvement in resolution that was obtained by reducing the temperature, but an operating temperature of 135°C appeared to be the lower limit for these compounds with the present apparatus unless a more sensitive detector was employed.

In the examination of a phenolic extract from a low-temperature coal tar, the separation of the total tar acids was abandoned for three reasons:-

1) Comparison samples were available for a boiling range of 180-250°C alone.

2) Little fractionation of compounds boiling above 250°C was obtained by gas chromatography.

3) The length of time required for the elution of the total tar acids in each run was excessive and, for the above reasons, unjustified.

Examination was therefore confined to the fraction 230-250°C distilled from the tar acid extract and containing probably 30 phenols at least. Identification of each constituent by gas-liquid chromatography alone was not possible with the stationary phases employed. The

technique was therefore used as a means of separating the phenolic extract into fractions containing a smaller number of constituents. For this purpose chromatographic columns with internal diameters of 1cm. and 2cm. were employed. These could accommodate larger samples than the normal 4mm. bore analytical columns. Probable compounds in each separated fraction were indicated by retention time data and confirmed by subjecting each fraction to infra-red spectroscopy. In this way some 28 tar acids were identified.

The stationary phases silicone grease and polythene were investigated but gave no improvement on the separations achieved with Apiezon L grease. The high operating temperatures used in the analysis of tar acids limits the choice of stationary phases and a suitable fixed phase can only be found by experiment.

3.4. Some Practical Problems in Gas-Liquid Chromatography.

(a) Heating Liquids.

Temperature control is maintained by the vapour of a boiling liquid. Since this liquid refluxes 8 hours per day for perhaps several months at a time, it must be stable against decomposition and oxidation. As the vapour jacket is constructed in copper tubing, corrosion by the heating liquid must also be considered. This precludes the use of the stable halogenated benzenes and toluenes.

Catalytic decomposition of the liquid by the copper jacket may also prevent the use of a heating liquid which is suitable when the vapour jacket is constructed in glass. In the work described cyclohexanone was used to maintain a temperature of 155°C, a pure cut being employed. After approximately five weeks the base line on the recorder became irregular and the deterioration increased over the next two days. When it was observed that it was now taking longer to heat the cold liquid to the reflux stage, the solvent was examined and was now found to resemble a lubricating oil in appearance and viscosity. There is a known reaction for cyclohexanone, in which $\frac{1}{6}$ of the ketone condenses to a double ring compound on refluxing for 116 hours, with $\frac{5}{6}$ of the ketone recovered. It is probable therefore that the ketone had condensed almost 100 per cent to form a multi-ring compound on refluxing for

5 weeks (more than 200 hours) in the presence of a copper catalyst.

Cyclohexanol (158°C) was substituted for cyclohexanone and proved satisfactory, its only disadvantage being that a small quantity of water (less than 1 ml.) was formed from day to day. This was also experienced with ethylene glycol monoethyl ether and 2-ethylhexanol. This difficulty was overcome by removing the first few mls. of the heating liquid in its initial "boil up".

(b) Stationary Phases.

For a given separation it is desirable to use a stationary phase which is of the same chemical nature as the compounds being analysed.

For the separation of high boiling tar acids liquid phases such as high boiling alcohols or glycols which contain hydroxyl groups, could not be used because of their possible loss from the column at high temperatures. In the absence of a hydroxyl group it would be desirable that an aromatic fixed phase be employed. However, benzyldiphenyl is unsuitable for use above 150°C and fluorene picrate starts to decompose at 130°C.

Therefore, in this work, choice of stationary phase has been limited by the high operating temperatures and a number of fixed phases which have appeared suitable from the chemical standpoint have had to be discarded.

Apiezon L stopcock grease has been used successfully

for several months at 183°C. In the course of this period the packing changed from yellow to a very dark brown in colour, but retention times were unaltered and the efficiency of the material does not seem to have been impaired. Both silicone grease and polythene were suitable at a temperature of 158°C.

(c) Column Packing.

After a new column had been used for a day, it was observed that "cracks" had appeared in the packing. These were removed by vibrating the column and pushing the packing down with a close fitting glass plunger in the same way as before. This process had to be repeated after the second, and sometimes the third day before no further "cracks" appeared in the packing. The column was now fairly tightly packed and in some cases a suitable flow rate could not be obtained without the use of the vacuum pump. The reason for the appearance of these "cracks", despite careful packing technique, is rather uncertain but the cause may have been incomplete removal of the solvent used in the distribution of the fixed phase. The elution of solvent traces by the nitrogen stream would make the packing contract with the subsequent appearance of "cracks". This does not, however, explain the recurrence of "cracks" after a second day's work with the column.

3.5 Discussion of Gas Chromatography Apparatus.

Little success was experienced in the earlier part of this work with an electrically-heated apparatus and rather than carry out the extensive modifications that were necessary, it was decided to change to a vapour-heated apparatus which would give greater uniformity of temperature. Nevertheless, electrically-heated units do possess some advantages over vapour-jacketed columns and well-designed units have been used by a number of workers[24,38]. The relative merits of both types of apparatus will therefore be discussed.

3.5.1. The Relative Merits of Electrically-Heated and Vapour-Heated Apparatus.

Recent electrically-heated units incorporate a system of fans to distribute the heated air and provide a uniform temperature throughout the column. Also, satisfactory base line stability is given and this may well have been achieved with the apparatus used in the earlier part of this work if the detector and chromatographic columns had been enclosed within the same heating jacket or if the detector had been designed with an air jacket between the detector block and heater.

Vapour-heated apparatus usually incorporates the detector and chromatographic columns within a single unit and both are heated by the vapour from the same heating liquid boiling under reflux. Uniformity of temperature therefore

depends on the purity of the heating liquid and on stable reflux conditions. No temperature gradient exists over the length of a vapour-jacketed column whereas a highly efficient fan system must be employed to prevent this occurring with an electrically-heated unit.

Changes in barometric pressure can affect the temperature of a vapour-heated column but will have no effect on the uniformity of column temperature. These changes can produce slight differences in elution times from day to day but by using relative retention times reproducible results can be obtained. Change in barometric pressure is probably not the only reason for slight alterations in elution times since these can also occur with electrically-heated units

To change the operating temperature of a vapour-heated unit the heating liquid must be removed, the column and boiler flushed out with acetone and the fresh distilled solvent added. Further delay is caused in heating the cold liquid to the reflux stage. It is therefore unsuitable to use two different operating temperatures in the same day. An electrically-heated apparatus, on the other hand, has a greater flexibility of temperature. The operating temperature can even be changed during a run if required.

The upper temperature limit of a vapour-heated apparatus is determined by the availability of a solvent which would be stable under reflux conditions for long periods at the high temperature. No such problem exists with an electrically-heated unit.

3.5.2. Recommendations for the Design of a Gas-Liquid Partition Apparatus.

Temperature Control.

It is felt that greater uniformity of temperature is given by a vapour-jacketed column. Also, design difficulties are fewer than those encountered with an electrically-heated unit, e.g. a fan system for distribution of heat, elimination of a temperature gradient throughout the column.

The chromatographic columns and detector should be enclosed within the same heating jacket.

Detector.

The katharometer has been used in this work and has proved fairly satisfactory. It has, however, two main disadvantages:-

1) Decrease of sensitivity with increase in operating temperature.

2) Possible decomposition of thermolabile compounds by the hot wire of the thermal conductivity cell.

The first disadvantage can be overcome by increasing the current supplied to the bridge, by the use of an additional amplifier between the detector and the recorder, or by the use of a mobile phase with a high thermal conductivity.

Of the remaining detectors, hydrogen microflare devices are considered unsuitable as they destroy the

compounds being separated. In the analysis of an unknown mixture it is frequently necessary to collect the separated compounds and submit them to mass spectrometry or infra-red spectroscopy.

The gas-density balance does not exhibit any decrease in sensitivity with temperature nor is there any possibility of decomposition of the compounds being analysed. Although no experience has been gained of this detector, it is nevertheless recommended for its consistently high performance over a wide range of experimental conditions.

Chromatographic Columns.

Straight analytical columns are recommended because a loss of efficiency is caused by the packing at the bends of a U-tube or spiral column.

Mobile Phase.

With a katharometer detector the choice of mobile phase may depend on the sensitivity required. Nitrogen and helium have been employed.

With the gas density balance nitrogen has proved satisfactory.

Inert Support.

Celite 535 containing 30 per cent stationary phase was found to pack down very tightly in the 4mm. bore columns and a suitable flow rate could not have been obtained in many cases without reduced outlet pressure. When the column

was packed loosely, "cracks" appeared after a short period of working. A coarser material such as "Sterchamol", although well packed in a column, should give faster flow rates and eliminate the necessity for reduced outlet pressure. Resolution of components would therefore be increased.

Introduction of Samples.

The micropipette method is preferred, its main advantage being that the sample is applied directly to the column packing.

APPENDIX I.

Correction for Gas Compressibility.

The assumption is made that the partial pressures of the substances to be separated are negligible relative to that of the stream of carrier gas.

Let

p_1 = pressure of gas applied to chromatogram.

p_o = pressure of gas at outlet.

p = pressure of gas at point distant x from the outlet.

v = linear velocity of gas at point x.

L = length of column.

t = time which elapses before the centre of the zone emerges from the column (the retention time).

F = volume of gas emerging from outlet in unit time.

V_R = tF = the retention volume of the centre of the zone.

V_R^o = limiting value of V_R as p_1/p_o tends to unity.

a = the area occupied by the gas phase in any cross-section of the column.

K = the column constant, a function of the viscosity of the gas phase and the tightness of the column packing.

then $$K\frac{dp}{dx} = \frac{Fp_o}{p} = av$$

Integrating to give the pressure along the column:

$$K\frac{p^2}{p_o} = 2Fx + Kp_o$$

or $$K = \frac{2Fxp_o}{p^2 - p_o^2}$$

or $$F = \frac{p_oK}{2x}\left[\left(\frac{p}{p_o}\right)^2 - 1\right] \quad .. \quad .. \quad (1)$$

Now

$$t = \int_0^L \frac{dx}{vR_F} = \int_0^L \frac{a\ p\ dx}{R_F p_o F} \quad .. \quad .. \quad (2)$$

Here R_F has the usual chromatographic meaning, that is, it represents the rate of movement of the zone of the substance under consideration relative to the rate of flow of the moving phase. In the present case the rate of flow of the moving phase increases continuously as it advances down the column, but the R_F remains constant and the rate of movement of the zone increases correspondingly. The R_F is a constant depending only on the substance to which it refers, the temperature, the nature and amount of the stationary phase and, in so far as the support is not inert, on its amount.

Rewriting Equation 2 in terms of pressures,

$$t = \int_{p_o}^{p_1} \frac{Kap^2\ dp}{R_F\ F^2\ p_o^2} = \frac{Ka\ (p_1^3 - p_o^3)}{3\ R_F\ p_o^2\ F^2}$$

$$V_R = K\ a\ p_o \frac{\left[(p_1/p_o 3) - 1\right]}{3\ R_F\ F}$$

Hence by (1), if $x = L$ then $p = p_1$

$$V_R = \frac{2}{3} \frac{aL}{R_F} \left[\frac{(p_1/p_o)^3 - 1}{(p_1/p_o)^2 - 1}\right] \quad .. \quad .. \quad (3)$$

As p_1/p_o tends to unity then V_R tends to $V_R^0 = \frac{aL}{R_F}$

Calculation of Column Efficiency.

Two methods of calculating the number of theoretical plates from the experimental curves have been described by Martin and James[3].

Method 1.

Let r = no. of theoretical plates in the column. The assumption is made that all the material (M equivalents) is put on in the first plate. The quantity occurring in the last plate at the maximum concentration

$$= \frac{M}{\sqrt{(2\pi r)}} \text{ equivalents}^{12}$$

Let q be the fraction of the original quantity occurring in any plate, and let the time taken for the centre of the zone to reach the last plate be t min. Therefore the time taken for contents of last plate to escape = t/r min.

Then Mq max. = $M/\sqrt{(2\pi r)}$ equivalents

and Mq max. r/t = maximum rate of escape.

= max. slope of experimental curve

= S equiv./min.

$$\therefore \quad S = Mr/t\sqrt{(2\pi r)} \text{ equiv./min.}$$

$$\therefore \quad r = \frac{2\pi S^2 t^2}{M^2} \qquad .. \quad .. \quad (4)$$

In the recorded chromatogram the peak height of the vapour (h) will be proportional to S

$\therefore$ $S = Kh$ where K is a constant (for a detector with a linear response).

The distance L to the centre of the peak is directly proportional to t

$\therefore$ $t = kL$

and the area (A) under the peak is proportional to the size of the original vapour sample since

$$M = \int_0^\infty Khdt = Kk \int_0^\infty h\, dL = KkA$$

$$\therefore \quad r = 2\pi \frac{h^2 L^2}{A^2}$$

Method 2.

The area between ordinates one standard deviation on either side of the peak of an error curve is 68.3 per cent of the total. From the theory[12] the shape of the chromatographic zone should approximate to an error curve and 68.3 per cent of the material should be included between plates $\pm \sqrt{r}$, where r is the total plate number.

The ratio of the time taken for the centre of the zone to emerge (t) to the time taken for the middle 68.3 per cent of the zone (T) = $r/2\sqrt{r}$

$$\therefore \quad r = \frac{4t^2}{T^2}$$

Figures obtained by the two methods for the same column show only fair agreement. This might be expected since experimental peaks only approximate to error curves. Also with either method it is usually not possible to calculate values of r with great accuracy, particularly as they depend upon the squares of measurements. Therefore small variations in the number of theoretical plates are of little significance.

APPENDIX II.

Paper Chromatography of Some Tar Acids.

Summary.

Paper chromatography has been used for the separation and identification of synthetic tar acid mixtures.

Investigation has been made of several spraying reagents to locate the tar acids on a developed chromatogram. Diazotised sulphanilic acid was the most useful while ultra-violet light was ideal for detecting spots without causing spreading.

The best method of separation was to couple the tar acids with diazotised sulphanilic acid and develop the chromatogram with methyl ethyl ketone saturated with water.

The use of methyl ethyl ketone was dependent on temperature control and R_F values were difficult to reproduce. However, if a control paper containing the suspected tar acids was run alongside the paper containing the mixture, the constituents were easily identified.

The compounds 2:4- and 2:5-xylenol and 2:3:5-trimethylphenol could not be detected on the chromatogram either when diazotised in a mixture or singly. Steric hindrance probably prevented coupling.

Apparatus.

Chromatography Vessel.

The vessel was a large wooden tank 16 x 24 x 30 inches, constructed of plywood. This was lined with $\frac{1}{8}$ inch sheet glass fitted at either side with two aluminium brackets which support three glass developing troughs when the vessel was used for downward development. Glass rods placed between the racks keep the papers from touching the sides of the troughs. A plate glass cover sealed to the tank with putty made the vessel gas tight.

The tank can be adapted for upward development by replacing the troughs with glass rods round which the paper is pinned, and dipping the paper in the troughs now placed on the bottom of the vessel.

Preparation of Solvent.

The organic solvent was shaken with water in the desired proportions and allowed to separate. The organic layer was used for developing the chromatogram and the aqueous layer for saturating the atmosphere.

Drying Cabinet.

Since the papers should be dried horizontally, shelves were made by stretching fine muslin cloth between eye-hooks. A fan in the base of the cabinet ensured a uniform temperature of 35°C.

The Detection of Tar Acids on Paper Chromatograms.

Spots of the tar acid solutions were made on the chromatographic paper using a micropipette. The capillary of the micropipette contained 0.001ml.

The only tar acid samples available at the time were:-

Phenol	2:4-Xylenol	3:4-Xylenol
o-Cresol	2:5-Xylenol	2:3:5-Trimethylphenol
m-Cresol	3:5-Xylenol	3-Methyl-5-ethylphenol
p-Cresol	2:3-Xylenol	4-Indanol.

Use of Ultra-Violet Light.

Using 0.001ml. of a 25% tar acid solution, the acetone evaporating and leaving the tar acid "spot", only phenol, o- and m-cresol failed to show up as dark blue absorption spots.

Use of Spraying Reagents.

If a spraying reagent is used it should, ideally, react only with the compound sought and not with any impurities, nor should it attack the paper. It is also an advantage if different colours are obtained for each specific substance since this aids identification. The results obtained with some spraying reagents are given in Table I.

Table I.

Reagent	Concentration	Colour-ation	Comments
Ferric chloride	2% aqueous	None	Reagent rejected.
Ferric chloride + potassium ferricyanide	1% $FeCl_3$ + 1% $K_3Fe(CN)_6$	Deep blue	Colour spread badly - rejected.
Millon's Reagent	1 part Hg + 2 parts fuming HNO_3. Soln. diluted with 2 vols. water.	Faint yellow or brown	Second spray produces colour. Corrosive, poor colour - rejected.
Phosphomo-lybdic acid	2% aqueous	Faint blue	Fairly suitable.
Ammonium vanadate	Aqueous satd. soln.	Slight trace of green.	Rejected.

Diazotised Sulphanilic Acid.

The sulphanilic acid (4g.) was dissolved in sodium hydroxide and the solution neutralised with hydrochloric acid. There were then added 50ml. of 10% hydrochloric acid and the mixture cooled to 0°C. To the solution 20ml. of 10% sodium nitrite were added slowly with stirring. The diazotised sulphanilic acid began to precipitate and so excess sodium hydroxide was added, the resulting solution being stored in a refrigerator

until required. When used as a spray, the solution was diluted with about ten times its volume of water.

The colour produced by the reagent with the tar acids ranged from orange to yellow but spread badly however, and gave in addition a coloured background. The reagent was therefore rather unsuitable.

Conclusions.

Of the methods of detection, the best results were obtained with ultra-violet light alone. The diazonium salt proved useful to show up phenol, o- and m-cresol, which did not appear under ultra-violet light.

The Use of Various Developing Solvents.

Spots of each tar acid were put along one edge of the sheet of filter paper and developed (downward) using various solvent systems:-

(a) n-Butanol/aqueous satd. sodium bicarbonate solution, paper buffered to pH8[39].

(h) Aqueous carbonic acid, pH4.2[40].

(c) Benzene/formic acid[41].

(d) Carbon tetrachloride/acetic acid/water[41].

Development was rapid and in all cases the spots were too close to the solvent front for any separation to be possible.

N-N-Dimethylformamide.

This solvent is miscible with water and as the tar acids are more or less insoluble in water, it was hoped that by varying the ratio N-N-dimethylformamide/water a separation could be obtained.

With 10 parts water to 1 of solvent long streaks stretching from the starting line were obtained for each compound.

With the mixtures 1:2, 1:2.2, 1:2.5, 1:3 of solvent: water, the phenols were merely pushed back from the solvent front as the water content increased without any improvement in separation.

Development of Tar Acids as Diazonium Salts.

The tar acids were coupled with diazotised sulphanilic acid and the coloured dyes developed with methyl ethyl ketone saturated with water[42]. The chromatographic paper was sprayed with 4% sodium carbonate and dried before use.

Test I.

Three papers each containing the twelve phenols were run by downward development for six hours. R_F and Rp values were calculated where:-

$$R_F = \frac{\text{distance moved by substance}}{\text{distance moved by solvent front.}}$$

$$Rp = \frac{\text{distance moved by tar acid azo compound}}{\text{distance moved by p-cresol azo compound.}}$$

The results are shown in Table II.

Table II.

Compound	R_F values			Rp values		
	1	2	3	1	2	3
Phenol	0.14	0.12	0.13	0.25	0.25	0.24
o-Cresol	0.22	0.22	0.25	0.40	0.47	0.46
m-Cresol	0.23	0.22	0.24	0.42	0.47	0.45
p-Cresol	0.55	0.47	0.54	1.0	1.0	1.0
3:4-Xylenol	0.63	0.53	0.58	1.2	1.1	1.1
3:5-Xylenol	0.40	0.40	0.38	0.73	0.85	0.71
2:3-Xylenol	0.38	0.39	0.37	0.69	0.83	0.69
2:4-Xylenol	)					
2:5-Xylenol	)	did not couple				
2:3:5-Trimethylphenol	)					
3-Methyl-5-ethyl-phenol	0.43	0.37	0.37	0.78	0.79	0.69
4-Indanol	0.21	0.21	0.21	0.38	0.45	0.39

Test II.

Separation was attempted of the following mixtures, made up from the recrystallised dyes:-

(1) Phenol, o-cresol, m-cresol, p-cresol, 3:4-xylenol and 3:5-xylenol.

(2) 3:4-Xylenol and 3:5-xylenol.

(3) 2:3:5-Trimethylphenol, 3-methyl-5-ethylphenol and 4-indanol.

Duplicate chromatograms were run for 16 hours by the ascending method, the individual tar acid dyes being run at the same time on two other papers. Most of the components of each mixture were separated, the R_F values being greater than those obtained in the previous test because of the increased development time (Table III). The only compounds not separated

Table III.

Compound	R_F values				Rp values	
	1	2	Separations		1	2
Phenol	0.14	0.16	0.20	0.19	0.17	0.21
o-Cresol	0.40	0.38	0.37	0.37	0.50	0.49
m-Cresol	0.37	0.35			0.46	0.45
p-Cresol	0.81	0.77	0.76	0.78	1.0	1.0
3:4-Xylenol	0.88	0.83	0.88	0.88	1.1	1.1
3:5-Xylenol	0.65	0.56	0.63	0.65	0.81	0.73
3-Methyl-5-ethylphenol	0.84	0.82	0.81	0.82	1.0	1.0
4-Indanol	0.45	0.44	0.44	0.44	0.55	0.55

were o- and m-cresol. These compounds could both be separated from p-cresol but not from each other.

Test III.

The previous mixtures were made up and this time diazotised as a whole, as would be the case in an actual analysis. The alkaline dye solutions were spotted directly on to the paper and developed for 16 hours by the ascending method using methyl ethyl ketone/water. The same separations as before were achieved.

Discussion of Results.

The R_F values varied between tests probably because the volatile methyl ethyl ketone is very sensitive to temperature variations. Closer agreement is obtained if R_P values are used.

In all cases streaks rather than round spots were observed. This may have been caused by the tar acids coupling in more than one position, development then causing the isomers to spread into a streak.

The compounds 2:4-xylenol, 2:5-xylenol and 2:3:5-trimethylphenol do not appear to couple, probably because of steric hindrance.

Chromatographing tar acid mixtures as the alkaline azo dye solutions appears to be a suitable method

for separation, but unless the chromatograms are run under standard conditions, it is safer to run a control paper containing the suspected phenols alongside the paper containing the mixtures.

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