

L I Q U I D - S O L I D A D S O R P T I O N S T U D I E S

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THE SEPARATION OF A LUBRICATING OIL

A thesis submitted for the degree of

Doctor of Philosophy

IN THE VICTORIA UNIVERSITY OF MANCHESTER

BY

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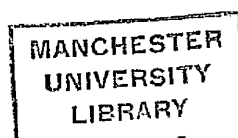
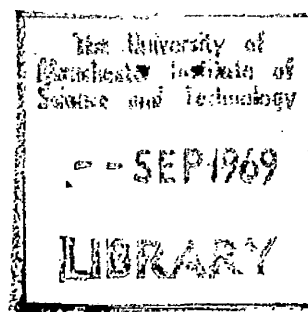
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Inside back cover scale for N_D^{25} v. volume of effluent graphs.

S U M M A R Y

A batch slurry method of separating oil fractions has been investigated and developed. It has been shown that by adsorbing most of the oil onto an adsorbent, and then desorbing it in stages, a fraction rich in polynuclear aromatic compounds can be obtained. The time taken to prepare this fraction was much less than would have been necessary by conventional chromatographic methods on an adsorption column.

By chromatographic analysis of the samples produced, it has been demonstrated that an equilibrium is established in each batch slurry stage, between concentrations in the adsorbed phase and the liquid phase for both polar and saturate compounds. Isotherms showing the relationship between the amount adsorbed and the amount in the bulk liquid phase have been determined for both types of compounds. These isotherms have been used to estimate the number of theoretical stages required for complete desorption of each type of molecule, and also illustrate the separation taking place between saturate and polar molecules at each stage of a batch slurry process. Application of these isotherms to column chromatography is also discussed.

A method of estimating the saturate content of an oil sample based on refractive index has been investigated, and a correlation depending on the type of separation used on the oil has been suggested.

An investigation into the separation of a test mixture by elution chromatography in an adsorption column has been carried out. It was found that several of the variables which have been reported to affect the separation considerably in frontal analysis did not appear to have a significant effect in elution analysis.

INTRODUCTION

A systematic analysis of the light lubricating oil fraction of petroleum has now been carried out for a number of years, and has developed along two main courses. In the U.S.A. a large programme sponsored by the American Institute of Petroleum, known as Research Project 6, has been concerned with the isolation and identification of individual compounds in petroleum. It has been estimated that about three thousand compounds exist in detectable quantities, although many millions of isomers are theoretically possible. So far, about 500 compounds have been identified.

In this country, the work has its origins in Lancashire cotton industry, where mill-workers were liable to develop skin cancer due to contact with oil used on the machinery. This disease became known as "mulespinners cancer", although it was also recognised in various forms in the coal-tar and shale-oil industries. Legislation was introduced to ensure the use of refined oils between certain limits of density and viscosity, but this did not attack the roots of the problem, and so, in 1948, work was started on lubricating oil analysis with a view to identifying individual carcinogenic compounds. This was sponsored by the Medical Research Council, in conjunction with the Institute of Petroleum Research Group No.2.

Oil separations were carried out in the Department of Chemical Engineering at Birmingham University, and since 1956 at the University of Manchester Institute of Science and Technology.

The methods used were (i) low pressure distillation, (ii) liquid extraction, (iii) liquid-solid adsorption chromatography. A more detailed account is given elsewhere by the author (2). All three of these methods have been used at Manchester, although the main emphasis has been on column chromatographic separations.

Part I of this thesis describes some preliminary investigations into column separations using a five-component test mixture. Part II is concerned with widening the application of adsorption to include a batch slurry process.

P A R T I.

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CHAPTER 1. LITERATURE SURVEY ON

ADSORPTION

1.1. Adsorption may be defined as the tendency of a solution to increase its concentration at a liquid-solid interface if by doing so the surface tension at the interface is reduced.

The phenomenon of adsorption has been known for many years, but the first recorded experiments were the classic work of Tswett, a Russian botanist, at the turn of the century. As he was working with naturally occurring pigments he called the process chromatography. Nowadays much of the work is performed on colourless compounds and the term "adsorption analysis" is preferred by many workers.

Following Tswett's work, and that of Day (see Chapter 2), many applications were found for solid-liquid chromatography in the field of dyestuffs, petroleum chemistry, vitamins, plant pigments, antibiotics etc.

Gas-solid adsorption has also been used, normally with charcoal, alumina or silica as adsorbents to purify gas streams, dry gases or extract valuable components present in small quantities.

An example of this is the Hypersorption Process (1) in which natural gas is continuously passed up beds of charcoal. Ethylene is adsorbed from the gas stream reducing its ethylene content from 6% to 0.1%, and the ethylene is recovered from the charcoal by desorption at over 92% purity. Ion exchange chromatography, and paper chromatography have been developed from these techniques to effect fine separations of very small quantities of materials.

In 1951, James, Martin and Synge developed what is now known as gas-liquid chromatography (G.L.C). They were interested in separating fatty acids and devised a method in which the sample was vaporised in an inert gas stream, and the sample components were distributed between a stationary liquid phase on an inert solid support, and the inert gas stream. It was found that good separation was achieved between the components and the mechanisms were very similar to adsorption chromatography except that the "adsorbent" was a liquid phase. This method has been developed at a phenomenal rate and is now a standard analytical tool for a whole range of compounds in chemistry, botany and zoology.

1.2. THE NATURE OF ADSORPTION

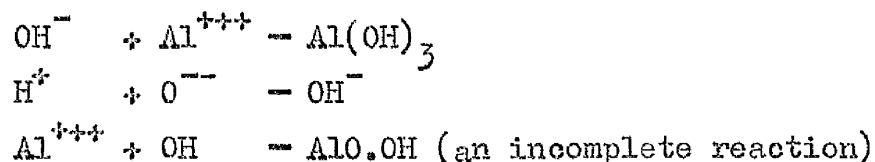
When a number of solutes are passed down a column, the relative positions taken by each solute depend on their free energy of adsorption, while their rate of travel down the column depends on their rate of desorption.

In practice, almost all organic compounds, except saturated aliphatic hydrocarbons, are retained on alumina, and as alumina has been used in this work, most of the discussion will refer to alumina.

It is well known that interfaces between water and non-conducting solids have a charge arising from an electrokinetic potential. This may be due to various causes, such as ionization of groups in the solid surface, orientation of the solvent molecules at the interface, or unsatisfied charges in the solid surface caused by previous mechanical treatment.

D.J. O'Connor et al (5) have shown that the latter can occur through grinding, or even simple handling and abrasion. This will leave Al^{+++} ions and O^{--} ions, and the surface will be in an activated state.

When water is adsorbed, it is ionised, and three reactions will take place:



Commercial alumina is prepared by low temperature (below 700°C) dehydration of alumina trihydrate and is a mixture of γ alumina, some $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and some Na_2CO_3 .

The electrokinetic potential depends on the pretreatment. Ignition below 400°C produces little loss of surface moisture and has little effect. As the temperature is raised, partial dehydration occurs, giving a surface of AlO.OH or $\gamma\text{Al}_2\text{O}_3$ which is the active form of alumina. Ignition higher than 950°C produces Al_2O_3 , and then the unreactive Al_2O_3 , and a surface layer of AlO.OH and a negative charge.

An examination of the relative retention of various types of molecules can give clues to the type of bonding involved. Strong adsorption is favoured by high polarity and an increase in the number of polar substituents or aromatic nuclei.

Recent work by Cumming et al (6) has shown that hydrogen bonding is an important factor, and that all compounds with an H atom capable of bonding are strongly adsorbed by Al_2O_3 . They were able to conclude that the whole external solid surface was covered by a monolayer, by consideration of the following facts for the adsorption of phenols, amines and aldehydes:

- a) Adsorption is very rapid, i.e. a few minutes, so that no penetration of the pores is occurring;
- b) The shape of the isotherm is consistent with the formation of a monolayer with the molecules orientated end-on;

c) Calculation of the amount adsorbed and molecular dimensions agrees with the values of the specific surface of the powder.

Hydrogen acceptor compounds, such as nitrobenzene, are less strongly adsorbed than hydrogen donors, probably due to the limited number of free OH^- ions on the solid surface.

Recent work by Klemm et al (7) and by Giles and McKay (8) has been concerned with aromatic hydrocarbons. Adsorbability is favoured by an increase in the number of double bonds, an increase in coplanarity, and a "symmetry number", based on the possible number of places where a molecule can attack itself to the solid.

O'Connor et al (5) have studied adsorption on alumina of grades I and II. Grade I is prepared by heating alumina to red heat, and cooling in a vacuum dessicator. Grade II is made by exposing Grade I to a damp atmosphere with stirring. They showed that although Grade I had a higher affinity for water, Grade II had a greater affinity for aromatic hydrocarbons, suggesting they were adsorbed on different sites. Further tests on silica and cellulose showed very little adsorption of aromatic hydrocarbons compared with alumina, and they came to the conclusion that the hydrocarbon forms an ionic complex with the alumina atoms which have a slight positive charge.

Little is known about desorption, but work by Giles (3) on the adsorption and desorption of p.nitrophenol from water suggests that adsorption and desorption isotherms are not the same.

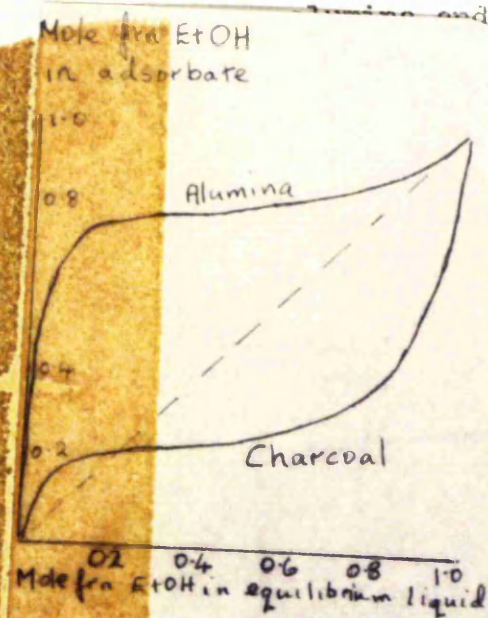
Thus, the advantage of alumina as an adsorbent are the presence at its surface of O atoms, OH^- , Al^{+++} ions, and possibly Na^+ ions depending on its pretreatment. It is suggested that most types of compounds are adsorbed on the outer surface only due to consideration of the short time to reach equilibrium.

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Giles estimated the amount of coverage of alumina by aromatic hydrocarbons to be about 0.1%, and in small isolated clusters, end-on oriented, and bound to the Al^{+++} ions.

A new approach to adsorption isotherms has been introduced by Kipling and Tester (9), and Kipling and Peakall (10), (11). These workers have considered individual isotherms for adsorption from a binary mixture instead of a "composite" one. Their work is based on the theory that in physical adsorption the adsorbed layer is one molecule thick on the solid surface. They have also shown that chemisorption takes place to a much greater degree than has ever been thought. The process creates new surfaces on which physical adsorption can follow: e.g. the lower aliphatic alcohols may be chemisorbed on alumina to give OEt and OH groups. These preferentially adsorb other hydroxyl groups.

For example, consider the system ethyl alcohol-benzene, adsorbed on alumina and charcoal.



Mole frn EtOH at equilibrium on alumina

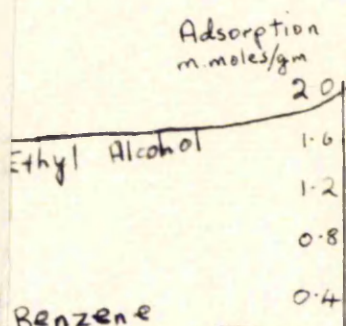
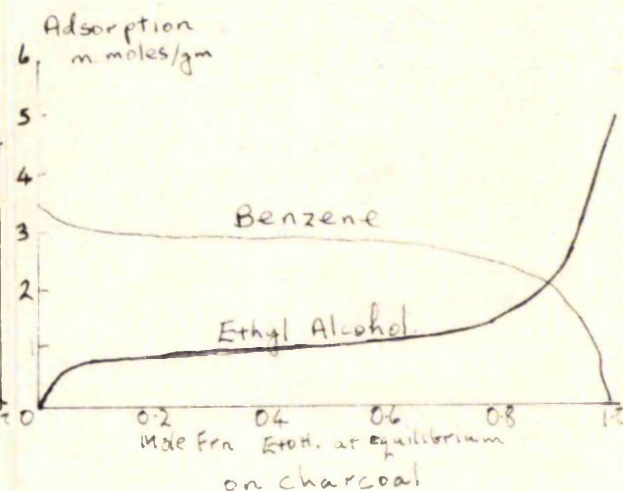


FIG. 11



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They concluded that on alumina the alcohol molecules are held by hydrogen bonds to the surface OH^- groups, these bonds being much stronger than the van der Waals bonds holding the benzene molecules, and so benzene can only occupy a small fraction of the surface. In the case of charcoal, it interacts strongly with the benzene molecules, while the alcohol OH group is likely to be directed away from the solid surface towards other alcohol molecules in the liquid phase.

In the case of the benzene-cyclohexane system, benzene was found to be always preferentially adsorbed, and the size and orientation of the molecules was nearly the same. Thus the relative adsorption depends only on the difference in interaction between the strong π bonding with the aromatic molecule, and the weak interaction with the saturated cyclic molecule.

An investigation into the nature of adsorption on alumina is given by Giles (3). For nonpolar, non-ionic compounds such as hydrocarbons, the extent of the surface coverage is only about 0.1%. The molecules are adsorbed on the Al^{3+} sites in small isolated clusters of molecules, orientated end-on to the surface. The bond is probably a π electron complex with surface aluminium atoms. This suggests that much of the theory derived later for the plotting of adsorption isotherms may be without a valid foundation, and more work needs to be done on the process of adsorption for a weakly adsorbed hydrocarbon.

1.3. ADSORPTION EQUILIBRIA

There are two main types of adsorption: physical adsorption and chemisorption.

Physical adsorption occurs when the bond formed between the liquid or gas and the solid surface is due to dipole interaction and electrostatic forces.

Chemisorption refers to the formation of a chemical bond between adsorbent and adsorbate. It is characterised by a heat of reaction as much as ten times higher than that of physical adsorption, and differs from an ordinary chemical reaction in that the reacting atoms of the solid surface retain their identity in the solid structure. Chemisorption is normally irreversible, or only reversible under special conditions.

Physical adsorption is a reversible process in which no changes in structure take place, and is the type observed in chromatography. It is considered further in the rest of this survey.

1.4. ADSORPTION CHROMATOGRAPHY

Adsorption chromatography is usually carried out in a column containing a fixed bed of adsorbent, and the solution may flow upwards or downwards over this bed, so that maximum contact of solid and liquid is obtained. Various separation techniques have been developed and these are described below. Batch processes, although included under the general heading of adsorption analysis, are treated in Part II.

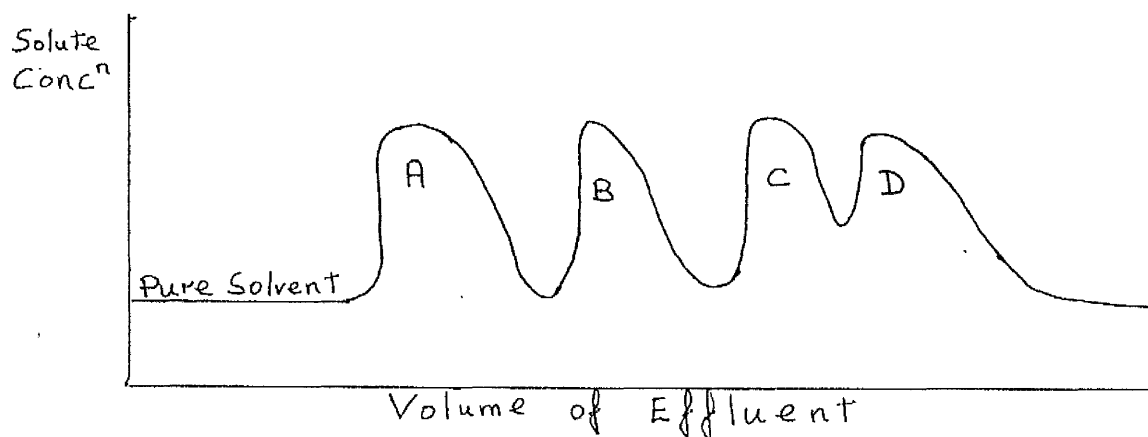
(i) Elution Analysis

The packed column is wetted with the first solvent to be used in the elution process. This can be either by introducing it in the feed,

or by wet-packing the column in the form of a slurry. The sample, dissolved in the same solvent, is then introduced to the column, and after it has all been charged, more of the solvent is added. This solvent is called the eluting agent, or eluent. For a multicomponent solute, the eluent will normally be more strongly adsorbed than only a part of this solute, and the remainder of the solute can be eluted with a more strongly adsorbed eluent. Under the influence of the eluent, the substances in the sample will travel down the column at velocities corresponding to their adsorption characteristics. Substances which are very weakly adsorbed will travel the faster, and if the column is long enough, and the respective isotherms are concave (see later), then each compound, or group of compounds, will separate into zones with ideally pure solvent in between.

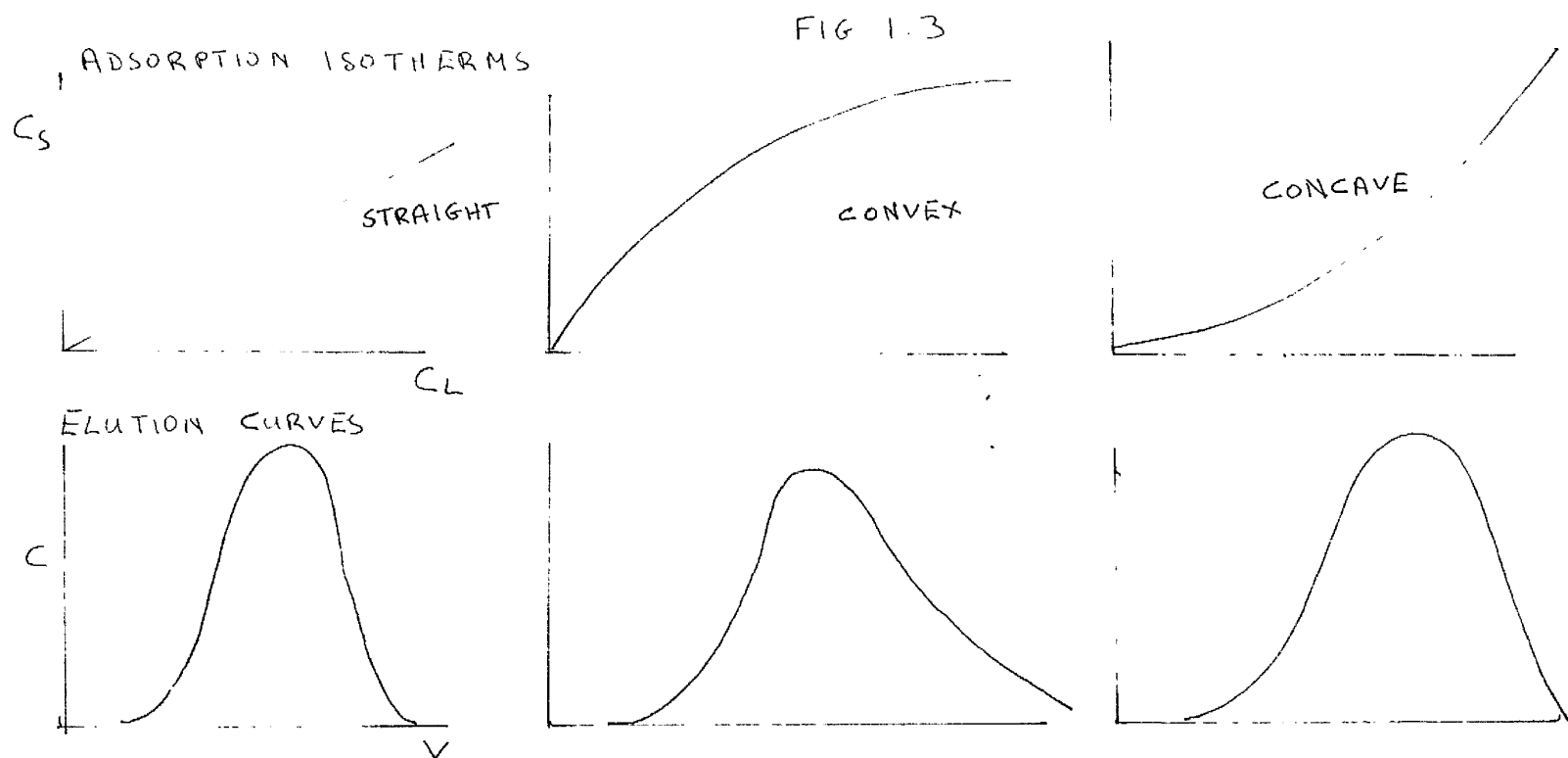
The sketch (Fig.1.2) shows the separation of four compounds by elution. Pure solvent emerges first, probably the prewetting volume, followed by pure A and pure B. These show complete separation, with the leading edge of the curve vertical, showing a sharp front, and tailing slightly at the rear, showing incomplete zone formation. Complete zone formation would be shown by a symmetrical Gaussian type curve. C and D have not been completely separated and the leading edge of D will in fact be a C-D mixture.

FIG 1.2



In practice, most of the substances could be eluted with a single solvent, due to the following of an adsorption isotherm, but for very strongly adsorbed compounds, an infinite column of eluent would be required, and so, it is more convenient to use a series of stronger eluents. Examples of this have been given by the author for lubricating oil separations (2).

The separation shown in Fig.1.2. is for a mixture of compounds having concave isotherms with the eluent. For varying shapes of isotherm, the elution curves will be as shown in Fig.1.3.



This demonstrates the dispersive effect of convex isotherms, as discussed later in section 1.5.

(ii) Gradient Elution Analysis

The operation is the same as in elution analysis, but the eluent is a mixture of solvents, usually a binary mixture in which the proportion of the stronger eluent increases uniformly. The advantage of this method is that blurring of the zones is reduced, as the tailing part of the zone is under the influence of a higher eluting power than the front of the zone. This effect however, also works between the zones, so that the zones will tend to be closer together.

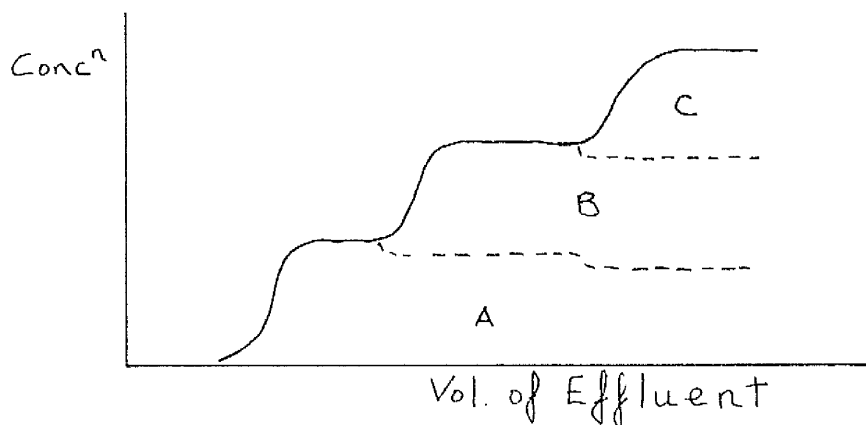
The rate of increase of elution power will depend on the relative adsorbabilities of the substances in the sample.

Narrower and higher peaks can be obtained, and this method reduces the possibility of one substance appearing in two peaks as can happen using a series of solvents in a step-wise process.

(iii) Frontal Analysis

This method requires a large volume of the sample, as the sample is passed continuously down the column, usually prewetted with a solvent, until the sample emerges with the same composition as the feed and the column is saturated. During passage down the column, each substance will travel with a different velocity, and so will separate according to adsorption affinity.

FIG. 1.4

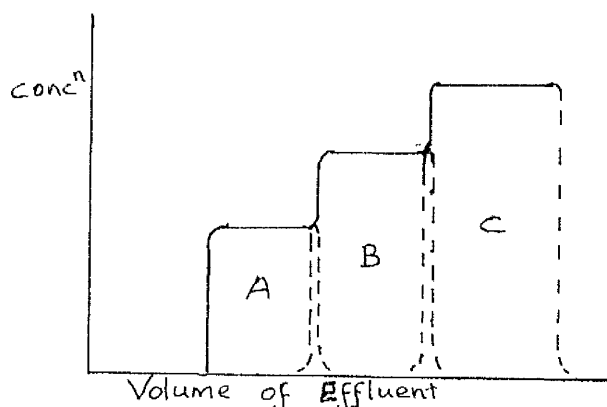


An experiment such as shown in Fig. 1.4. cannot give a quantitative analysis of the sample, but will give an idea as to the number of components present, which in many cases is all that is required.

(iv) Displacement Analysis

In this method, the column is prewetted with a weakly adsorbed solvent, and the sample is then charged usually in a solution of this same solvent. A solvent is now charged to the column which is more strongly adsorbed than any component of the sample. The components will separate among themselves, and the most weakly adsorbed will appear first in the effluent.

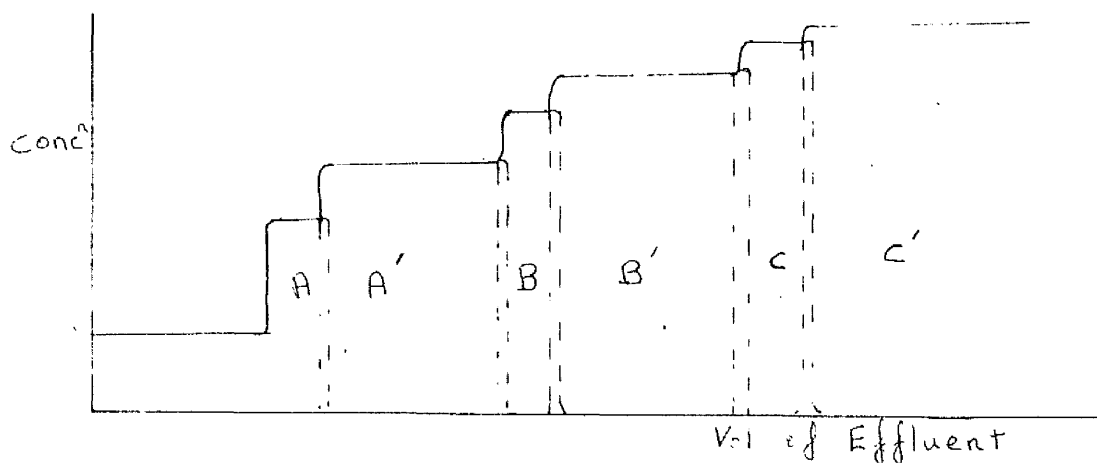
FIG. 1.5



The resulting effluent curve will be as shown in Fig. 1.5., and in this case, if equilibrium has been reached, there should be sharp divisions between A,B and C. It should be noted that once the equilibrium has been reached, an increase in column length will not lead to any improvement in the separation.

This method can give good separations, but the difficulty is in separating the zones of pure substances. This can be overcome by CARRIER DISPLACEMENT ANALYSIS, in which a substance which is adsorbed intermediately between the substances to be separated. For a simple mixture, it should be possible to place a carrier between each component.

FIG 1.6



If the carriers (A, B, C etc...) are easily separated, from the components of the sample, then good separation can be obtained (3).

(v) Thin layer Chromatography

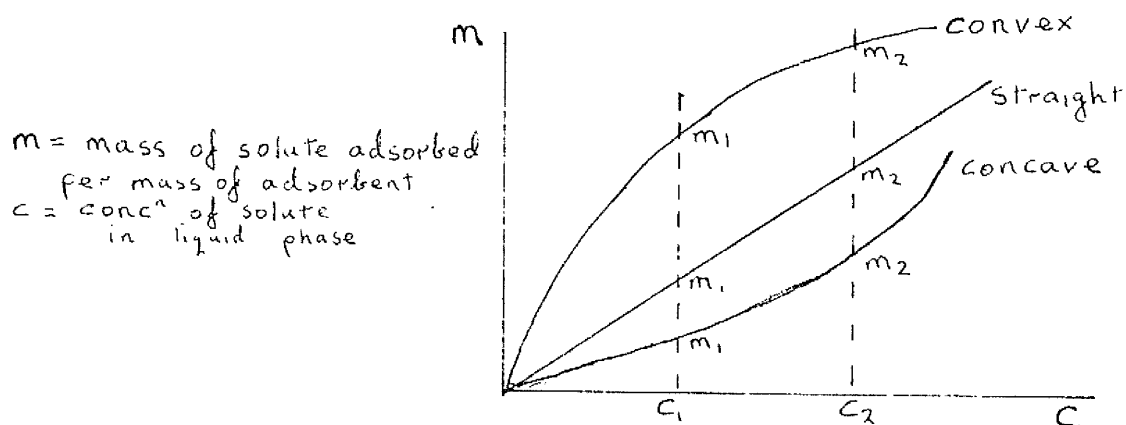
Here the adsorbent is bound by an adhesive onto a glass plate. The sample is introduced as a spot on the adsorbent (alumina and silica are frequently used), and the plate is then held vertically in a vessel containing the eluent. The eluent travels up the plate, and the spot is eluted to form bands of its components. These can be identified by spot tests, or fluorescent methods.

1.5. ADSORPTION ISOTHERMS

An adsorption isotherm is a representation of the equilibrium relationship between the amount of solute in the stationary phase, and the amount of solute in the mobile phase at a constant temperature. It can be compared with vapour-liquid equilibrium diagrams used in distillation.

The isotherm of a system can most easily be determined by contacting a binary mixture of known concentration with a known weight of adsorbent. The three main types of isotherm are shown below. (Fig. 1.7)

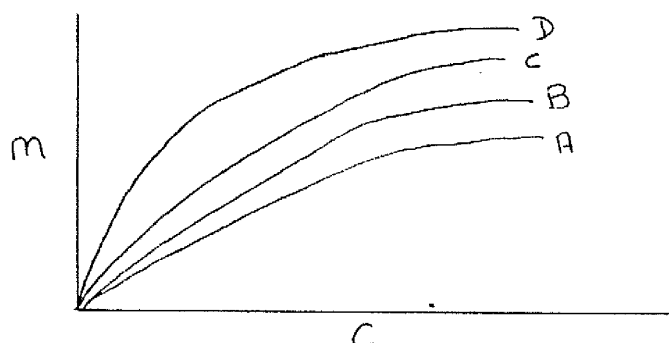
FIG. 1.7



Although the isotherm depicts the equilibrium relationship between an adsorbent and adsorbate, it may also be used for design purposes. For example its position relative to the positions of other isotherms shows in what order a group of components will appear in the column effluent, and the tendency of the adsorption zone to sharpen or to diffuse.

The rate of travel down the column is shown by the slope of the isotherm. Consider a group of compounds A,B,C,D, all with convex isotherms when individually brought to equilibrium with the same adsorbent and solvent.

FIG. 1.8



If this group of compounds were to be separated on a column, then A, being the least adsorbed, would appear at the bottom of the column first. This family of curves is only true for one solvent-solute-adsorbent system, and by varying the system, the curves may be more or less separated, and their positions may be interchanged, leading to better separations.

The same principles apply also to concave, and straight isotherms. The sharpness of the zone varies according to the type of isotherm, and to the technique used.

The simplest case is the straight isotherm, where the proportion of solute in the adsorbed phase does not vary with concentration. These conditions only occur in adsorption chromatography at low concentrations of the order of 1:1000 solute:adsorbent ratios. They are observed more frequently, however, in partition, and ion-exchange chromatography. Once the zone has formed, it will travel at constant rate, giving a zone of constant height.

The convex isotherm, the type most common in hydrocarbon systems, leads to a sharpening, or a concentration of the adsorption zone in frontal analysis. Reference to Fig. 1.7. shows that a larger proportion of the solute will stay in solution at C_2 than C_1 (assume $C_2=2C_1$). It follows that the substance will travel more rapidly through the column at higher concentrations. In elution analysis, the higher solute concentration is at the leading edge of the zone, and therefore the zone will tend to become more diffuse, giving rise to a "tailing" effect.

The concave isotherm, by the same reasoning as above, will lead to diffusion and spreading of the zone in frontal analysis. In elution analysis, the regions of lower solute concentration will move faster, and therefore the adsorption zone will become sharper.

1.6. MATHEMATICAL EXPRESSION OF ADSORPTION ISOTHERMS

An adsorption isotherm is a relationship between the average concentration in the adsorbed phase, on the solid surface y^* or c , and the equilibrium concentration in the bulk liquid phase x^* or c^* . These concentrations are usually expressed in vol.,mol. or wt%, in terms of the preferentially adsorbed component. In this work, it is assumed that adsorption and desorption take place on a molecular basis, with one molecule being displaced by another molecule, but since it is almost true to say that equal volumes are displaced, volume% will be used here for the sake of convenience.

The earliest expressions were the Langmuir isotherm

$$y^* = \frac{k_1 k_2 x^*}{1 + k_2 x^*}$$

and the Freundlich isotherm

$$y^* = k(x^*)^n \quad (\text{where } k_1, k_2 \text{ and } n \text{ are constants}).$$

Some adsorption isotherms may be expressed by these equations, usually at low concentrations, as their derivations are based on the assumption that no solvent is present in the adsorbed phase, and therefore in this case y^* is equal to wt. solute adsorbed/ unit wt. adsorbent, which is usually written as "a".

The Freundlich isotherm is a simple empirical relationship based on experimental observation.

The Langmuir isotherm is derived from theoretical considerations and has been developed by other workers to satisfy more realistic conditions (4).

Koble and Kerrigan made assumptions on polymerisation and dissociation, and produced the equation:

$$c_s = \frac{Lk'(C_A)^n}{1+k'(c_A)}$$

Brunauer, Emmett and Teller assumed that adsorption was multilayer and expressed c_s in the form

$$c_s = \frac{B_1 B_2 c_A}{(1 - \frac{c_A}{c}) (1 + (B_2 - 1) \frac{c_A}{c})}$$

For multisolute monolayer adsorption, the Langmuir isotherm becomes

$$c_s = \frac{\sum_{i=1}^n \frac{k_i c_i}{1 + \sum_{i=1}^n k_i c_i}}$$

c_A is concⁿ of A (p.a.c.) in fluid phase.

c is concⁿ of A (p.a.c.) in solid phase.

$B_1, B_2, k, n, L, k', k_i$ are empirical constants

c_i is concⁿ of component i in fluid phase, where i varies from A to n .

The difficulty with many of these expressions is that the many constants are difficult to determine for a particular system, although in a logarithmic form some constants can be obtained graphically.

A convenient method of expressing the isotherm may be developed for a binary mixture, where A is the p.a.c., according to three sets of conditions.

(i) Only A is adsorbed, and only A enters the pores.

wt. adsorbent = m

pore volume = V_p

volume of solution initially = V , of concentration x_0

At equilibrium, concentrations are y^* or a in adsorbed phase,
 x^* in liquid phase.

initial volume of A = Vx_0

final volume of A in solution = $(V-a)x^*$, as a volume "a" has been adsorbed.

$$\therefore a = Vx_0 - (V-a)x^* = Vx_0 - Vx^* + ax^*$$

$$a(1-x^*) = V(x_0 - x^*)$$

$$\therefore a = \frac{V}{m} \frac{(x_0 - x^*)}{(1-x^*)} \quad \text{mls/gm adsorbent.}$$

It is possible that $a = V_p$ in this case.

(ii) Both components are adsorbed, but only adsorbed molecules exist in the pores.

initial concentration of A = Vx_0

final concentration of A in liquid phase = $x^*(V-V_p)$

concentration of A in adsorbed phase = y^*V_p

$$\therefore y^*V_p = Vx_0 - x^*(V-V_p)$$

$$y^* = \frac{Vx_0}{V_p} - \frac{x^*V}{V_p} + \frac{x^*V_p}{V_p}$$

$$y^* = \frac{V}{V_p} (x_0 - x^*) + x^*$$

and $a = y^*.V_p$

$$\therefore a = V(x_0 - x^*) + x^*V_p \quad \text{mls/gm.}$$

(iii) Both components adsorbed; and the pores contain the adsorbed phase and also some of the bulk liquid phase.

initial volume of A = Vx_0

volume of A in pores in bulk phase = $x^*(V_p - V_a)$

volume of A in bulk liquid phase = $x^*(V - V_p)$

volume of A in adsorbed phase = y^*V_a

} where $V_a =$
vol. adsorbed

$$\therefore Vx_0 = x^*(V_p - V_a) + x^*(V - V_p) + y^*V_a$$

$$\therefore Vx_0 = x^*(V - V_a) + y^*V_a$$

$$\therefore y^* = \frac{V(x_0 - x^*)}{m(V_a)} + \frac{x^*}{m} \quad \text{mls/gm}$$

This contains two unknowns, y^* and V_a , there being no way of determining V_a independently.

As an approximation, an expression can be derived as follows:

$$\text{amount adsorbed of A} = Vx_0 - x^*(V-V_p)$$

$$\therefore a = \frac{V}{m} (x_0 - x) + \frac{x^* V_p}{m} \quad \text{mls/gm.}$$

$$\text{and } y^* = \frac{V}{m} \frac{(x_0 - x^*)}{V_p} + \frac{x^*}{m}$$

These two expressions would be the same if $V_a = V_p$, and as the difference could be very small, the latter expression may be used in some circumstances.

Large errors will occur if the pores are large, and V_p is many times greater than V_a . Thus dividing by V_p instead of V_a will lead to y^* being too low.

1.7. THEORETICAL ADSORPTION STUDIES

Many theoretical treatments of adsorption can be found in the literature, some derived from experimental results, and some derived from analogies to other unit operations such as liquid-solid- or liquid-liquid extraction, and distillation.

Adsorption Efficiency.

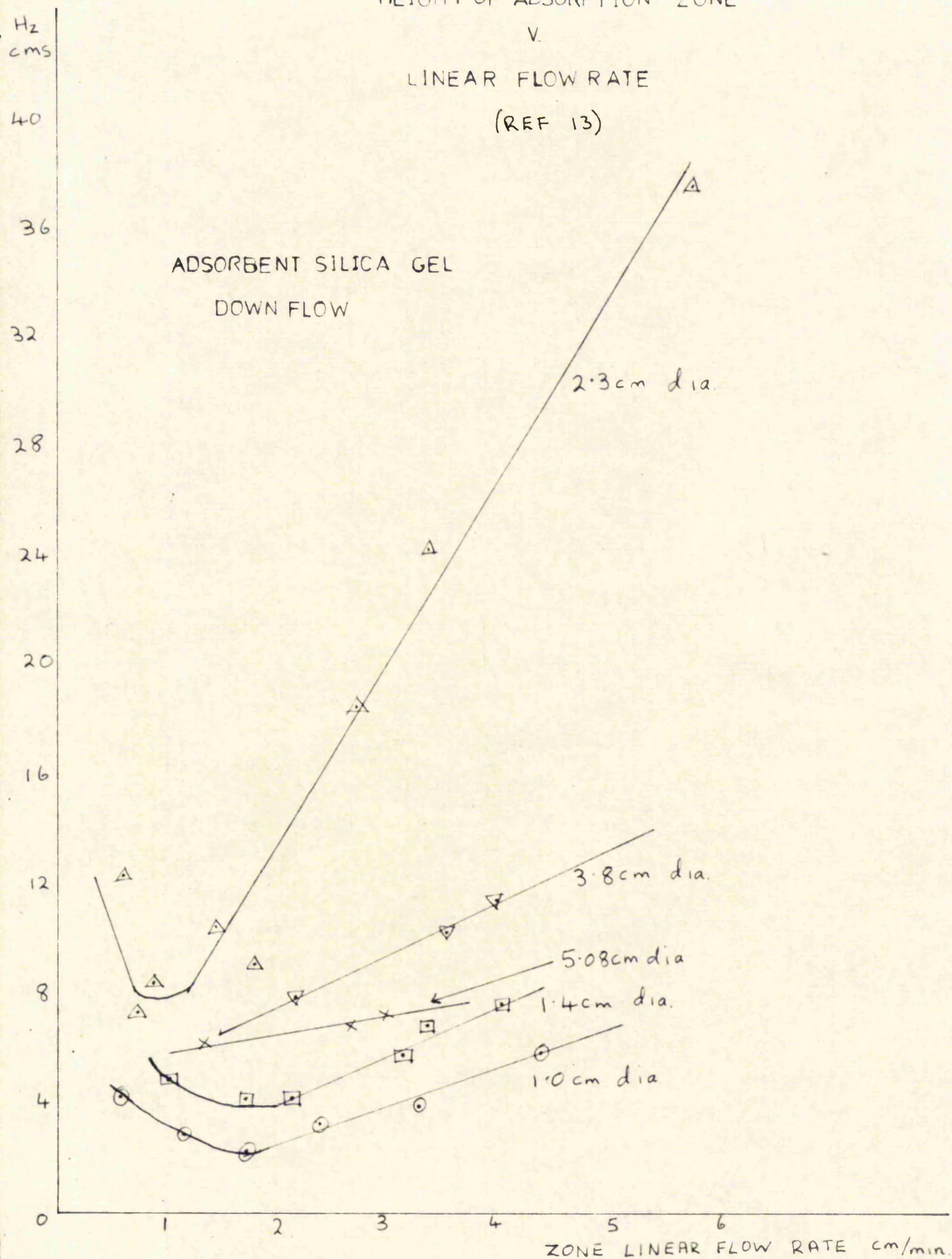
The method proposed by Fink et al. (12) was to define the most efficient separation as that in which an adsorbed compound, such as a liquid hydrocarbon, was recovered in excess of 98% purity when displaced with methanol. The efficiency was calculated as a percentage of the theoretical volume. They found that separation efficiency is proportional to tube length divided by diameter squared, and inversely proportional to particle size.

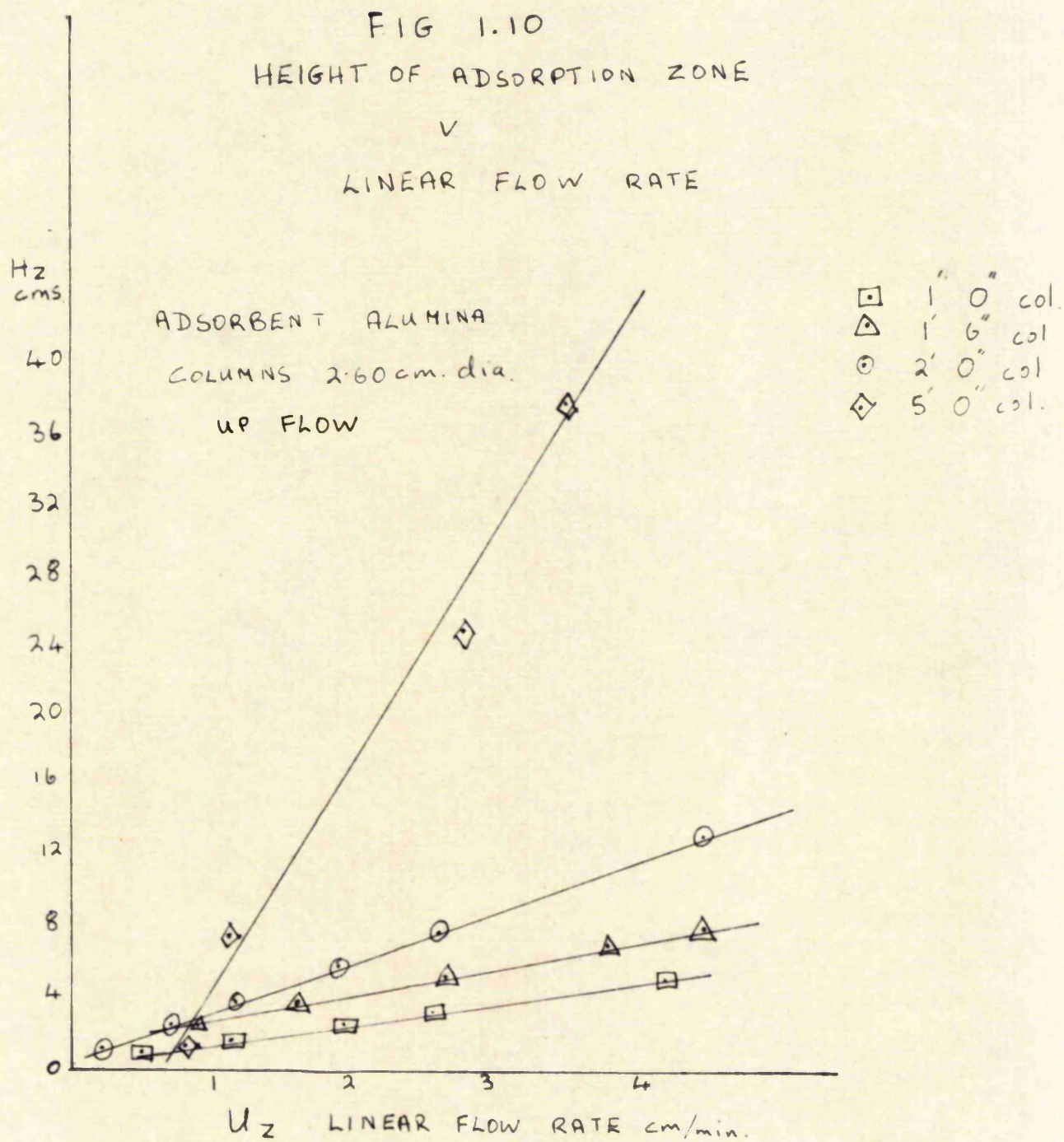
HEIGHT OF ADSORPTION ZONE

V.

LINEAR FLOW RATE

(REF 13)





REF. 14.

This approach has been furthered by Chambers (13) on down flow work, who studied the separation of benzene and iso-octane by frontal analysis (see Chromatography Techniques). The variables studied were tube length and diameter, fluid composition and velocity.

The separation efficiency was determined in terms of the "height of adsorption zone, h_z ", this being the length of column in which the liquid concentration changed from $x'' = 0$ to $x'' = x_0$.

The main conclusions were:

(i) h_z increases with bed length.

(ii) An optimum flow rate was found for all diameters and lengths, and for both alumina and silica. For tubes between 1.0 and 2.3 cms. dia. the relationship found for silica gel was $h_z = 1.3D^2U'_z$, where U'_z = velocity of the adsorption zone.

Fig. 1.9. shows the minimum h_z values for various columns, giving optimum adsorption conditions.

(iii) For diameters greater than 2.3cms., it was concluded that channelling led to divergence from the above equation, but for alumina, h_z was proportional to U'_z for a 3.8cms.dia. column.

(iv) For the system studied, solid phase diffusion was the controlling mechanism.

Ibbotson (14) followed this work by a study of up-flow conditions, and also a variation of the liquid system, to investigate the effect of density difference.

He reached the same conclusions as Chambers about the controlling mechanism, but for up-flow, he found no optimum velocity. Fig. 1.10. shows typical results for 2.6 cms. dia. columns on alumina. However, optimum diameters of 1.4cms. for silica and 1.0 cm. for alumina were found.

He also found that if the density of the p.a.c. is greater than that of the displaced liquid, then up-flow gives greater efficiency. In a comparison of up and down-flow, the latter was more efficient for small diameters (below 1.4), while up-flow was more efficient for diameters of 1.4 to 2.6 cms.

The concept of an adsorption zone, and its use in column efficiencies, was developed by Michaels A.S. (15) for ion-exchange work, and later by Moison and O'Hern (16). They, however, used this concept in calculating heights of theoretical transfer units (H.T.U.) and related this to Reynolds Number, bed depth and particle size.

Its use in adsorption theory was recognised by Schmelzer, Molstad and Hagerty (19). They made an extensive study of the system toluene-n.heptane-silica gel, and by using the H.T.U. concept were able to accurately predict the shape of the breakthrough curve in columnar separations.

Many empirical equations have been derived for prediction of the separation by an adsorption column. A review of these is given by Badhwar (17). He also gives a review of analytical techniques, using partial differential equations. He showed that:

$$H.T.U. = \frac{\rho V_p}{K_s a} \cdot U'_z$$

where $K_s a$ = overall solid phase mass transfer coefficient;

He also suggested that an empirical relationship derived by dimensional analysis of the form given below was possible.

$$\frac{K_{s \text{ adp}}}{U'_z} = A (Re'_z)^{g-1} \cdot \left(\frac{M}{D_s} \right)^{-c} \cdot \left(\frac{L}{d_p} \right)^f \cdot \left(\frac{d_T}{d_p} \right)^b$$

The left-hand side is similar to the Stanton Number, and the right-hand side includes the zone Reynolds Number, D_s is diffusivity, and the other terms have their usual meaning. He modified an equation given by Lapidus and Amundson (18) to include a diffusivity term, giving

$$D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - \frac{\partial (u_g c)}{\partial x} = \frac{\partial c}{\partial t} + \frac{1-\epsilon}{\epsilon} \gamma \frac{\partial c_s}{\partial t}$$

and developed a method of determining $\frac{\partial c_s}{\partial t}$.

A simplified form of this equation was solved, assuming that U_g , the settling velocity due to density difference, and the longitudinal diffusivity, D , were 0. He was thus able to predict the effluent curve for columns up to 10 cms in length, but suggested a different method of solution to predict the performance of larger columns, as the computer was not large enough to store all the necessary instructions and data.

CHAPTER 2. OIL SEPARATIONS BY ----- CHROMATOGRAPHY -----

2.1. CHROMATOGRAPHY OF PETROLEUM FRACTIONS

Some of the earliest work on the fractionation of petroleum was carried out by Day (20). He realised that oil samples from different parts of the Pennsylvania oil field were of different composition, ranging in colour from black and green to red and even to white. He was able to demonstrate that these oils all came from the same source, and had been separated by a "fractional diffusion" process through the porous limestone. By percolating oil through beds of fullers earth, he obtained many fractionations according to hydrocarbon type.

The first serious attempt to isolate and identify hydrocarbon types and individual components was begun in 1927 by the American Petroleum Institute under Research Project 6 (21). A detailed study of chromatography, starting with the adsorption of synthetic mixtures on silica, led to the separation of petroleum fractions in 63'x1 $\frac{3}{4}$ " dia. columns. It was shown that it was possible to determine accurately the aromatic content of a given sample. In a quantitatively controlled experiment using a synthetic mixture resembling a gas-oil fraction, elution with pentane, butane or propane, separated the sample into aromatic and non-aromatic fractions to within 1% of the expected composition.

A gas-oil fraction was separated into samples identified as n.paraffins, monocycloparaffins, alkyl benzenez, mixed aromatics and cycloparaffins, and polynuclear aromatics.

A lube-oil fraction was separated on silica by elution with iso-octane, benzene, and 2 propanol in sequence. On refractionation of the aromatic fractions, a good separation was achieved into mono. and dinuclear aromatics, eluted with iso-octane, and tri.nuclear, eluated with benzene. It was found that alumina was better than silica for the separation of aromatic types.

The solvents shown in table 2.1. have been used in the chromatography of petroleum fractions. In most cases, the last solvent, usually an alcohol or other highly polar compound, has been used as a desorber to remove all remaining adsorbate from the column. The first solvent is one very weakly adsorbed, and in fact some of those used are among the most weakly adsorbed known.

Irish and Karhum (22) eluted a lube-oil with different primary solvents, and found the order of increasing elution ability to be:

n.hexane

cyclopentane

50% n.hexane/2.3 dimethylbutane

iso-hexenes

2.3 dimethylbutane = cyclohexane = n.heptane.

Only 2.3 dimethylbutane and n.heptane were sufficiently weak to separate the oil eluted by n.hexane, but using a lower column load, even n.hexane would separate the fraction into peaks.

TABLE 2.1. SOLVENTS USED IN ELUTION CHROMATOGRAPHY.

<u>Ref.</u>	<u>Primary</u>	<u>Secondary</u>	<u>Tertiary</u>
23.	n.pentane	methanol	
23.	"	cyclohexanol	
23.	"	iso propanol	
23.	"	3 methyl- 1 butanol	
24.	iso pentane	benzene	
25.	n.heptane	acetone	
26.	"	benzene	
27.	decane	1.octanol	
28.	"	cyclohexanol	
28.	iso pentane	diethyl ether	
28.	40-60° pet. ether	" "	
29.	di.isopropyl benzene		
30.	pentane		
30.	butane		
30.	propane		
31.	cyclohexane		
29.	n.pentane	benzene	1:3 ethanol- benzene
32.	pentane	C.Cl ₄	chloroform ether
33.	"	"	ether
33.	"	"	acetone
34.	iso-octane	benzene	methanol
34.	iso-octenes	"	2 propanol
35.	n.heptane	"	pyridine
22.	n.hexane	"	chloroform- acetone
28.	n.pentane	"	chloroform- acetone
36.	"	1.pentene	benzene chloroform- acetone
28.	iso pentane	C.Cl ₄	ether acetone benzene

A systematic analysis of oil samples into five homogeneous fractions has been described by Snyder (37). Using an oil to adsorbent ratio of 1/100 on alumina, the oil sample was eluted with pentane, a pentane-benzene mixture and a benzene-methanol mixture in succession.

A U-V spectrometer was used to detect the separate zones, and fractions containing saturated hydrocarbons, mono-aromatics, diaryomatics and saturated monosulphides, polyaromatics and polyfunctional sulphides, and oxygen and nitrogen compounds were obtained. The average contamination by overlapping of fractions was 3%. By analysing these fractions on a low voltage mass spectrometer, over 1500 compounds have been identified.

Snyder has also described a method of separation at much lower concentrations which give linear adsorption isotherms (38).

Details of large scale oil separations are given by Bornemann, Finke and Heinze (39). They separated 2kg. of oil on silicagel in a 6m. x 10cm. dia. column by elution with iso-octane, benzene and methanol. Further fractionation on silica gel was carried out on each fraction, and details of many physical properties, together with the results of chemical analyses are given. A review of methods of ring analysis is also given, and two designs for continuous solvent stripping of the filtrate are described.

2.2. WORK BY THE MEDICAL RESEARCH COUNCIL "CARCINOGENIC ACTION OF MINERAL OILS COMMITTEE".

Adsorption chromatography was first used in this project by Carruthers at Glasgow, and later at Exeter Universities. He separated, on alumina, a picric acid extract from an acetone extracted Kuwait oil, using petroleum ether, benzene, and methanol as solvents. By further chromatography and crystallisation of molecular complexes, a considerable number of compounds were isolated (40). They were identified by elemental analysis u-v. spectra, the formation of derivatives and comparison with authentic compounds (41).

So far 45 compounds have been isolated from the crude lubricating oil. The carcinogens identified were all polycyclic aromatic hydrocarbons derived from 1.2 benzantracene, which were not recognised previously as being constituents of uncracked mineral oils. No new carcinogen has yet been identified, though it is suspected that there are unknown carcinogens in the oil.

One difficulty in chemical investigation has been the high sulphur content of the Kuwait oil. The acetone extracts used by Carruthers, which were similar to the oils used in this thesis, contained 5-6% sulphur, and it was estimated, assuming one atom of sulphur per molecule, that 35-40% of the molecules contained sulphur.

Adsorption was first used in the Department of Chemical Engineering by Ray (42). He was working on a Kuwait furfural extracted oil fraction known as KX₇₋₈ (boiling range 380-390°C), which had been obtained at Birmingham University by distillation. Details of this operation are given by King (43).

Ray compared the elution of KX_5 (boiling range 370-375) on silica and alumina, and found silica to give the better separation. However, several changes were noted in the silica runs, when the samples were tested biologically, as the samples had reduced activity, suggesting oxidation or polymerisation had occurred. Alumina was thought to have a slight effect, though not as much as silica. By refractionation of some oil samples produced by elution, he was able to obtain good separation of aromatics and non-aromatics.

A comparison of the elution powers of primary solvents has been carried out by the author (2), using petroleum ether, n.pentane, n.hexane, cyclohexane, carbon tetrachloride and trichloroethylene as primary solvents, in turn, followed by benzene and methanol. It was found that only petroleum ether 40-60° was a better eluent than iso-octane. This justified the rather arbitrary choice of iso-octane for elution chromatography in the work of Ray, Parr (44) and Ibbotson (45). Separations were also carried out using a series of solvents: petroleum ether 40-60°, n.pentane, iso-octane, n.hexane, cyclohexane, carbon tetrachloride, benzene and methanol. Some of these solvents had very similar adsorption characteristics, and much mixing was observed, giving rise to a type of gradient elution effect. Without more sophisticated means of analysis, it was not possible to say whether the resulting oil separation was significantly better than when using only one primary solvent. It was suggested that at least one solvent between iso-octane and benzene would give better separation of polynuclear aromatic materials. Reduction in the oil/adsorbent ratio from 1/12 to 1/24 and 1/100 showed better separation of molecular types, especially of straight-chain paraffins from other non-aromatics.

2.3. EFFICIENCY STUDIES

Efficiency studies carried out by Chambers (13), (46), (47) and Ibbotson (14), as well as furthering our knowledge of the process of adsorption, have been with a view to obtaining improved oil separations on the large scale columns constructed by Parr (44) and Ibbotson (48). Factors considered were:

- 1) L/D^2 ratio,
- 2) direction of feed,
- 3) rate of fluid flow.

Variations of these three factors have been tried, and oil separations have been judged to be improved, but as improvement in oil separation is very difficult to judge, the true value of these results is not known. They showed that by variations in the flow rate of 1, 2 and 4 ft/hr., the 2 ft/hr. run showed the highest benzene peak, and better separation of the iso-octane peaks, suggesting more efficient adsorption on the alumina.

This work is, however, not sufficient to give a good design basis for a column for oil separation. Ibbotson obtained an increase in h_2 , the height of the adsorption zone, for 2 cm to 5 cm for a $5' \times \frac{3}{4}"$ dia. column, suggesting more than 50% decrease in efficiency for an increase in flow rate of 1 cm/min. to 4 cm/min.. The difficulties in relating this work are:

- 1) A different separation technique has been used.

While oil is separated by elution, all efficiency studies have been carried out using a frontal analysis technique, and the shape of the effluent curve has been investigated. This technique is not suitable for the separation of a complex oil, as individual groups of compounds cannot be detected. For a very simple oil extraction, a carrier frontal analysis may be of interest.

2) The system used, iso-octane/benzene is not close enough to the characteristics of lubricating oil samples.

Eagle and Scott (49) suggest that for a kerosene distillate, one can treat the sample as a binary mixture of aromatics and non-aromatics similar to the toluene/iso-octane system for adsorption on silica gel. However, the conclusion of many other research workers is that at present different solid-liquid systems cannot be compared. It is suggested that future work might be concentrated on studies similar to Chambers and Ibbotson, but using an elution technique on a synthetic test mixture of pure known components, similar in properties to the oil fraction under investigation.

CHAPTER 3. PRELIMINARY EXPERIMENTS

IN ADSORPTION CHROMATOGRAPHY

3.1. INTRODUCTION

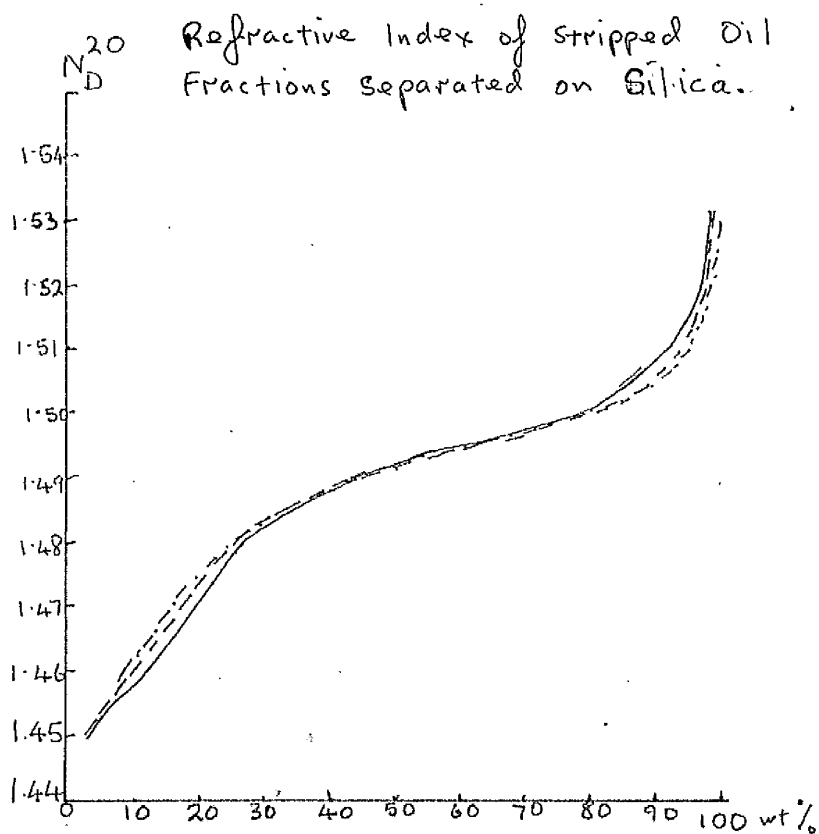
One of the aims of the work in this thesis was to investigate a stagewise slurry process for the separation of a lubricating oil, and to compare the separation with that obtained by the use of a column. It was realised that to make an accurate comparison, a lubricating oil was not a good experimental material, due to difficulties in analysis and comparison of fractions. It was therefore decided to use a test mixture of pure hydrocarbons. A series of column separations were carried out using this test mixture, not only to provide a means of relating the efficiency of a batch slurry process to column efficiency, but also to obtain some idea of the relationship between the effect of column variables using elution and frontal analysis methods.

Much work has been carried out over the past years in this department into the efficiency of the adsorption process using either silica gel or alumina. The variables studied have included:

- direction of flow,
- column diameter,
- nature of adsorbent,
- particle size,
- wet or dry packing.

In all cases, the technique used has been frontal analysis with a binary mixture, usually benzene-iso-octane. The only previous approaches to the problem of relating frontal analysis to elution analysis studies have been by Smit (33) and Ibbotson (14).

FIG. 3.1.

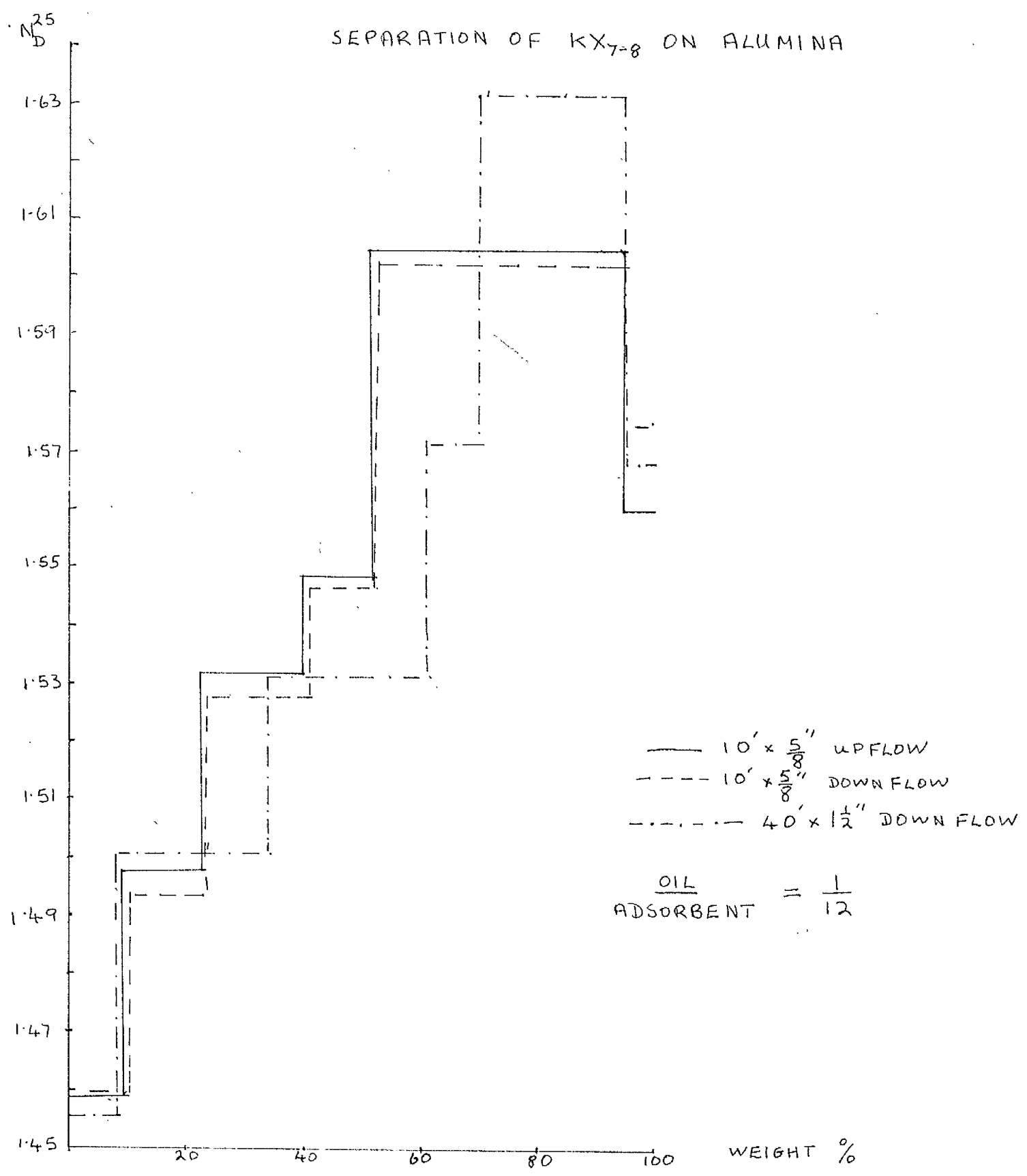


curve:	A	B	C
diam. cm.	5.8	2.9	1.45
length cm.	301	302	310
wt. SiO_2 gm.	5242	1345	336
density of packing gm/ml.	0.66	0.67	0.66
oil weight gm.	60.145	15.525	3.754
adsorbent/oil.	87.2	86.6	89.6

(REF. 33)

FIG 3.2

SEPARATION OF KX_{7-8} ON ALUMINA



Smit carried out separations of a lubricating oil on columns of different diameter by elution, and found very little change in the refractive index of the oil fractions (Fig. 3.1.). He concluded that the efficiency was independent of column diameter, providing that the oil/ adsorbent ratio was constant.

Ibbotson compared separations of KX₇₋₈ (boiling range 380-390°C) on alumina to investigate the effect of diameter, direction of flow and flow rate (14), (45), (44). Fig. 3.2. shows the results of three separations on alumina, the figures being for eluent-free oil fractions. Fraction 1 consisted only of non-aromatic material, and fractions 1-4 were eluted with iso-octane, fraction 5 with benzene and fraction 6 with methanol.

Ibbotson concluded that the 10' x $\frac{5}{8}$ " column showed greater efficiency, due to the fact that more oil was retained on the column, after iso-octane treatment, to be eluted with benzene. However, the 40' x $1\frac{1}{2}$ " column gave a much better separation of polynuclear aromatics with benzene. The question of column efficiencies will be mentioned in chapter 4. The difference between upflow and downflow runs may or may not have been significant.

3.2. SELECTION OF TEST MIXTURE AND ADSORBENT

The major difficulty with oil separations is the accurate analysis of the column effluent. One way of overcoming this is to use a synthetic test mixture composed of a small number of simple components in similar proportions of molecular type as the original oil. The synthetic should be amenable to some simple form of analysis.

When this stage of work was first considered, it was hoped to obtain extended use of an "F and M 720" gas chromatographic instrument for analysis, and a test mixture was chosen for initial experiments.

However, as only a very limited use of the instrument was possible, the results have been analysed mainly by refractive index. If it had been realised that this method of analysis would have to be used, a more suitable test mixture could have been selected. If the method proved useful, then it would be possible, at some future date, to simulate an oil by using high molecular weight pure components.

The components chosen were: n.hexane, methylcyclohexane, benzene, toluene and xylene. Data on these solvents, as well as on the adsorbents, are given in Appendix 1. The adsorbent used in all this work was alumina 100-200 mesh.

The sieve analyses show a higher proportion of fine material than in that used by Ibbotson. This is probably due to handling, sintering due to heat of adsorption released, and perhaps most important, sintering on regeneration at 450°C . Adsorption isotherm tests show that the adsorption capacity of the alumina has not been decreased, possibly due to an increase in surface area, but further regeneration may affect the pore structure and pore volume of the adsorbent.

The two main adsorbents which have been used in the separation of petroleum fractions are alumina and silica gel. The A.I.P.R.P.6 has used mainly silica, but other workers, such as Heftmann and Giles (3), have only worked with alumina. Silica has been found to have a greater adsorption capacity, though alumina has been found to be better for the separation of different types of aromatic molecules (21), (50). Activated charcoal has also been used (50) to give partial separation of straight-chain paraffins from other hydrocarbons. Silica has been suspected of causing some chemical change in the adsorbate by oxidation or polymerisation, and for this reason all oil separations carried out in connection with the M.R.C. work have been on alumina.

The effect may possibly be reduced by jacketing all columns with cooling water to dissipate the heat of adsorption, which is greater for silica than alumina. It has also been suggested that the action of daylight can give rise to coloured compounds from oil fractions (33). Evidence of changes due to silica gel are given by Ray (42).

Alumina is known to cause changes in esters and fatty acids, but no effect on hydrocarbons has been recorded. Thus alumina was chosen for all this work, except in Experiment 20, where the relative extent of adsorption between alumina and silica is seen.

3.3. APPARATUS USED AND MEANS OF ANALYSIS

The layout of the fractionating column is seen in Fig. 3.8. with details of the support plates in Fig. 3.9.

For different sizes of columns, and variation in feed direction, or the use of several columns in series, the feed reservoir and support plates could be used in different positions.

The adsorbent, which had previously been regenerated at 450°C , and stored in polythene lined drums, was kept at $115-125^{\circ}\text{C}$ for at least 8 hours before use, and then allowed to cool in a dessicator. Packing was carried out by pouring the alumina through a funnel into the column, with one support plate in position, and at the same time vibrating the column with a "Pifco" hand massager. When all the alumina was charged, the column was vibrated over its whole external surface to ensure even packing. This took about 5 mins. and was continued until there was no further fall in the bed height.

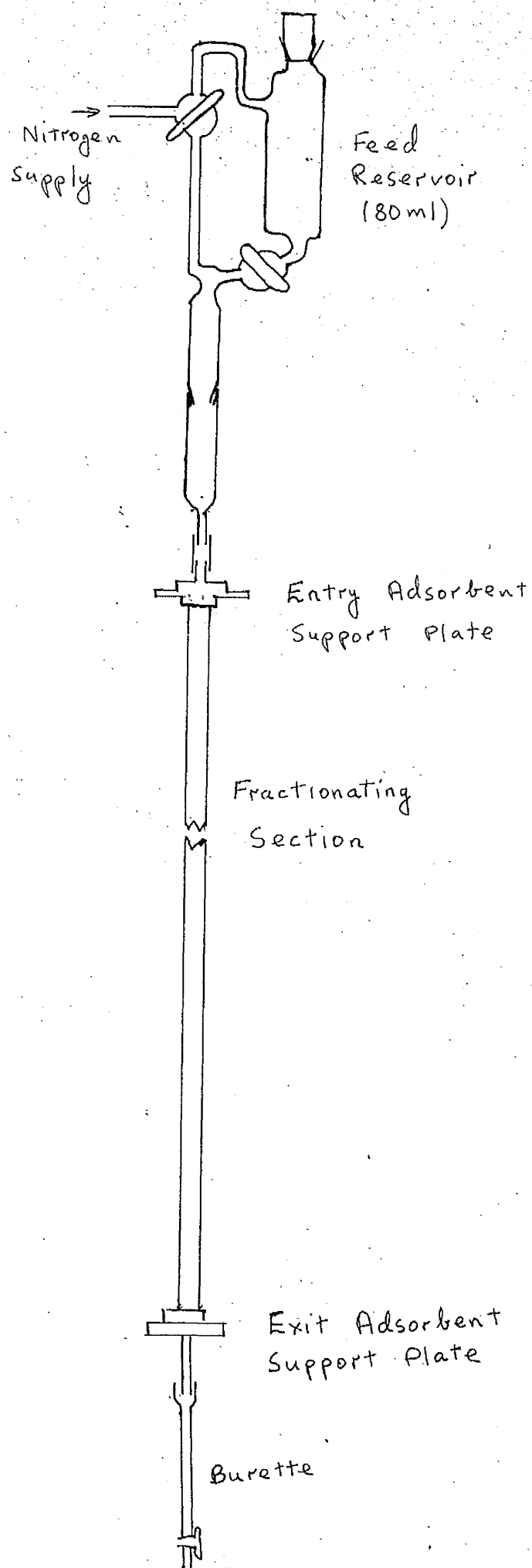
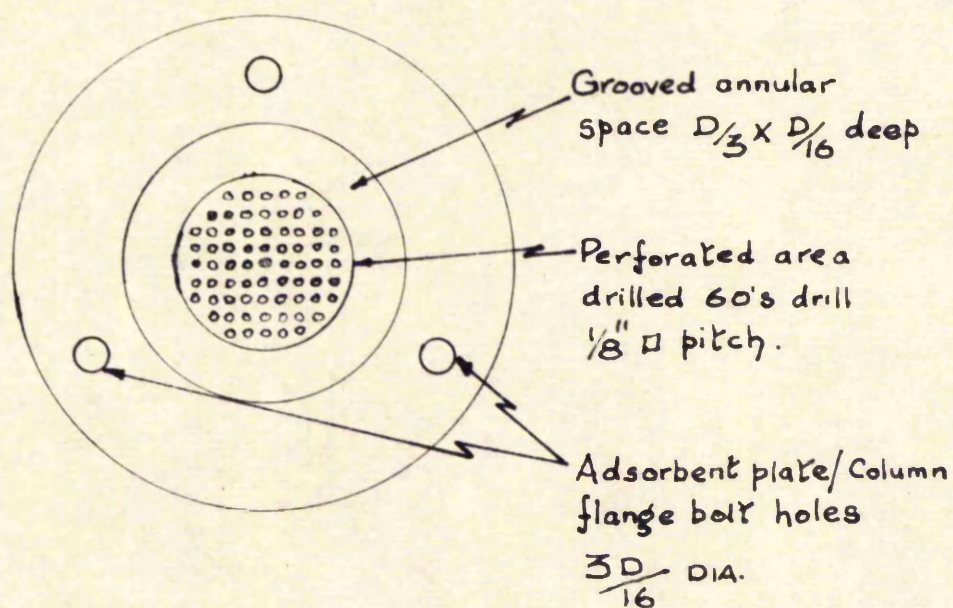
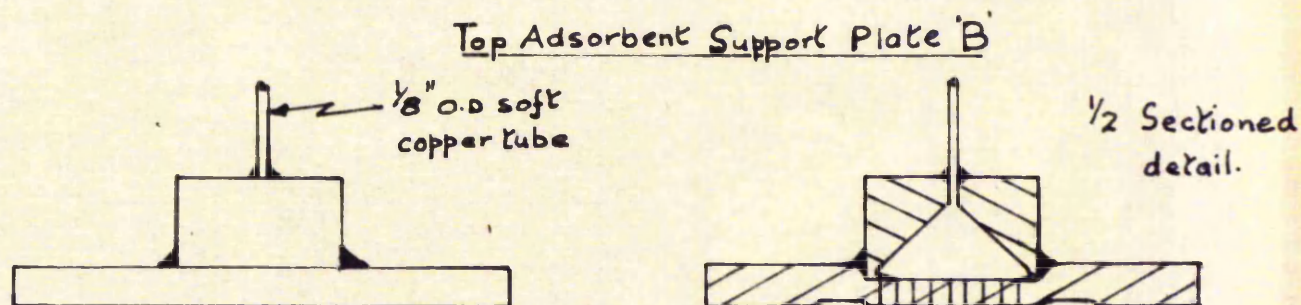
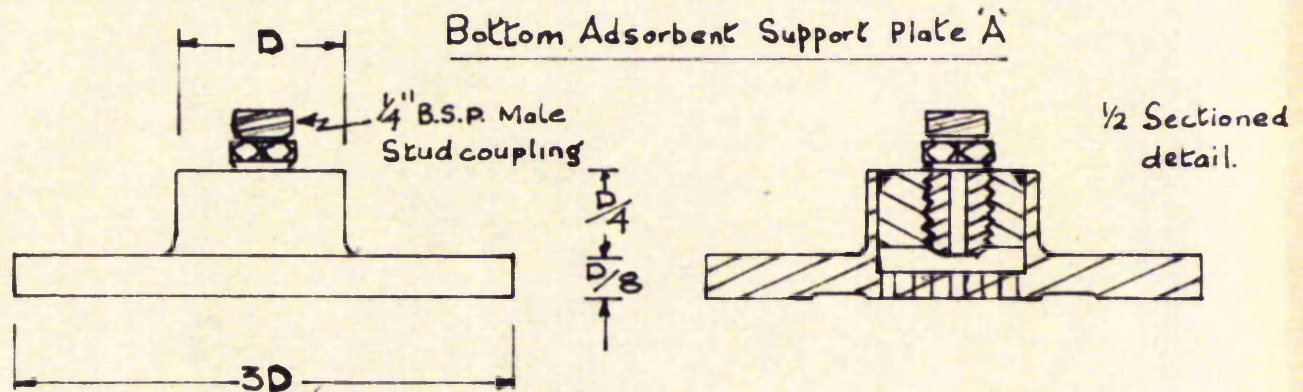


FIG. 3.8

ARRANGEMENT OF
FRACTIONATING COLUMN.

ADSORBENT SUPPORT PLATES DETAIL.

Fig 3.9



Material of Construction — CAST BRASS

Areas shown thus  silver soldered

SCALE :- $\frac{1}{2}$ FULL

Failure to do this efficiently sometimes led to streaking (where the front travelled down one side of the column through an "easy" channel, and instead of being horizontal was spread over up to 1ft. of the bed). The column was the topped up to ensure it was completely full, which meant that there was no change of bed expansion and cracking due to changes in pressure.

The experiments were carried out according to the standard techniques of displacement or elution analysis. Measured volumes of the solvents were charged to the feed reservoir, and thence to the column. The three-way-tap system meant that liquid could be charged with no change in the pressure of the system.

The components of the test mixture were analysed by G.L.C. on an F and M 720 instrument.

The operating conditions were:

- 2 columns in series : 6' x $\frac{1}{4}$ " and 1' x $\frac{1}{4}$ " .
- liquid : silicone rubber S.E. 30 (10%).
- support : diatoport W.
- injection temperature : 150°C.
- column temperature : isothermal 80°C.
- carrier : helium 50mls/min.
- detector : thermal conductivity cell.

The n.hexane, methylcyclohexane and xylene showed the presence of trace impurities which would have to be removed for further quantitative G.L.C. analysis. However further purification was not proceeded with, as it was learned at this time that the instrument would not be available for full-time use, which was necessary for the many hundreds of samples envisaged. Five samples from Experiment 21 were analysed to give an indication of what was happening in the column to supplement the refractive index readings.

In spite of this, it was thought worthwhile to continue with test mixture separations, in order to give a pointer to future work in this field. The samples were characterised by refractive index, which showed separation between saturates and aromatics, although separation between the aromatic molecules themselves was difficult to follow due to the similarity of the refractive indices. The instrument was an Abbe refractometer, which gave a refractive index for the sodium D line. The temperature was kept at $25 \pm 0.05^\circ\text{C}$ by a thermostatically controlled water bath with external circulation. The accuracy was ± 0.0001 units. The symbol N_D^{25} used throughout this thesis refers to the refractive index at 25°C for the sodium D line.

3.4. SUMMARY OF EXPERIMENTS WITH TEST MIXTURE (table 3.1).

Notes

1. The final desorber was methanol in all cases.
2. The letters H,M,I,B,T,X, refer to n.hexane, methylcyclohexane, iso-octane, benzene, toluene and xylene respectively.
3. The rate of flow was kept approximately constant at $2\text{ft.}/\text{hr.}$

TABLE 3.1.

<u>Expt.No.</u>	<u>Graph.No.</u>	<u>Type</u>	<u>Dir'ct. of Flow.</u>	<u>Column</u>	<u>Absorbent</u>	<u>Activation Temp.</u>	<u>Mesh Size</u>	<u>wt. Adt. sorbent.</u>	<u>Dry or Wet pack- ing</u>	<u>Freshet Solvent.</u>	<u>Test mixture.</u>	<u>Eluent.</u>
17	3.3.	Displacement	Down	5' 5/8"	Alumina	120°C.	400-200	300	Dry	4.5ml.H ₂ O	1.5ml.HBTX	-
18	"	"	"	"	"	"	"	284	"	"	5ml.HBTX	"
19	3.4.	Elution	"	"	"	"	"	275	"	"	5ml.HMBTX	150ml.I
20	"	"	"	"	Silica	"	28-200	311	"	"	"	100ml.I
21	3.5.	"	"	"	Alumina	"	150-240	274	"	"	"	"
22	"	"	Up	"	"	"	100-200	280	"	"	"	"
23	"	"	{ Down Up	{ 3' 1/8" 5' 5/8"	"	"	"	{ 480 277	"	60ml.H	"	80ml.I
24	3.6.	Displacement	as above	"	"	"	"	as above	"	20ml.H	"	-
25	"	Elution	Down	5' 5/8"	"	400°C.	"	280	Wet	I	"	80ml.I
26	"	"	"	5' 5/8"	"	"	"	280	Dry	4.5ml.H	"	"
27	3.7.	"	"	5' 1/8"	"	120°C.	"	843	"	"	"	"
28	"	"	{ Down Up	{ 5' 5/8" 5' 3/8"	"	"	"	{ 248 103	"	"	"	35ml.I

FIG 3.3

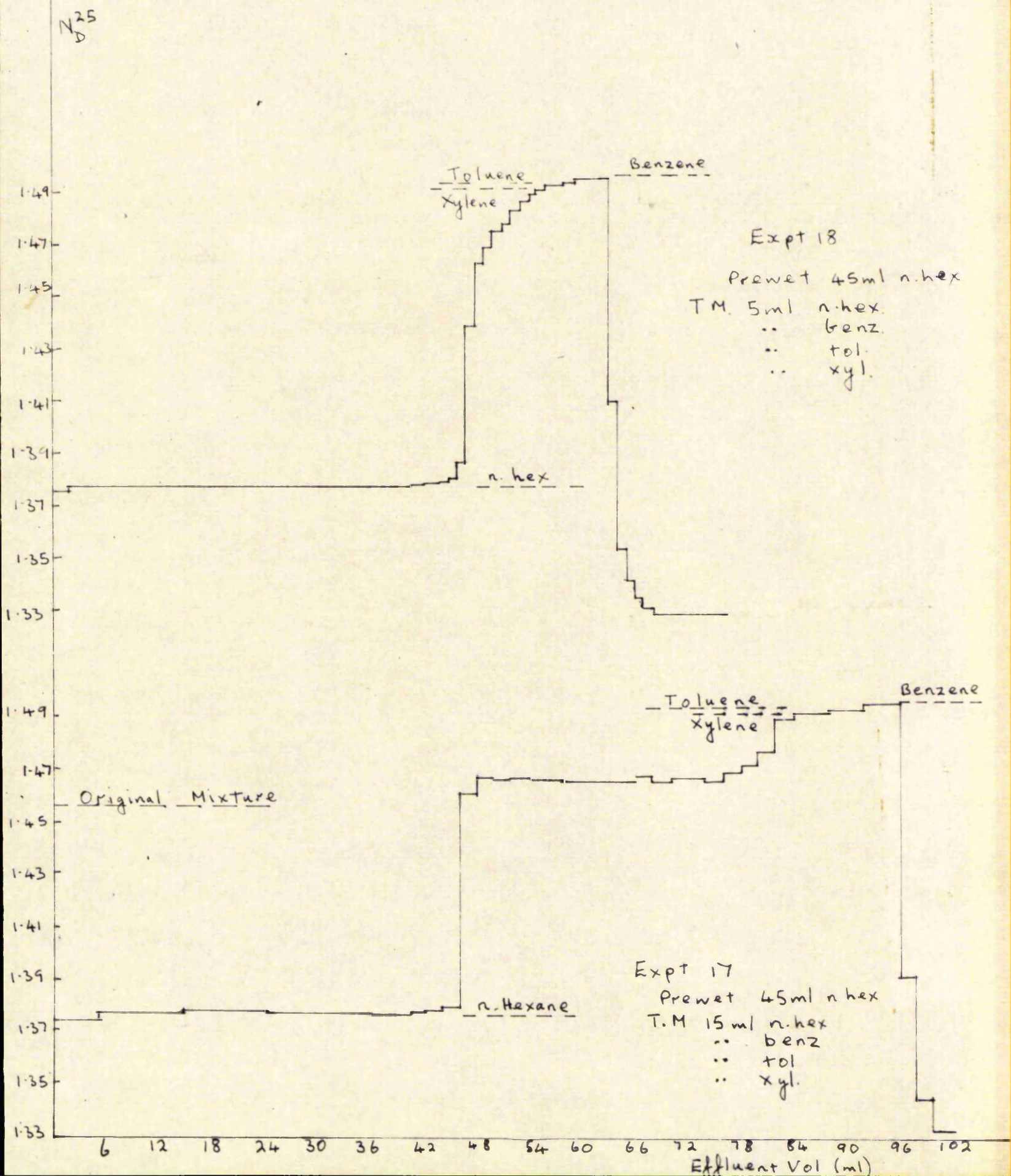


FIG 3.4

N_D²⁵

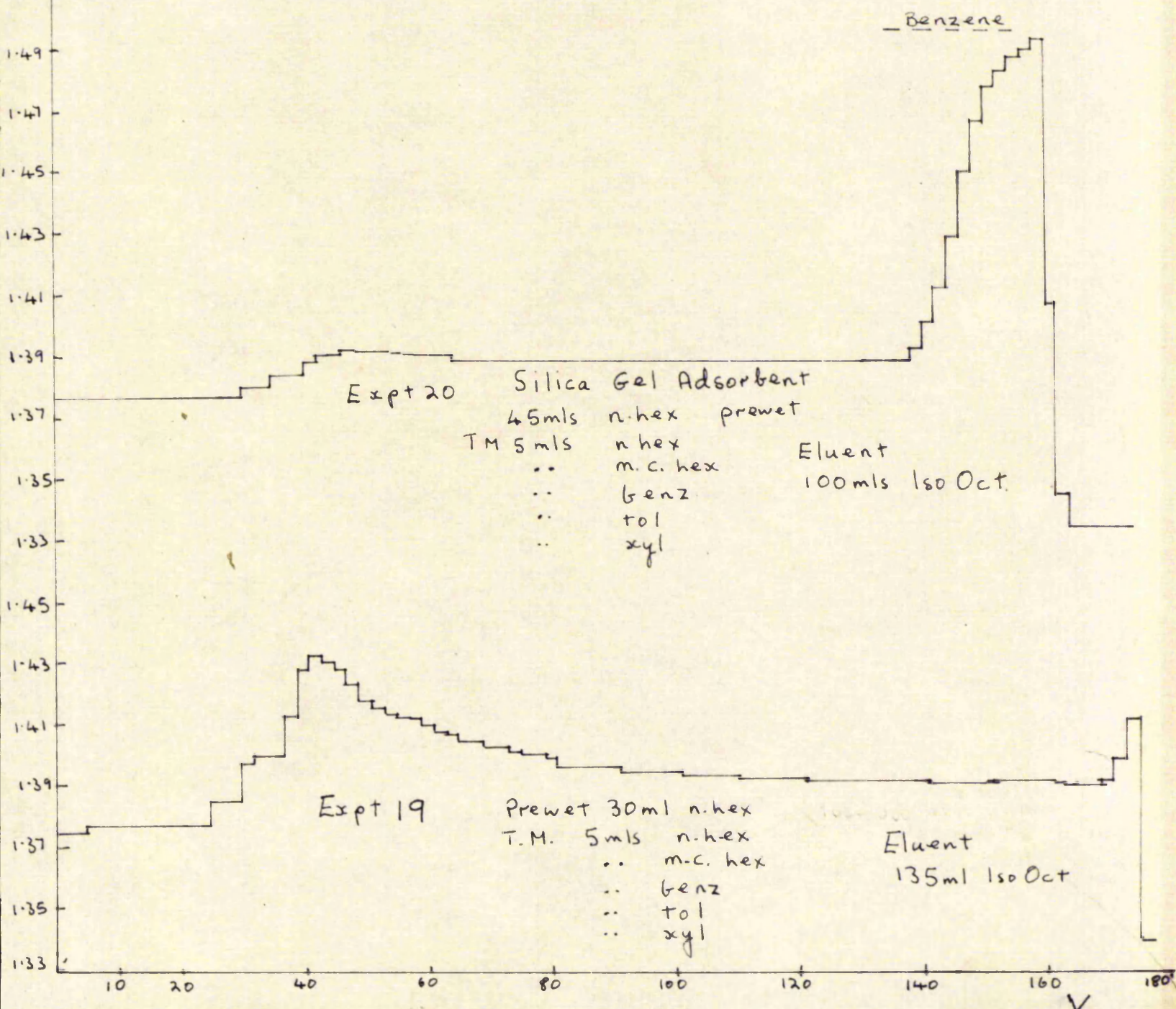


FIG 3.5

N₂
D

Expt 23

2 columns 3'x1", 5'x $\frac{5}{8}$ "

Prewet 60ml n-hex

T.M. 25ml

Eluent 80ml Iso Oct

Expt 22

Prewet 45ml n-hex

T.M. 25ml

Eluent 100ml Iso Oct

UPFLOW

Expt 21

150-240 # Alumina

Prewet 45ml n-hex

T.M. 25mls

Eluent 100mls Iso Octane

20

40

60

80

100

120

140

160

180

V

FIG 3.6

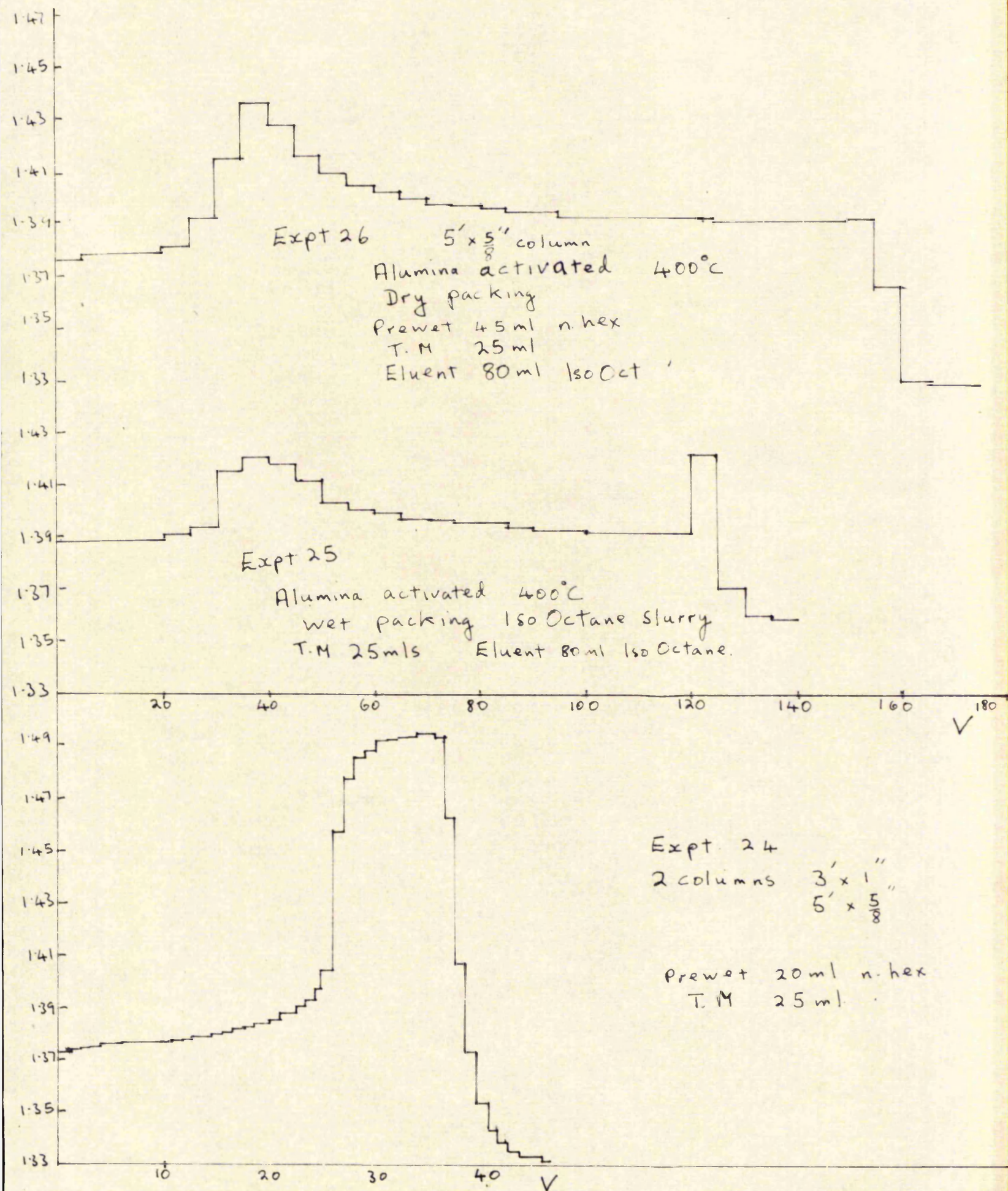
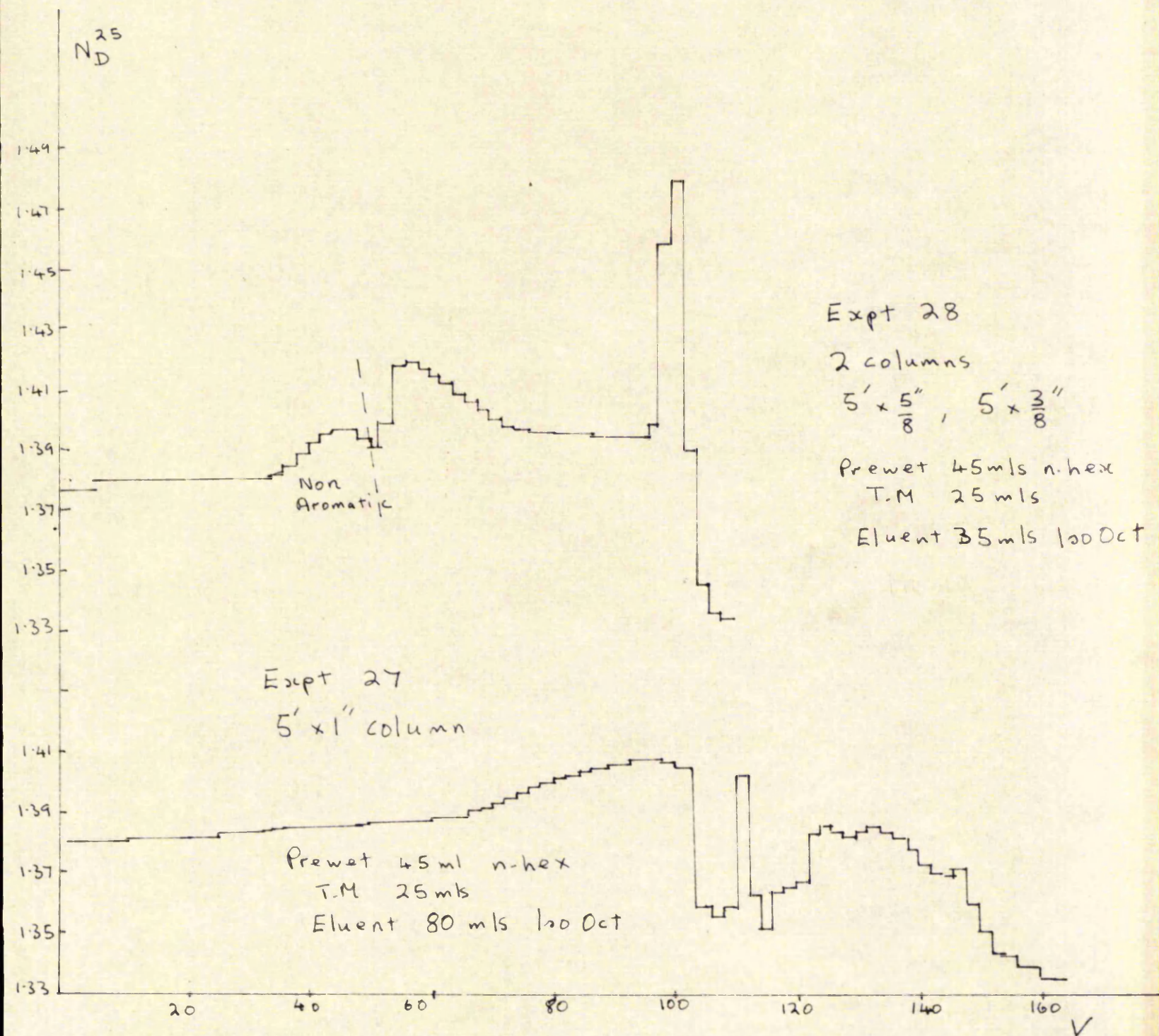
N_D²⁵

FIG 3.7



3.5. DISCUSSION OF RESULTS

Due to the fact that only refractive index was used to characterise the samples obtained, a complete analysis of the results is not possible. However, various trends can be observed, and the difference in refractive index between the aliphatic and aromatic compounds enables an estimation of the separation achieved to be made. The efficiency of separation was judged by the separation of aliphatic and aromatic compounds, the separation of individual compounds and the amount retained on the adsorbent after elution to be displaced by methanol. It was not possible to use the formolite test due to the presence of traces of aromatics in almost every sample.

1). Wet and dry packing. Experiments 25 and 26, Fig. 3.6.

It can be seen that the dry packing in experiment 26 gives the higher peak, even though the difference in primary solvents used meant that expt. 25 would have been expected to give the higher peak, due to the higher refractive index of iso-octane. However, a small amount of test mixture has been retained on the adsorbent for desorption by methanol in the wet-packing run. It has been reported elsewhere (17) that wet-packing gives greater efficiency than dry-packing for frontal analysis; but in this case, the advantage is not obvious. Difficulties in handling the slurry, and slight channelling effects due to caking, render this method not worthwhile unless a large improvement in efficiency is noticed.

2). Activation Temperature. Experiments 19 and 26, Fig. 3.4., 3.6.

The purpose of activating the adsorbent at 400°C (when it was assumed to have no free water adsorbed in the pores) was to see if any more adsorption sites were made available.

In experiment 26, using the 400°C . activated alumina, the peak is slightly higher, rising at 1.436, compared with 1.432 in experiment 19, though the peaks are almost the same shape. This suggests that adsorption may not necessarily be affected by water content of the adsorbent, due to the fact that different bonding mechanisms are involved, and that water and hydrocarbon molecules may not compete for the same sites. As increasing the water content is known to reduce adsorption capacity, it is possible that the value of the water content is very important. Work in this department by Pendlebury (51) may give a better solution to this problem.

3). Column Diameter. Experiments 19, 23, 27, 28. Fig. 3.4, 3.5, 3.7.

Experiment 19, using 275 gms. alumina in a $5' \times \frac{5}{8}"$ column may be compared with a similar experiment using 757 gms. alumina in a $3' \times 1"$ column and a $5' \times \frac{5}{8}"$ column in series (No.23). In the latter, nearly three times as much adsorbent has been used, and the separation has been improved as the aromatics have been held on the adsorbent and were quite well separated from the aliphatics. This shows the improvement due to increasing the adsorbent/ adsorbate ratio. The use of a narrow column after a wide column meant that the primary separation into zones took place in the wide section, while the finer separation between each component occurred in the narrower column.

Experiment 27 shows the use of a large diameter column containing the same weight of adsorbent as in Expt. 23. In spite of a streak which resulted in some mixing of the methanol front, it can be seen that the separation is not as good as No. 23, with no sudden increase in refractive index of the effluent.

Experiment 28, carried out in two 5ft. columns of narrow diameter, shows that with the use of only 27% more adsorbent than in experiment 19, the separation is much better than in all other experiments, giving two peaks eluted with iso-octane, the first one being almost entirely non-aromatic, and a high peak in the methanol front showing good separation between the iso-octane eluent, the aromatic material and the methanol desorber. This suggests that the use of a narrow column (in this case $\frac{3}{8}$ ") does much to improve separation efficiency.

4). Comparison of Silica Gel and Alumina. Experiments 19,20. Fig.3.4.

The silica did not give a much better separation than alumina, although the results obtained were very different. The alumina in experiment 19 gave slight separation of aliphatics, as seen by the step in graph 3.4. at $N_D^{25} = 1.400$, and then a wide peak showing little separation and a small amount held on the adsorbent to be desorbed by methanol. Silica, in experiment 20, gave a very small peak with iso-octane, containing perhaps half the aliphatics, and a very high peak in front of the methanol desorber containing the aromatics and also some aliphatics, as shown by the very gradual rise from iso-octane (1.389) up to the peak at 1.494. It is thought that deactivating the silica in some way would have resulted in none of the aliphatics being held on the adsorbent, but being eluted with iso-octane, giving good separation. This demonstrates the greater adsorption capacity which silica gel has compared with alumina for hydrocarbons. The difference in particle size range is not thought to have contributed to this effect.

5). Displacement Chromatography. Experiments 17, 18, 24. Fig. 3.3, 3.6.

Experiment 17 shows that the column was overloaded with much of the test mixture emerging almost unchanged. Reducing the amount of test mixture in experiment 18 to one third of experiment 17 shows that separation is beginning, but a column several times the length of the one used would have been necessary to achieve separation into zones of pure components. Using two columns in experiment 24 shows an improvement, but the result is still nowhere near as good as using an elution technique. Although there is a sharp rise in refractive index, much mixing of the zones is evident.

6). Mesh Size. Experiments 19 and 21. Fig. 3.4. and 3.5.

It was expected that the 150-240 mesh. in experiment 21 would have given the better separation, due to the more uniform packing obtained with smaller particles and the greater surface area available for adsorption. However, only a marginal advantage was observed. The iso-octane peaks are almost identical in shape, but the finer alumina gives a higher peak in front of the methanol desorber. G.L.C. analysis of some samples from experiment 21 showed how the experiment was progressing. The samples numbered on the graph were described as follows:

1. The bulk of the sample formed by hexane, with less than 10% of methylcyclohexane.

5. Three main components, in the following order of concentration iso-octane, xylenes and toluene.

Methylcyclohexane and benzene in lesser concentrations, and about the same order of magnitude.

14. Main component: iso-octane; secondary components in order of concentration: toluene, xylenes, benzene.

20. Main component: iso-octane; secondary components in order of concentration: toluene, xylenes, benzene.

7). Direction of Flow. Experiments 19 and 22. Fig. 3.4 and 3.5.

It was concluded by Ibbotson (14) and Badhwar (17) that upflow would give better separation where the more strongly adsorbed component was also of the higher density. In this case, the S.G. of the aromatics was about 0.86, and the aliphatics about 0.7. It can be seen that upflow in experiment 22 gives slightly better separation into two peaks in the iso-octane fraction. A higher peak in front of the methanol desorber shows that slightly more aromatic material has been held on the adsorbent, and not eluted with the iso-octane.

3.6. CONCLUSIONS ON TEST MIXTURE SEPARATIONS

1). A preliminary investigation has been made concerning the effect of several variables on column efficiency. These were:

- Wet and dry packing,
- Activation temperature,
- Column diameter,
- Particle size,
- Direction of flow.

A comparison between alumina and silica has also been made, and the techniques of elution and displacement chromatography have been compared.

2). From these experiments, it seems that the amount of adsorbent and column diameter have noticeable effects on elution analysis. Several columns of narrow diameter will effect a good separation between aromatics and non-aromatics. Ibbotson found that for upflow on alumina a 1.0 cm. dia. column was the most efficient, and this is in agreement with these studies. In experiments 23, 27 and 28, the flow was upwards in the narrower diameter columns, but in this case the effect of upflow was not distinguishable from other effects.

3). It was not possible to detect much separation among the aromatic components due to the very similar refractive indices. For a small detailed study, a test mixture should be more carefully chosen.

4). GLC analysis was found to be useful in showing where each component began and ended. When used quantitatively, it will give many possibilities for evaluating column efficiencies.

3.7. PARTITION CHROMATOGRAPHY

This technique was developed by Martin and Synge (52) and LeRosen (53). The mixture to be separated is distributed between two liquid phases, one of which is adsorbed on a stationary solid support and the other mobile. The principle is similar to gas-liquid chromatography. (G.L.C.). It is sometimes difficult to distinguish this technique from adsorption chromatography. If adsorption takes place to the extent that a multilayer is formed, and the adsorbed layer acts as a solvent, then the conditions for partition chromatography exist. In this case, the distinction in terminology is not important.

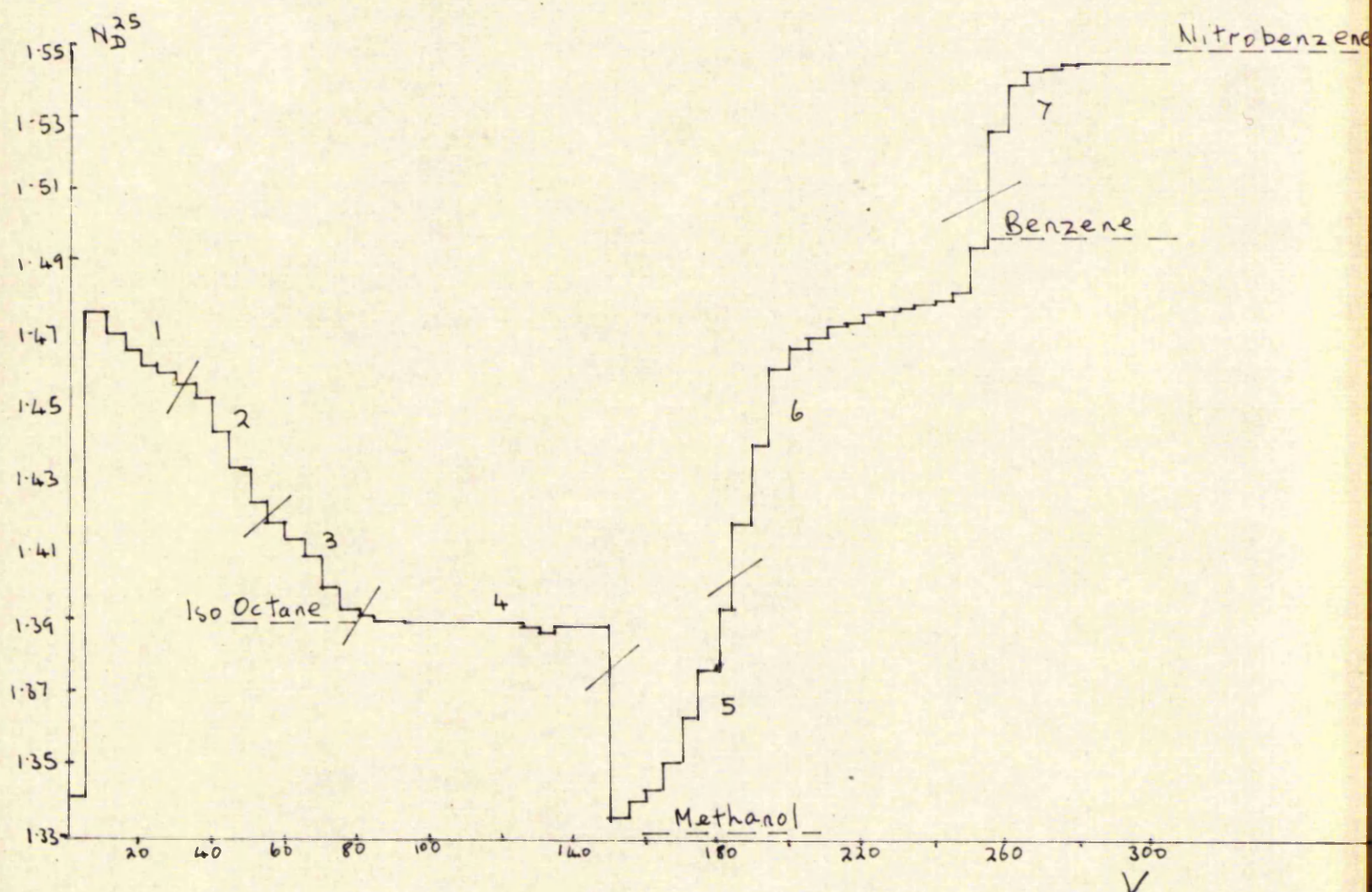
Martin and Synge separated acetylated amino-acids on a column of silica on which was adsorbed an aqueous phase, using a 1% solution of n.butanol in chloroform as eluent.

The application of this technique to mineral oils was carried out by Mair et al (54). They used a column packed with silica gel, on which was adsorbed methyl cellosolve, or methyl carbitol. The sample of oil was charged to the top of the column and was followed by heptacosaflluoro-tributylamine ($(C_4F_9)_3N$ or perfluorocyclic ether ($C_{18}F_{16}O$).

FIG 3.10

Expt 16

Partition Chromatography.



As the fluoro. chemical passed down the column, an interchange of molecules took place. The paraffins concentrated in the mobile phase, while the cycloparaffins concentrated in the adsorbed phase. Using a column containing 155 gms silica gel with 139 mls. of stationary phase, a 10 mls. sample was separated.

As the separation of normal and cycloparaffins is usually very difficult, it was thought worthy of investigation; but because the solvents above were not readily available, methanol was used as the stationary phase. After elution with iso-octane and benzene, nitrobenzene was used as desorber, as this was one of the few compounds more strongly adsorbed than methanol.

A sample of 22 gms. of oil was charged to a 5' x $\frac{5}{8}$ " column containing 261 gms alumina. The oil used was KX₆ (boiling range 375-380°C) and $N_D^{25} = 1.5460$. Further data are given in Appendix 1.

Results.

The result of the experiment is seen in Fig. 3.10.

Most of the oil appeared in the iso-octane peak, with the refractive index returning to that of pure iso-octane. Droplets of methanol in iso-octane then appeared (the two are immiscible), and then benzene mixed with methanol, followed by the nitrobenzene desorber.

The samples obtained were bulked according to the numbers on the graph, and stripped of solvent.

<u>fraction No.</u>	<u>wt%.</u>	<u>N_D^{25}</u>
1	31.5	1.5409
2	32.1	1.5382
3	9.6	1.5576
4	0.92	1.6020
5	0.46	not sufficient for N_D^{25}
6	0.46	
7	-	
	<hr/> 75.2%	

This does not show much separation, and all but 0.46% was removed by the iso-octane. The reason for the appearance of methanol after iso-octane is not clear. It was expected that due to their great differences in adsorbability and immiscibility, very little methanol would appear at this stage, but it would appear before the nitrobenzene. It could not have been displaced by the oil, as in this case the oil would have been retained on the adsorbent. It may be that lowering the column load and the more selective use of solvent phases will give better results. Solvents which are miscible in all concentrations would improve the mass transfer process.

P A R T II.

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CHAPTER 4. BATCH SLURRY SEPARATIONS

4.1. INITIAL CONSIDERATIONS

For some time now, the work of the M.R.C. committee has been concentrated on the strongly adsorbed polynuclear aromatic compounds which are usually in the benzene eluate of a chromatographic separation. To obtain samples for further analysis, it was necessary to go through the whole process of elution chromatography, including elution with iso-octane.

The 40' x $1\frac{1}{2}$ " columns in this department have been shown to give reasonable separation into molecular types, particularly of aliphatic from aromatic material. However, for the primary separation of polynuclear aromatics (material eluted with benzene), from simpler aromatic material (eluted with iso-octane), it appeared as if the columns might have been operating more efficiently than necessary, with a resultant wastage of time.

The efficiency of the separation must be judged by the result required; for a complete oil separation, the column is nowhere near efficient enough to give separation into zones of pure compounds.

Reference to Fig. 3.2. shows an example of this efficiency. Ibbotson concluded that the 10' column was the more efficient, as more oil was eluted with benzene, showing that it had been retained on the adsorbent. However the 40' column gave a much higher refractive index benzene eluate, with poorer separation of the rest of the oil by iso-octane. Clearly with respect to current M.R.C. work, the 40' column has given the best result. If the separation of the iso-octane eluate material could be cut out altogether, a great deal of effort could be saved.

As well as efficiency considerations, time was also an important factor. To complete the separation of 3kg. of oil, by charging 1kg. to each of the three 40' columns available would take at least two months, including over a week of shift work while the columns were running continuously. As the result of a request from Dr. Carruthers in Exeter, for a large sample of the benzene eluate, the large scale batch slurries (see chapter 5) produced the sample from 20kg. of oil in two months, instead of the "one year plus" it would have taken on the column.

A further consideration was that for large scale separations, the column was not suitable as an industrial process, due to low throughput, high pressure drop, difficulties in packing and unloading the column, and excessive time required.

It seemed that the possible ways to overcome these difficulties included the following:

- 1). Increase the oil/adsorbent ratio.

This would increase the throughput, but would not give a good benzene eluate sample, due to overlapping of zones of other compounds. Also this does not solve the time problem.

- 2). Vary the water content of the adsorbent.

This could make the separation less efficient, with only the strongly adsorbed material remaining on the adsorbent, but is still time-consuming.

- 3). Using a longer column.

This would give good separation of a benzene eluate, and by using the same oil/adsorbent ratio the throughput could be increased. However, the pressure drop would be greater, and it would be even more time-consuming than above.

4). A very useful benzene eluate could be prepared by following the method of 1) and rechromatographing the benzene eluate obtained; the time required would be twice as long however.

5). As the part of the oil required was the most strongly adsorbed, and therefore the most difficult to desorb, the oil could be completely adsorbed onto an adsorbent, and then the part not required could be desorbed. As this would be a batch process, the time factor could be overcome easily, and there would be no pressure drop considerations. Alternative 5) was considered further, as at the time it seemed to have the following advantages:

(i) by the simple mixing of a large volume of oil and adsorbent, the problem of time became negligible;

(ii) It was thought that several stages of contact between the oil-saturated adsorbent and an eluting solvent would leave only that part of the oil which was required;

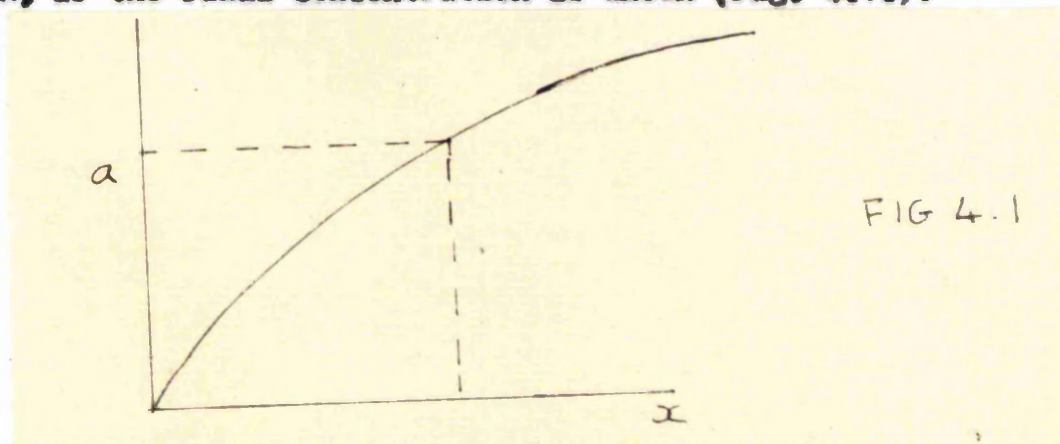
(iii) The mixing and filtration stages, with the accompanying evaporation of the oil solutions and distillation of solvents, could easily be carried out on a large scale. "Scale up" did not depend on time, as with using larger adsorption columns.

LITERATURE SURVEY RELATED TO BATCH SLURRYING

4.2. BATCH ADSORPTION PROCESSES

The batch processes considered in the literature are of a different type from those considered in this thesis. They are usually similar to a cascade process of equilibrium distribution, as used in liquid-liquid or liquid-solid extraction.

A simple batch process, similar to that used in determining isotherms, consists of contacting a known amount of adsorbent with a solution, and adsorbing one or more solutes, preferentially with respect to the solvent. The amount adsorbed can be read off from the isotherm graph, if the final concentration is known (Fig. 4.1.).



Sanders (55) improved the efficiency of batchwise adsorption when using it in the decolourisation of sugar solutions with charcoal. He related concentration to colour, so that he could measure progress by colourimetric means. The process was described quite well by a Freundlich isotherm in the form

$$\frac{V(C_0 - C)}{m} = KC^n$$

where $V(C_0 - C)$ is the amount of colour removed by m gm. of charcoal.

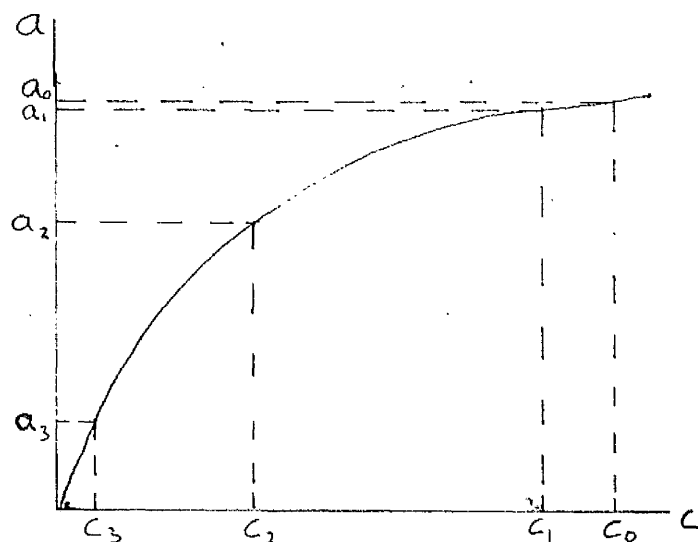


FIG 4.2

The solution enters with concentration C_0 and leaves with concentration C . Fresh adsorbent is contacted with the final stage to adsorb amount a_3 . The partly spent adsorbent is then contacted with the penultimate stage and so on, adsorbing a smaller amount each time. For a 4 stage process, only one third the amount of adsorbent was required with the isotherm of Fig. 4.2. The number of stages required can be calculated from the equation by letting $C_0 - C$ equal ΔC for each stage.

The refining of petroleum with fullers earth is similar to the above process, though on a continuous scale.

4.3. SOLID-LIQUID EXTRACTION (LEACHING)

Leaching is the extraction of a material from a solid with a solvent, and is used extensively in ore extraction, sugar beet extraction and vegetable oil production; the solute is usually uniformly distributed throughout the solid, and therefore the extraction tails off exponentially, as solvent penetration becomes more difficult, due to diffusion.

Assuming that a thin liquid film is controlling the process, the equation for mass transfer may be written as

$$\frac{dM}{dt} = \frac{K'A(C_s - C)}{b}$$

A = area of solid-liquid interface

M = mass solute transferred

b = thickness of liquid film

K' = diffusion coefficient

C = concentration on bulk solution

C_s = concentration of saturated solution in contact with the solid

In a simple countercurrent system for coarse solids, the solid is contained in a number of tanks and the solvent flows through each in turn. The first vessel contains solid which is almost extracted, and the last contains fresh solid. After a time, the first tank is disconnected and fresh charge is introduced at the far end of the tank system. This system requires frequent interruption, and countercurrent flow is not obtained in the units themselves. A true continuous process is obtained in a classifier in which the solid is moved countercurrent to the liquid by means of a rake with baffles.

4.4. LIQUID-LIQUID EXTRACTION PROCESSES

In these processes, the partition between a raffinate and an extract phase is governed by the partition coefficient of the form $C_1/C_2 = K$ at equilibrium, which corresponds to the isotherms in adsorption. The partition isotherms can be convex, straight or concave as shown in section 1.5. for adsorption. The attainment of equilibrium depends on diffusion through two films, one in each phase at the phase boundary.

A scheme for multiple-contact pseudocountercurrent extraction is shown in Fig. 4.3. for the complete removal of a solute from one phase to another (56).

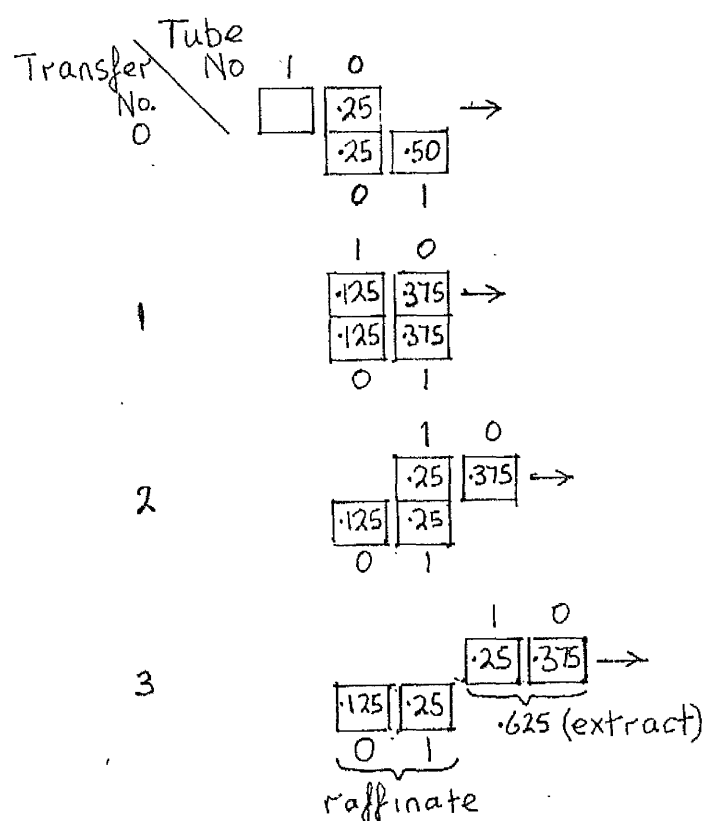


FIG 4.3

The solution to be extracted is divided into n convenient portions in separating funnels, and the funnels, or tubes, are numbered $0, 1, 2, \dots, n$. The first tube, numbered 0 , is shaken with an arbitrary volume of extractant, and the extract layer transferred to the next in line, tube 1 . A volume of extractant equal to that used in the first stage is added to tube 0 , and tubes 0 and 1 are equilibrated. The extract layer from tube 1 is transferred to tube 2 , the extract from tube 0 to tube 1 , and fresh solvent added to tube 0 .

In the case in Fig. 4.3., 100 mls of a solution containing 1.000 gms. solute are to be extracted with 100mls. solvent. The solution and extract solvent are both divided into two portions. As the extract portions are moved to the right, they pick up more solute until 0.625 gms. have been extracted.

This can be compared with a multiple contact non-countercurrent method which consists of dividing the extractant into four equal parts, and contacting each part with the solution.

If V mls. of a solution (phase I) containing W gms. of solute are repeatedly extracted with 1 mls. of solvent (phase II), and W_1 is the weight of solute remaining in phase I after the extraction, the distribution is

$$\frac{W_1 / V}{(W - W_1) / 1} = K$$

$$\therefore W_1 = W \frac{KV}{KV+1}$$

After a second extraction, W_2 gms. remain in phase I, and

$$W_2 = W_1 \frac{KV}{KV+1} = W \left(\frac{KV}{KV+1} \right)^2$$

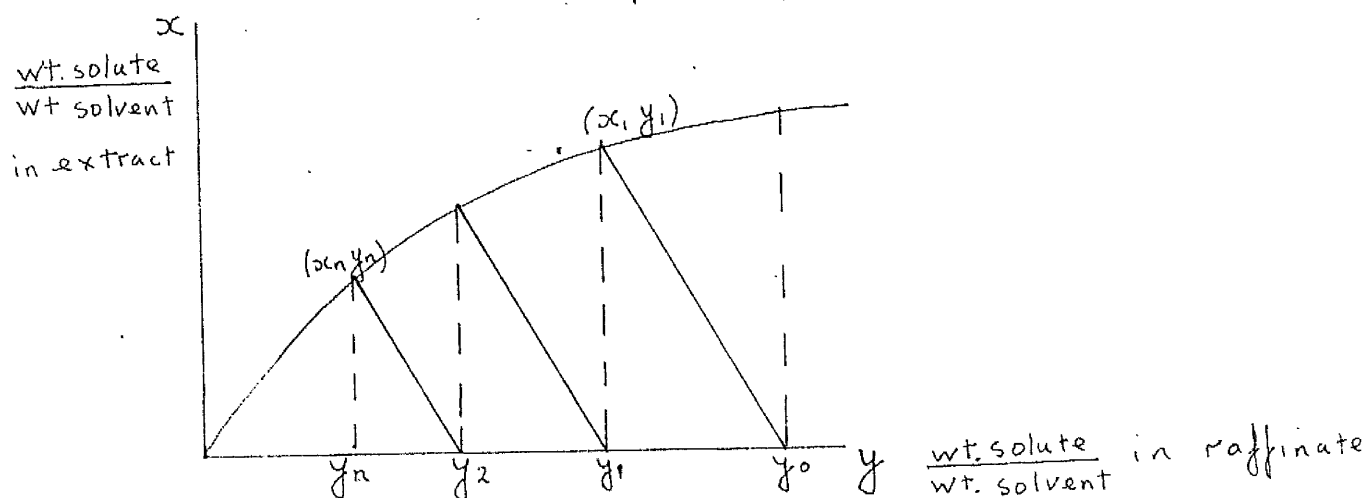
Similarly, after n extractions ,
$$W_n = W \left(\frac{KV}{KV+1} \right)^n$$

In the previous example, it can be shown that using the above equation 0.5904 gms. of solute could be extracted compared with 0.625 gms. for the same number of operations.

If the solution and extractant were divided each into four portions, and contacted according to Fig. 4.3., then 0.7265 gms. could be extracted. This would involve 16 operations, and any further subdivision would be considered laborious.

In the case of non-linear partition isotherms, the extraction process is similar to that shown for sugar decolourisation in Fig. 4.2.

FIG. 4.4



In Fig. 4.4., the partition ratio is decreasing with increasing concentration.

If a solution of y_0 gms. solute in R gms of pure solvent are contacted with S gms. of pure extract solvent which is immiscible with the solution,

then a line of slope $-\frac{R}{S}$ drawn through y_0 will give the distribution x_1, y_1 in the two phases at equilibrium. To reduce the solution concentration to y_n , n stages would be needed.

If a continuous countercurrent process were carried out, in a packed column for instance, then the number of theoretical stages could be found from the partition isotherm graph.

For partially miscible solvents, ternary equilibrium diagrams are used.

The separation shown in Fig. 4.3. can be represented graphically. For a two component solute mixture, due to different partition ratios, the components will move at different rates along the line of tubes.

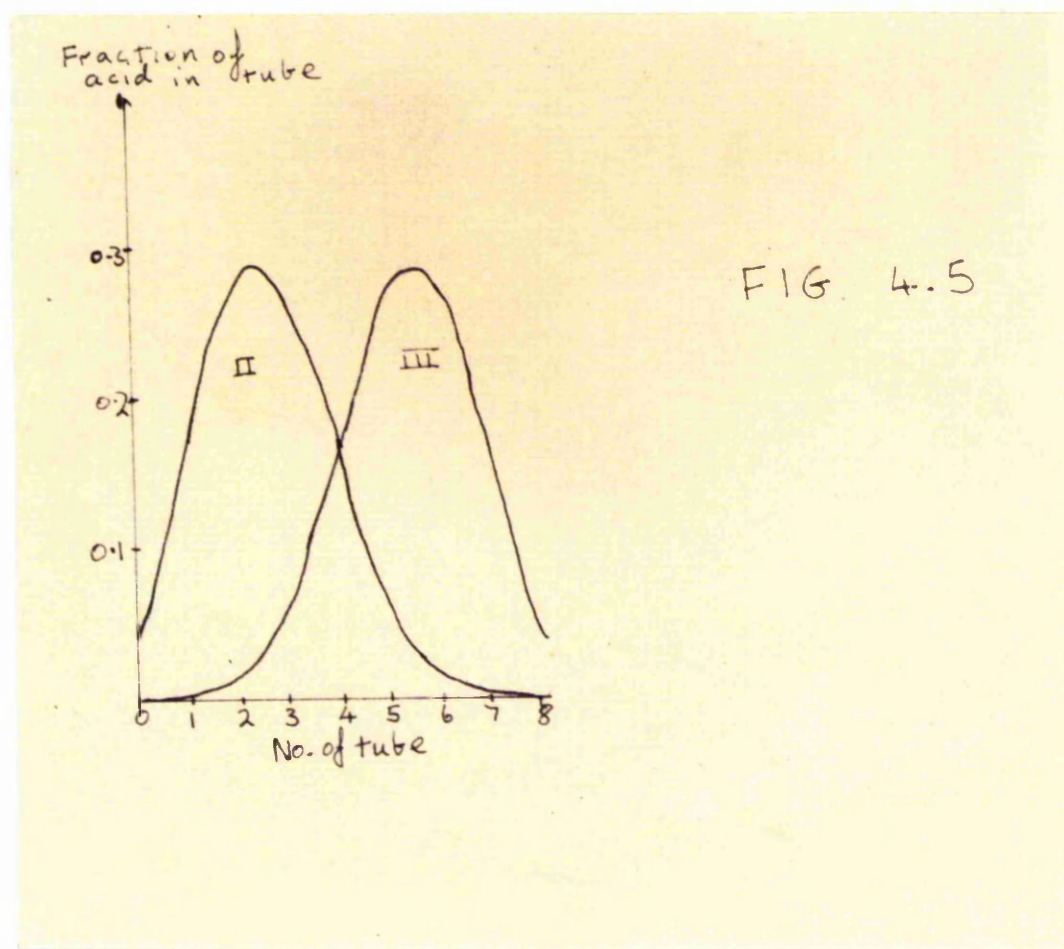
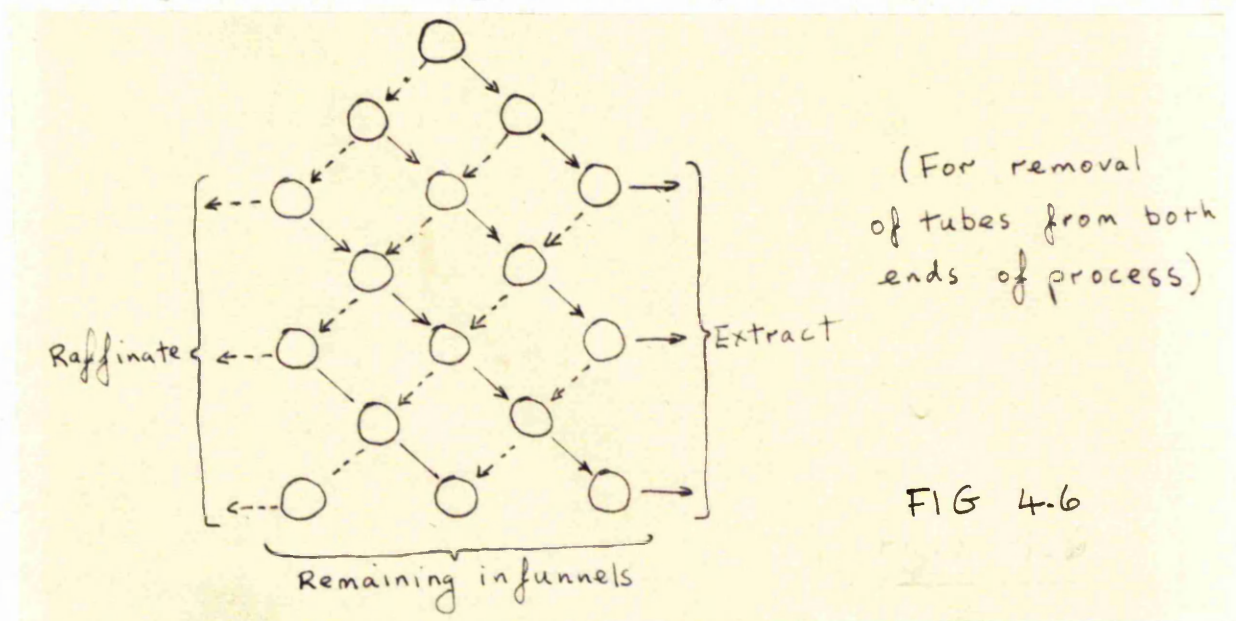


FIG. 4.5

Fig. 4.5. shows the extraction of a mixture of propionic and butyric acids, represented by curves II and III respectively, in an eight transfer process. Tube No.8 could be withdrawn, as it contains essentially butyric acid, and replaced by an empty tube. After proceeding one stage further, tube 8 could again be withdrawn and replaced by an empty tube. Soon however, propionic acid would appear in significant quantities. This is very similar to an adsorption elution process.

The process can be represented diagrammatically as shown in Fig. 4.6.



Each circle represents an equilibrium contact, dotted arrows represent the solution, or raffinate phase, and the solid arrows represent the extract phase. The volumes at each stage are always the same, due to the introduction of fresh extractant.

A development of this technique has been the Craig automatic counter-current distribution apparatus containing up to 400 tubes. The solution is placed in each tube, and the extractant placed on top of it. By varying the angle of the tubes, the phases are mixed, and then the tubes are tilted to allow the extract phase to decant into the adjacent tube. At the end, the extract can be removed, and replaced by fresh solvent. By recycling this last extract phase to the first tube, many thousands of transfer stages can be obtained, resulting in the complete separation of otherwise inseparable material.

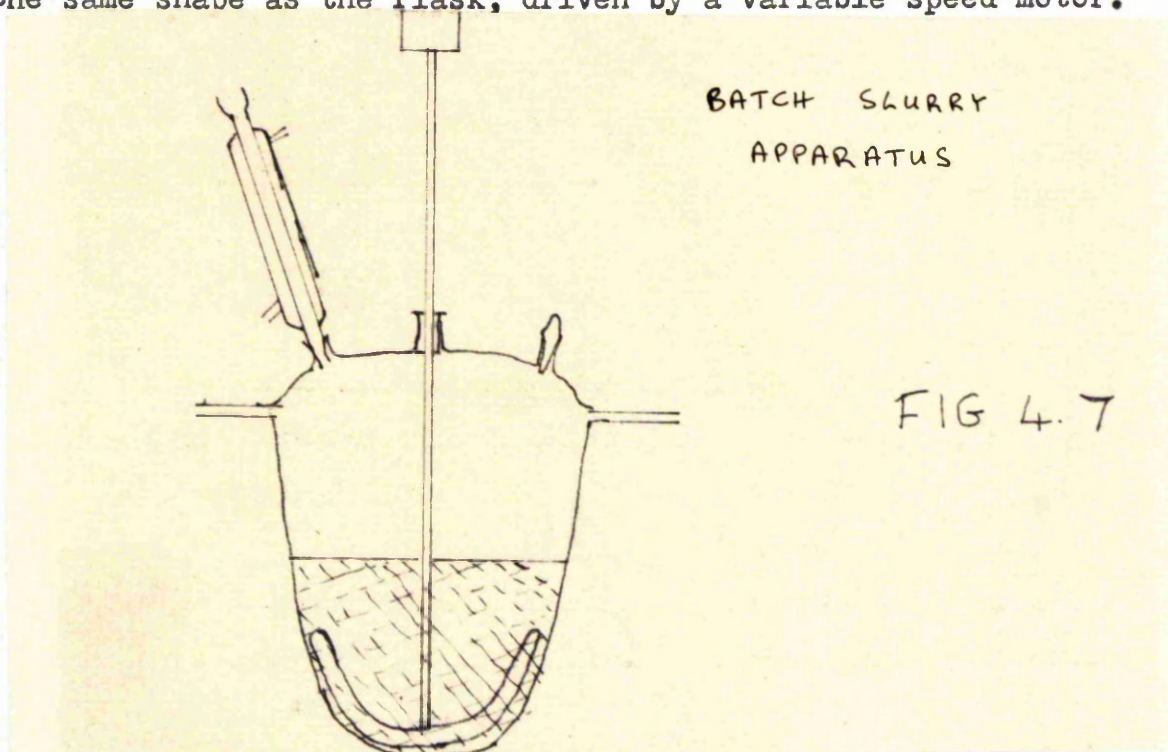
4.5. PRELIMINARY EXPERIMENTS IN BATCH SLURRYING

Three experiments on oil separation were carried out on alumina using a Kuwait extract oil of boiling range $375-380^{\circ}\text{C}$, and known as KX₆. The oil was produced in earlier work on this project by vacuum distillation, and has been separated on the large column by Higgins (57). It was also separated by the author on a $5' \times \frac{5}{8}"$ column, using the elution technique described earlier. Similar results were obtained to those from the $40'$ column.

Experiment 1 was carried out using an oil/adsorbent ratio of $1/5$. It was realised that the first stage would give very little separation, and so it was considered worthwhile to increase the inefficiency by increasing this ratio in order to be able to use more oil. This could give samples large enough to analyse further. The amount of solvent used in each stage was determined by the amount needed to form a slurry which could be stirred to give good liquid-solid contact. This volume was found to be about equal to the weight of alumina numerically, i.e. 100 mls solvent with 100 gms. alumina. Only one iso-octane stage was used, and as not much separation was obtained, experiments 2 and 3 had four iso-octane stages in order to leave only high refractive index material on the adsorbent.

4.6. APPARATUS AND TECHNIQUE

Analytical data on all materials used are given in Appendix 1. The apparatus, shown in Fig. 4.7., consisted of a wide-neck reaction vessel, open to atmosphere through a condenser, and an anchor stirrer the same shape as the flask, driven by a variable speed motor.



The alumina was kept at $115-125^{\circ}\text{C}$ for 8 hours, and allowed to cool in a closed vessel. It was then quickly weighed into the reaction vessel, and about half the iso-octane was poured in to saturate the adsorbent and dissipate any heat of adsorption produced by the oil. The weighed amount of oil was then poured in and the weighing bottle washed with more iso-octane. The remainder of the iso-octane was then added, and the flask top was fitted.

The spare entry point in the top was used either for charging more liquid, checking the slurry temperature, or taking liquid samples. The experiments were carried out at room temperature, which usually varied between 19 and 22°C.

The stirrer was then started, and by observation was run at the minimum speed to keep all the solid particles in motion, and was usually about 120 r.p.m.

Two hours were allowed for equilibrium to be established, and then the slurry was vacuum filtered in a Büchner funnel.

To avoid any oil loss, the same piece of filter paper was used throughout the experiment.

When the alumina was dry, with no free liquid in the filter cake, the solid was returned to the reaction vessel, and an equal volume of fresh solvent to that used in stage I was charged.

Stirring was carried out for another two hours, and so on for each stage.

The iso-octane/oil solution was then freed of solvent in a rotary vacuum stripper (see below).

The weights and refractive indices of all samples were then determined.

4.7. ANALYSIS OF SAMPLES

1). Refractive Index.

All readings were taken at 25°C on the Abbé instrument previously described in section 3.3. It has been reported that errors can arise from the use of refractive index alone to characterise oil fractions (28).

Saturates have been recorded with N_D^{20} above the usual limit met in lubricating oil fractions (1.48).

eg. 1.3 dicyclohexylcyclohexane	N_D^{20}	= 1.494
cis decalin		= 1.4811
9-n butylperhydroanthracene		= 1.5049.

Aromatics exist below the usual limit (1.49)

eg. 1 phenyloctadecane		= 1.481
1 phenyldodecane		= 1.474

However, these compounds may only exist in trace amounts in the oil used, and were not thought to have any effect on the refractive index.

2). Formolite Test.

This was used to identify samples which contained aromatic hydrocarbons. The test was used as a spot test, according to the modification by Sagarra (58).

"A spot of the filtrate was taken with a glass rod, and mixed with five drops of concentrated sulphuric acid on a clean white tile. A spot of 40% formaldehyde was placed on the tile, and slowly mixed with the acid mixture. The presence of aromatics was shown by the development of coloured bands.

3). Specific Gravity.

This was measured at 20°C with a capillary stoppered bottle according to the Institute of Petroleum Standard Method (59).

Some measurements were also taken at 25°C in order to determine the temperature coefficient in case a correlation of specific gravity against refractive index could be used to identify molecular types. It was attempted to determine the S.G. of small oil samples (approx. 0.1-0.3gms), but it was not possible to obtain reliable results. The methods used are reviewed in Appendix II.

4). Sulphur Content.

This was carried out according to the Institute of Petroleum Quartz Tube Standard Method (59). The method consisted of burning the oil sample in a stream of purified air to SO_2 , CO_2 and H_2O . The SO_2 alone was absorbed by bubbling the exit gases through 3% v/v H_2O_2 to produce H_2SO_4 . The acid solution was titrated with $\frac{N}{10}$ NaOH solution to give the sulphur wt%.

4.8. REMOVAL OF SOLVENT FROM OIL SOLUTIONS

This was carried out in a rotary film evaporator (Buchi, Switzerland). The flask was held at the end of a rotating arm which was at an angle of about 30° above the horizontal. The rotating flask was kept in a water bath at approx. 60°C .

Evaporation took place from the thin film of liquid adhering to the glass surface on rotation, and the solvent was condensed by a double surface cold water condenser, and collected in a flask.

A cold trap containing a solid CO_2 /kerosine mixture protected the vacuum pump from solvent vapours. The system was operated at a pressure just low enough to enable solvent to be collected. When no more solvent condensed, the collecting flask was emptied, and the maximum vacuum of less than 1mm. Hg. was applied for about 20 minutes.

A non-hydrocarbon-soluble grease, prepared according to I.P. Standards was used to obtain air tight joints.

4.9. EXPERIMENTAL DETAILS

Experiment 11.

Separation of KX_6 by chromatography. (see Fig. 4.8).

$N_D^{25} = 1.5460.$	Column 5' x $\frac{5}{8}$ " Downflow.
wt $Al_2O_3 = 265$ gms.	250 mls. Iso-Octane
wt oil = 21.8 gms.	130 mls. Benzene
	Desorber Methanol

Volumes of solvents used were in proportion to those used on the 40' column.

Experiment 1.

Batch Slurry Separation of KX_6 . wt Al_2O_3 100gms., wt oil 19.2 gms.

Stage 1. 130 mls. Iso-Octane

" 2. 100 mls. Benzene

Stage 3. 80 mls. Benzene

" 4. 80 mls. Methanol.

Experiment 2.

Batch Slurry Separation of KX_6 . wt Al_2O_3 100gms., wt oil 18.4gms.

5 successive iso-octane stages of 100 mls. each.

2 successive benzene stages of 100 mls. each.

1 Methanol stage of 100 mls.

Experiment 3.

Repeat of experiment 2. wt Al_2O_3 100gms., wt oil 19.1 gms.

Solvents were used exactly as in Experiment 2.

TABLE 4-1.

Experiment No.	Solvent.	Stage No.	wt% of original oil.	N _D ²⁵ of Stripped oil.
1.	Iso-oct.	1.	33.9	1.5298
	Benz.	2.	34.4	1.5425
	Benz.	3.	4.68	1.5565
	MeOH.	4.	2.60	1.5630
			<u>75.58</u>	
2.	Iso-oct.	1.	36.4	1.5265
	"	2.	28.8	1.5348
	"	3.	7.61	1.5455
	"	4.	3.76	1.5564
	Benz.	5.	11.42	1.5941
	"	6.	4.35	1.6008
	"	7.	1.63	1.6024
	MeOH.	8.	3.81	solid
			<u>97.48</u>	
3.	Iso-oct.	1.	42.4	1.5262
	"	2.	23.0	1.5360
	"	3.	10.5	1.5484
	"	4.	4.72	1.5618
	Benz.	5.	8.90	1.6049
	"	6.	3.67	1.6097
	"	7.	1.57	1.6096
	MeOH.	8.	2.62	solid
			<u>97.38</u>	
11.	Iso-oct.	1.	10.55	1.4490
	"	2.	28.0	1.4800
	"	3.	16.0	1.5306
	"	4.	5.4	1.5508
	"	5.	4.13	1.5472
	Benz.	6.	17.0	1.5999
	"	7.	16.5	1.6236
	"	8.	1.38	1.6150
	MeOH	9.	0.3	solid
			<u>99.24</u>	

4.10. DISCUSSION OF RESULTS

The chromatographic separation gave an iso-octane portion which consisted of two overlapping peaks, the first being "formolite negative". The stripped oil fractions are shown in Fig. 4.9 and details given in Table 4.1.

The fractions were bulked according to the diagonal lines on the N_D^{25} v. volume of effluent graphs. The letters N.A. mean non-aromatic and that each sample in the group between the diagonal lines gave a formolite negative reaction. The benzene eluate gave a sample of high refractive index material in fraction 8.

Experiment 1 (Fig. 4.9.) does not show very good separation, the reason being that not enough material was displaced from the alumina by the iso-octane. This means that the benzene has displaced a lot of low refractive index material, giving a fraction of mixed hydrocarbon types. Experiments 2 and 3 (Fig. 4.10) were an improvement on this technique, the four iso-octane stages removing 75-80% of the oil compared with 64% on the column. This should have led to higher refractive index material appearing in the benzene stages, but in fact both experiments gave much lower indices.

This must have been because of isotherm considerations, -at all concentrations, and with all solvents, some of the oil will be in the bulk liquid phase, and it is not possible to obtain complete separations by this means. It must be assumed that there will be always some contamination of fractions in batch stages.

Reference to the sugar decolourising in Fig. 4.2 shows that only four theoretical equilibrium stages were used. In experiments 2 and 3, eight theoretical stages were used, but on an adsorption column, using elution chromatography, many times that number of stages would be obtained, giving less contamination of fractions.

FIG. 4.8

25
 N_D

-1.63

-1.59

-1.49

-1.47

-1.45

-1.43

-1.41

-1.39

-1.37

-1.35

-1.33

Expt 11

Fractionation of KX_6

on alumina

$5' \times \frac{5}{8}"$ column.

Eluate fractions

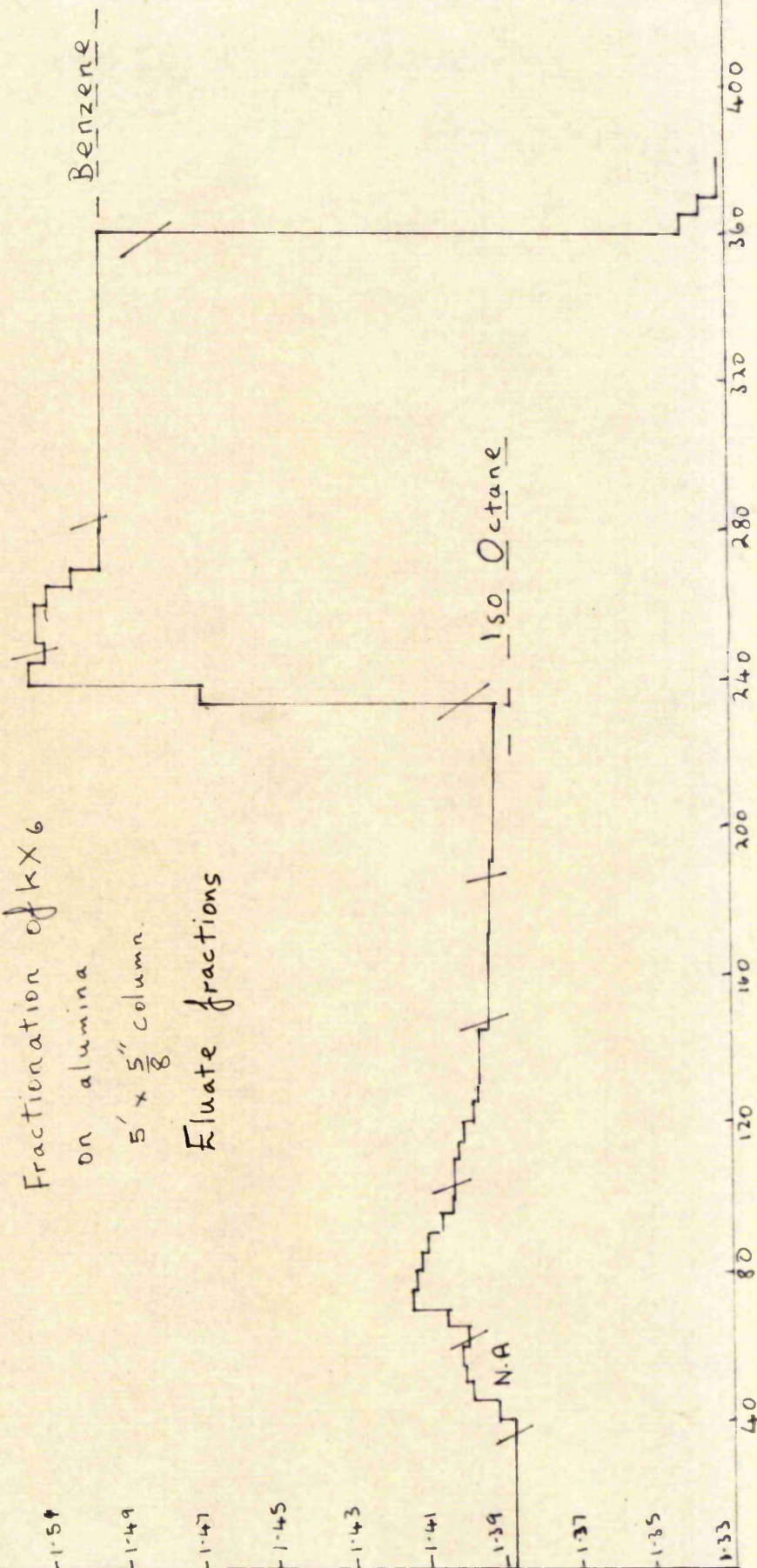


FIG. 4.9

Refractive Index of Stripped Oil Fractions

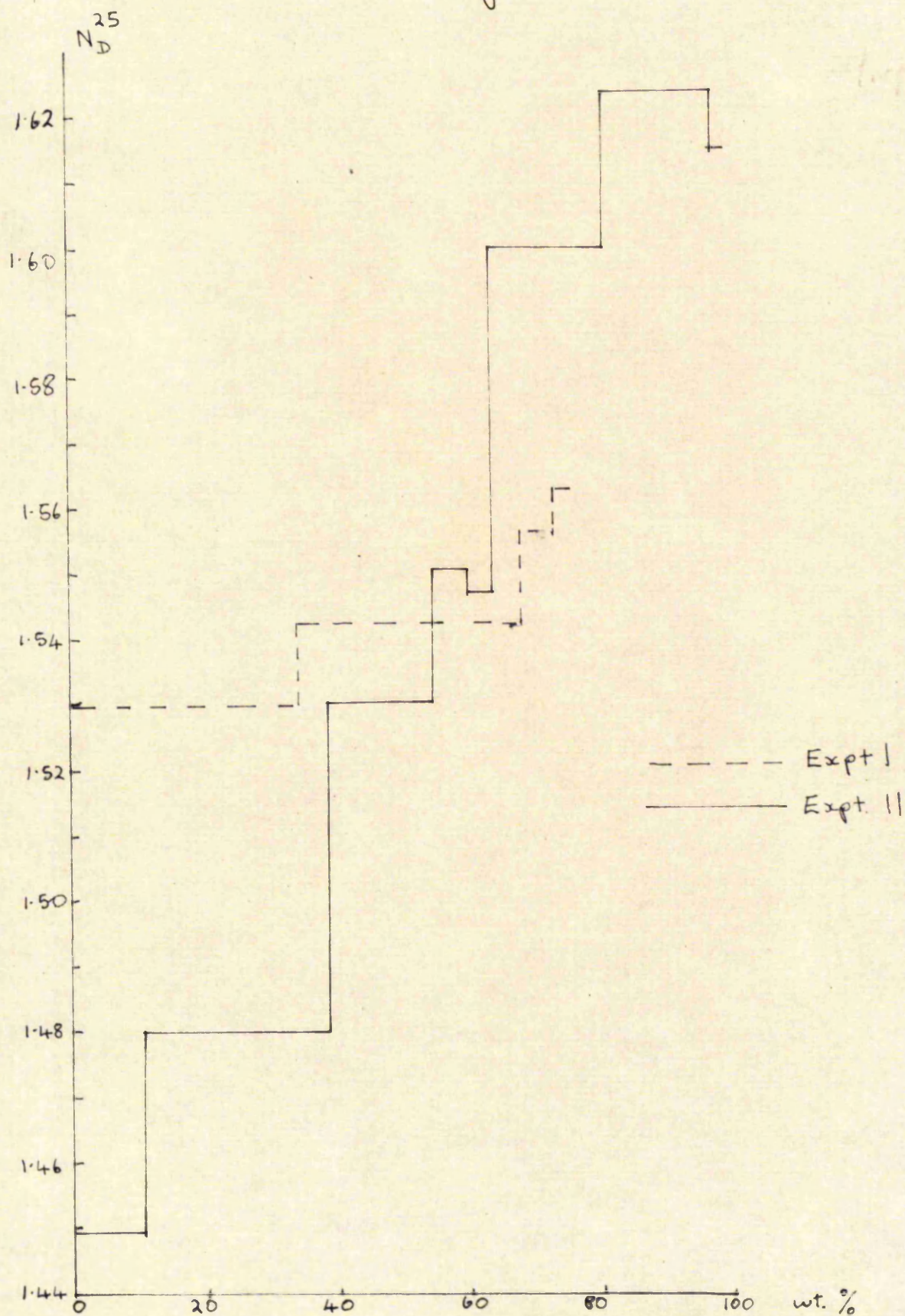
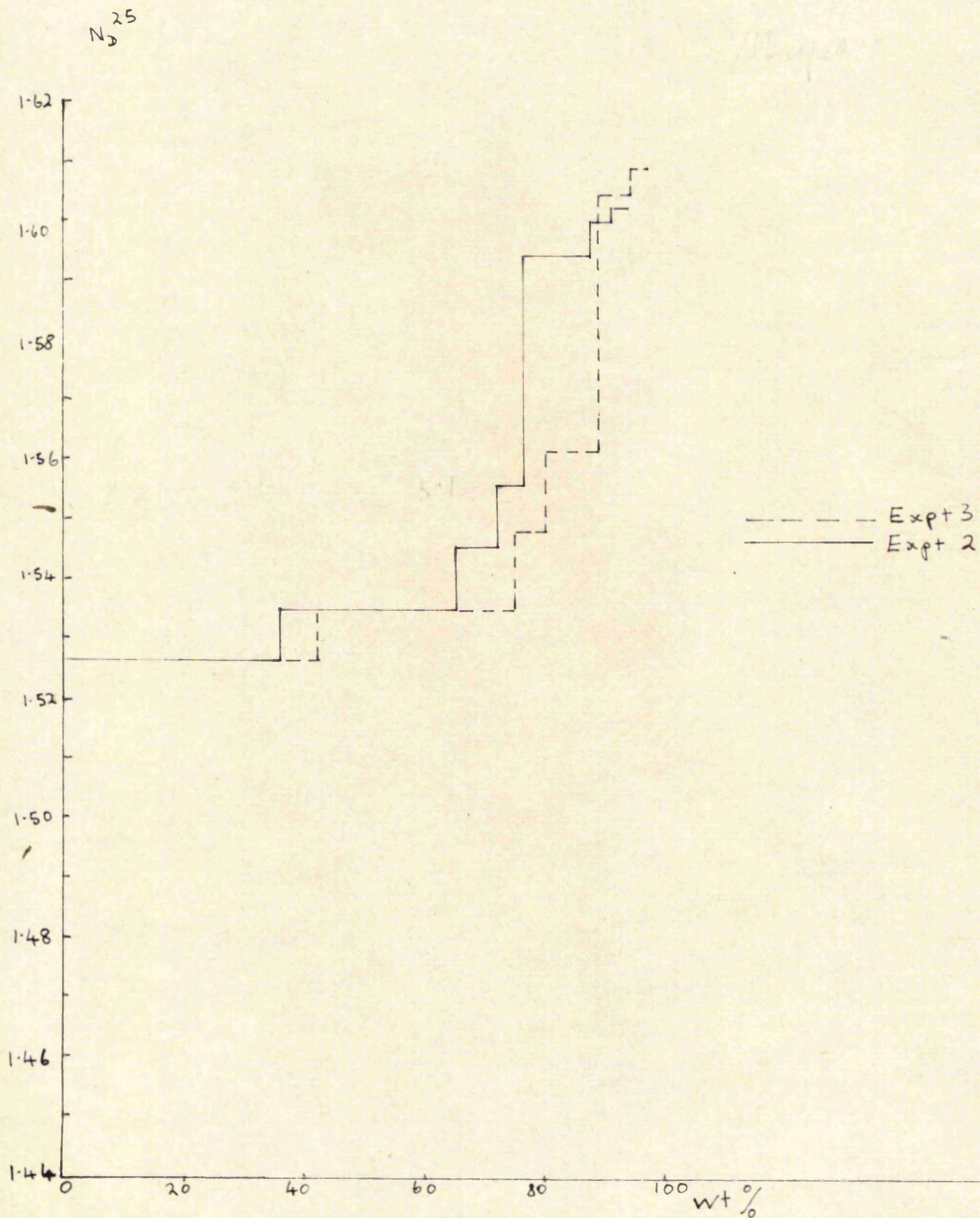


FIG 4.10.
stripped oil fractions



4.11. CONCLUSIONS

The experiments carried out so far have not shown an improvement over column separations, but the results were of great interest in understanding the oil adsorption/ desorption process.

A refinement of this process may lead to even better separations.

It seems that larger fractions ^{can} ~~used~~ ~~to~~ be obtained, which can be re-separated by chromatography, so that the course of the process can be studied, with reference to the appearance of non-aromatic and polynuclear aromatic material in each fraction.

The use of a test mixture may also help to overcome some of these problems, by more efficient analysis. (see Chapter 6).

CHAPTER 5. FURTHER BATCH SLURRY

EXPERIMENTS

5.1. INTRODUCTION

Following the analysis of the results of experiments 2 and 3, it was decided that a larger scale of operation was required, to provide large enough samples for further analysis by chromatography. It was thought necessary to start with approximately six times the oil used previously, and this was separated in two experiments to give a check on the reproducibility of the process. On completion of the analysis of these experiments, a request was received from Dr. Carruthers at Exeter University for about half a litre of polynuclear aromatic material and the preparation of this by large scale batch slurry separations is described in this chapter, together with the details of the chromatographic analysis of each fraction. The results of all these experiments are discussed in Chapter 6.

5.2. BATCH SLURRY SEPARATION OF 120gms. OF KX₆. EXPERIMENTAL DETAILS.

The same apparatus and materials were used as previously. Two experiments were carried out, each using 4 iso-octane stages, 3 benzene stages and 1 methanol stage (Expts. 4 and 5).

The amounts used in each experiment were:

wt oil KX ₆ :	60gms.
wt alumina :	300gms.
volume of solvent:	300mls. of fresh solvent at each stage.

As the two experiments were found to be reproducible, the corresponding stages were blended to give a larger sample for analysis; each iso-octane fraction was divided into three parts:

1. for reference,
2. for chromatographic analysis,
3. for blend of all iso-octane fractions to be chromatographed for comparison purposes.

There was not enough benzene fraction to divide in this way, and so all the benzene fractions were blended for chromatography.

The sample analysis obtained from each stage was separated on alumina by elution chromatography in a 5' x $\frac{5}{8}$ " column. The solvents used were in this case:

- 40mls. iso-octane, prewetting solvent;
- 20mls. iso-octane, to rinse oil container;
- 140mls. iso-octane, for elution;
- 80mls. benzene, for elution;
- 200mls. methanol, for desorption.

The usual oil/ adsorbent ratio used for oil separations in this department has been 1/12 for alumina. This has been fixed as a balance between the need for large samples for further analysis, and the poor separation due to overloading the alumina by exceeding its adsorption capacity. In the analyses of the batch slurry fractions however, there were not the required amounts of oil available (usually about 20gms.).

The weights separated were:

<u>Expt. No.</u>	<u>Fraction No.</u>	<u>wt. oil.</u>	<u>adsorbent/oil ratio.</u>
<u>6</u>	4/1 & 5/1	16.3gms.	16.6
<u>7</u>	4/2 & 5/2	9.9gms.	36.6
<u>8</u>	4/3,4 & 5/3,4	6.9gms.	25.8
<u>9</u>	4/1,2,3,4 & 5/1,2,3,4	16.5gms.	16.0
<u>10</u>	4/5,6,7 & 5/5,6,7	18.4gms.	14.3

5.3. RESULTS

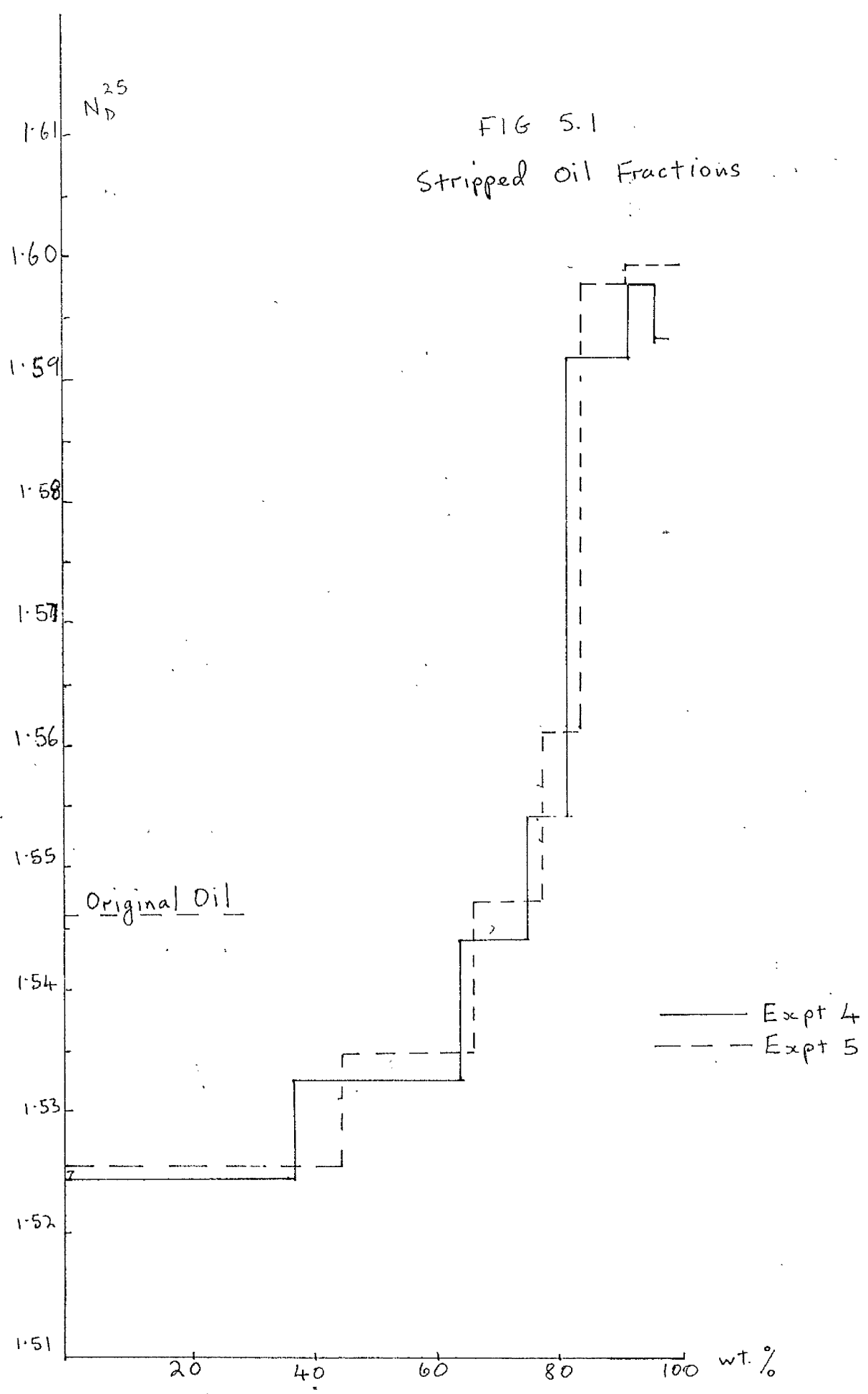
The results of the batch slurry experiments are shown in Figs. 5.1 and ~~5.~~ .

The chromatographic separations of the fractions obtained are depicted in Figs. 5.2 - 5.3 , and the refractive indices of the solvent-free samples in these separations are shown in Figs. 5.4 - 5.6.

The batch slurry experiments showed very similar results to those of experiment 2 and 3 (Fig. 4.10.), but the benzene stages did not give fractions of quite as high refractive index, ~ 1.60 in Expt. 5 compared with 1.61 in Expt. 3.

About 40% of the oil was recovered in the first stage, and about 80% of the oil was removed by iso-octane altogether in four stages. Thus no separation of the non-aromatics was possible. The oil from the last iso-octane stage was of a higher refractive index (1.56) compared with the last iso-octane fraction of the column separation (1.547) as shown in Fig. 4.9.

The graphs of refractive index v. volume of effluent show the effect of reduction in the oil/ adsorbent ratio. Good separation into two peaks is shown in the iso-octane eluate of Expt. 6, the first of which is wholly non-aromatic. It is likely that the first peak is composed of straight-chain paraffins, and the beginning of the second peak will be branched-chain paraffins and naphthenes, merging with the zone of mono-nuclear aromatics. Experiments 8 and 9 also show good separation, but the oil concentrations are too low for good separation of the peaks to be observed.



Expt 8
Fractionation of
Iso Frn 4/3,4
5/3,4.

NA.

NA.

Expt 7
Fractionation of
Iso Frn 4/2, 5/2

NA

NA

Expt 6
Fractionation of
Iso Frn 4/1, 5/1

NA

NA

1.33

40

80

120

160

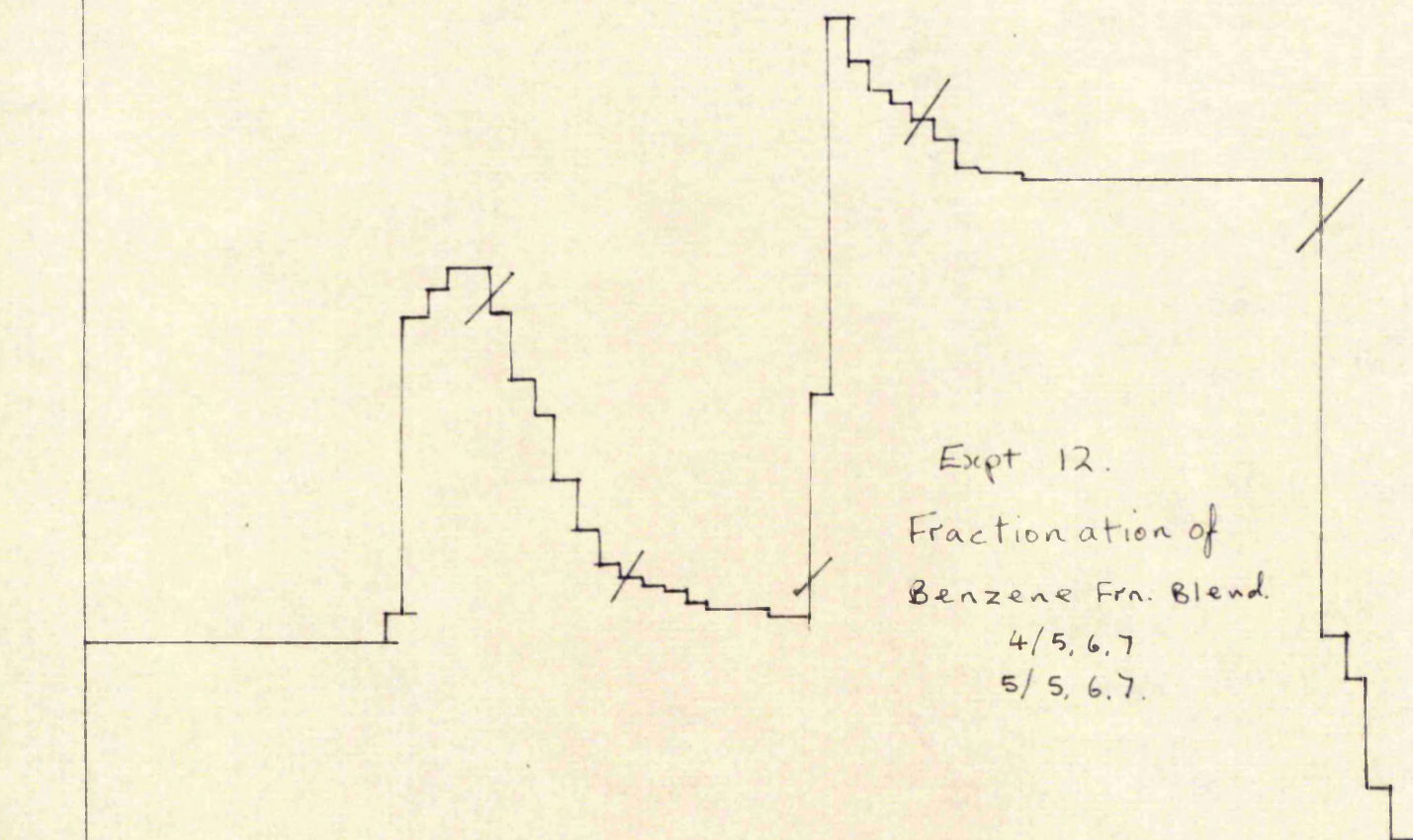
200

240

280

320

V



1.33

Expt 9
Fractionation of
Iso Frn Blend
4/1, 2, 3, 4.
5/1, 2, 3, 4.

NA

NA

1.33

40

80

120

160

200

240

280

320

V

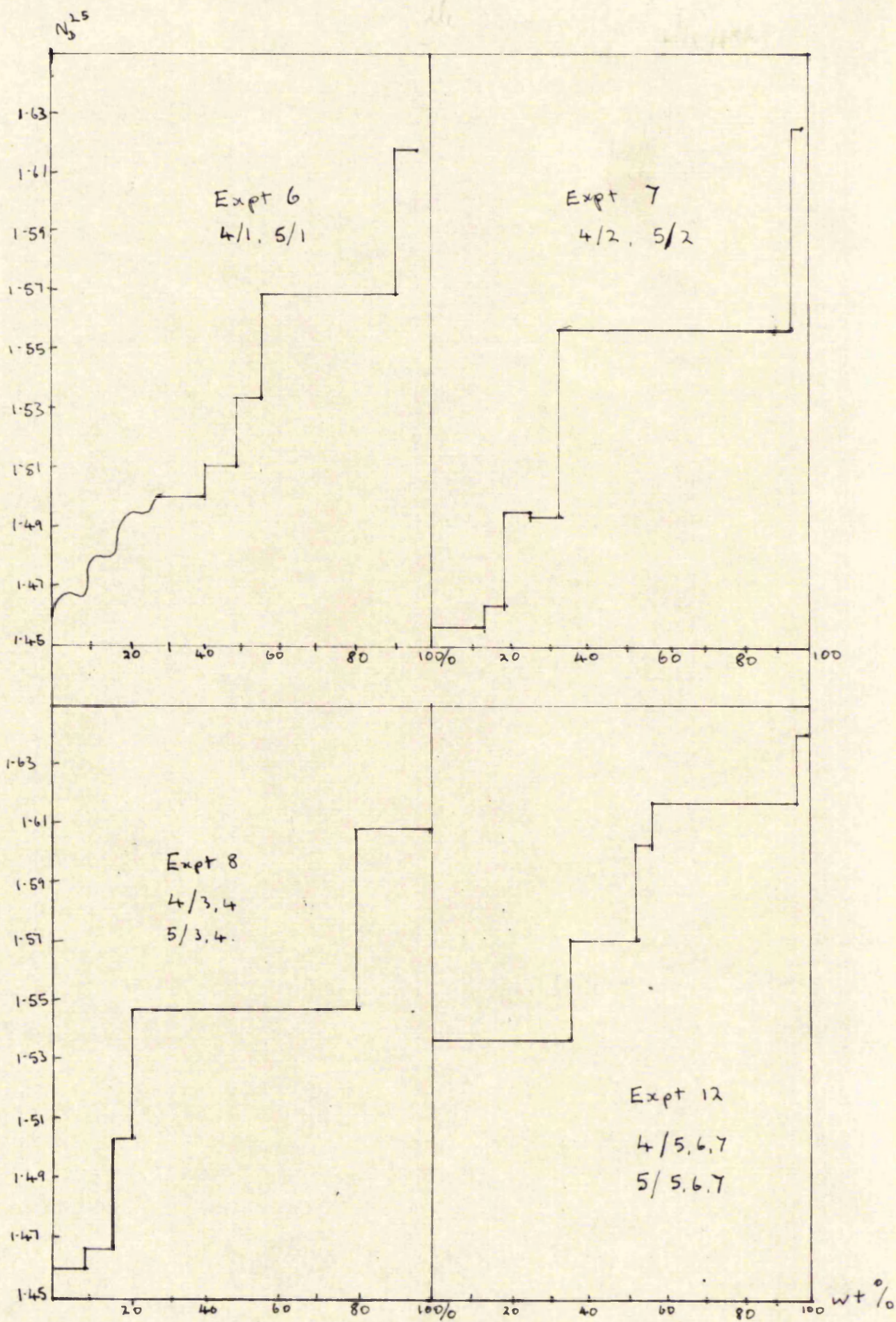
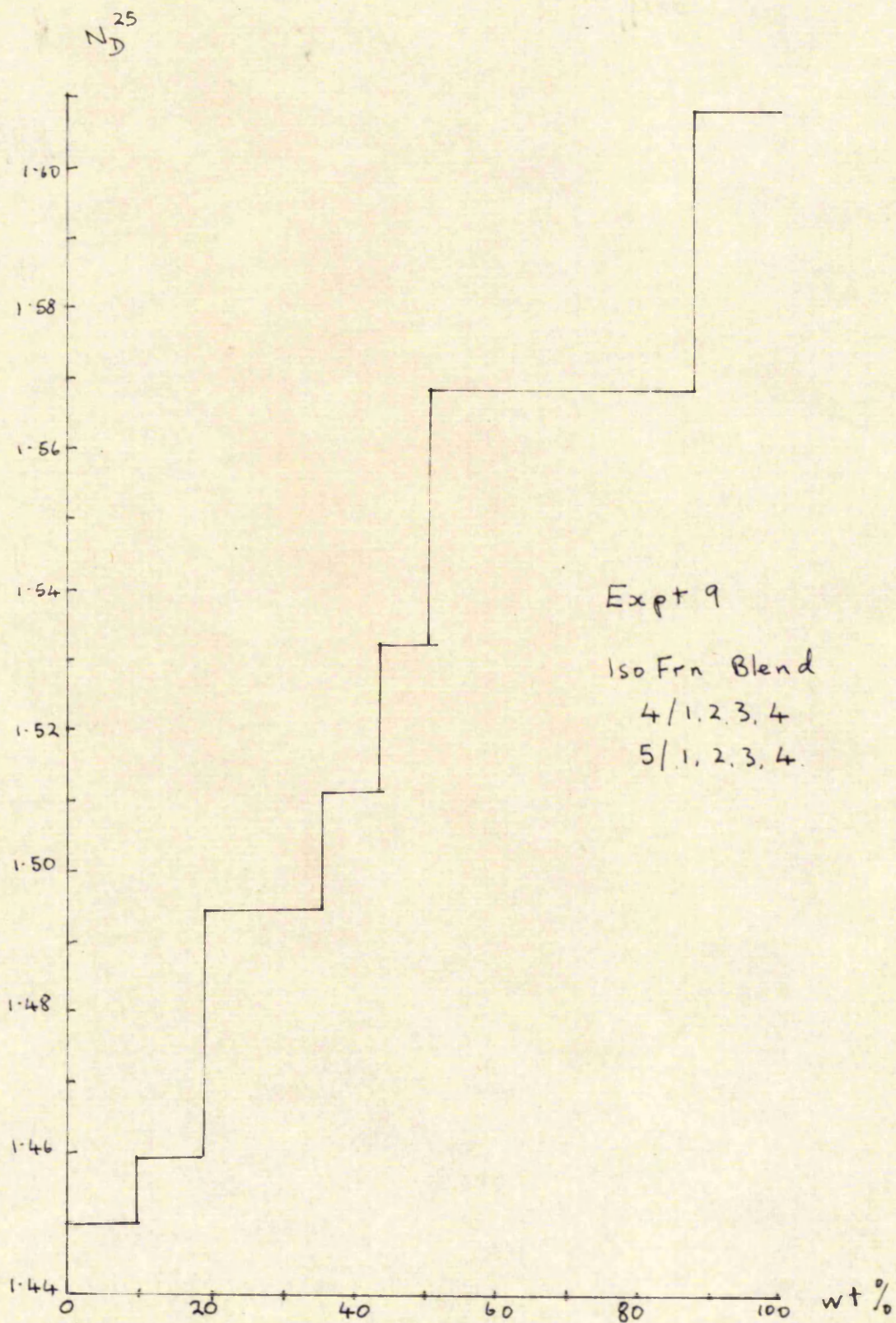
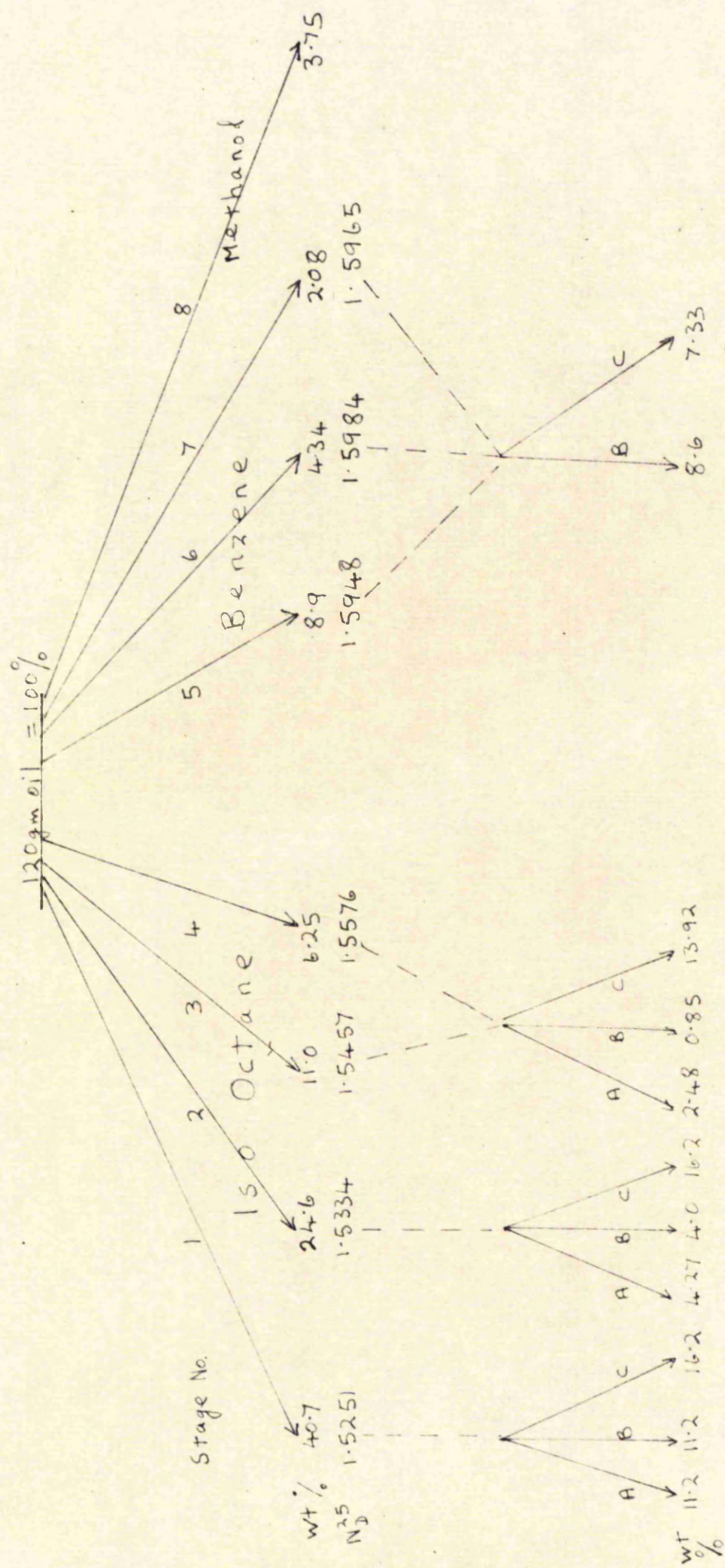


FIG 5.5 .





Note

A and B eluted with Iso Octane C eluted with Benzene

Fractions A combined to give 17.95% non-aromatics (iso octane frn.)
 " " " 24.60% aromatics (" ")
 " " " 53.65% (benzene ")

FIG 5.6

A further experiment was carried out to try and obtain better separation of the large fraction from the first stage of the batch slurry. The first stage was carried out in the normal manner, using:

300gms. alumina,

300gms. iso-octane,

60gms. oil (KX₆).

The resulting filtrate contained 44.8% of the oil, and the solvent-free product had a refractive index of 1.5238. This product was then recont~~rac~~-acted with fresh alumina and iso-octane in the same amounts as above, and it was found that the filtrate contained 36% of this product of $N_D^{25} = 1.5038$, leaving 64% of this product remaining adsorbed on the alumina. Thus it seems probable that, by the addition of two or three stages, good separation at both ends of the refractive index scale could be achieved. Samples of high concentration of non-aromatic material may appear in the filtrates after recont~~rac~~acting the oil from the first few stages with fresh adsorbent. This is discussed further in Chapter 6.

It is evident from these results that an equilibrium is being established between the adsorbed phase and the fluid phase. It is notable that non-aromatic material appeared in stage 3, whereas it is known to be very weakly adsorbed on alumina. In chromatographic separations, it is displaced by iso-octane, instead of being eluted, as is slightly more strongly adsorbed material. To explain these results further, a knowledge of this equilibrium is required. To investigate this, a series of experiments were carried out.

5.4. OIL-SOLVENT ISOTHERMS

Three series of experiments were carried out:

- a). the pore volume of the alumina was determined;
- b). keeping the oil/adsorbent ratio constant, the amount of solvent was varied (Expt. 14);
- c). the solvent/adsorbent ratio was kept constant, and the amounts of oil increased (Expt. 15).

a). Determination of Pore Volume.

This was carried out according to the method proposed by Innes (60) and developed by Harrison (61) and Badwar (17). It has been shown to be comparable with nitrogen pore volume determinations to within 0.01 mls/gms.

A sample of alumina was weighed into a conical flask, fitted with rubber bung. The flask was clamped onto a mechanical shaker. The dry alumina did not adhere to the sides of the flask on shaking. Water was added from a burette until the alumina first adhered to the sides of the flask. It was assumed that at this point the pores were full of water, and that the water on the surface of the particle caused this adhesion. Using 25gms. of alumina, the method was sensitive to the addition of 0.1 ml. of water. These determinations were reproducible to within 0.005 mls/gms. and gave an average pore volume of 0.285 mls/gms.

b). Variation of Volume of Solvent.

The ratio of oil/adsorbent was kept at 1/5 by using each time 100.0gms. alumina, and 20.0gms. oil. It was not possible to work in the region of high oil concentration, using a small amount of solvent, due to the impossibility of stirring the mixture.

The results are shown in table 5.1., and depicted in Fig. 5.7.

After stirring for two hours, the slurry was allowed to settle, and then a volume of the solution was pipetted into a flask which was fitted onto the rotary film evaporator for solvent removal.

TABLE 5.1.

(N.B. $KX_6 N_D^{25} = 1.5460.$)

<u>vol.iso-oct.</u>	<u>vol.sample.</u>	<u>N_D^{25} sample.</u>	<u>N_D^{25} stripped oil.</u>	<u>wt.oil.</u>
*120mls.	35mls.	1.4096	1.5140	4.5gms.
150	35	1.4070	1.5108	3.8
200	35	1.4021	1.5246	2.6
250	35	1.4018	1.5222	1.7
300	40	1.3997	1.5234	2.1
400	60	1.3958	1.5292	2.2

The oil/solvent isotherms were calculated according to the formula:

$$Ac = \frac{v}{m} \left(\frac{x_0 - x}{1 - x} \right) \quad \text{gms. oil / gms adsorbent.}$$

and the total amount of oil in the pores was found by:

$$At = Ac + (vp - Ac)x.$$

At could be checked in this case by a mass balance on the recovered oil. The adsorbed phase concentration = $At / vp = y$.

A sample calculation shows how Ac is obtained, taking the values marked * on tables 5.1. and 5.2.

wt. oil charged = 20gms. density = 0.968 ∴ volume = 21.7mls.

volume iso-octane added = 120gms. ∴ total volume of solution = 141.7mls.

pore volume = 28.5mls. ∴ volume of phase at equilibrium = 113.2mls.

wt. oil in solution = $\frac{4.5}{35} \cdot 113.2 = 14.5\text{gms.}$ ∴ wt. oil adsorbed = 5.5gms.

$$x_0 = \frac{20}{141.7} = 0.1414 \text{ gms/mls.}$$

$$\frac{v}{m} = \frac{141.7}{100} = 1.42 \text{ mls/gms.}$$

$$x = \frac{4.5}{35} = 0.129 \text{ gms/mls.}$$

These values are set out in Table 5.2. and Fig. 5.7 .

TABLE 5.2.

<u>x_0 gm/ml.</u>	<u>x gm/ml.</u>	<u>$\frac{v}{m}$ ml/gm.</u>	<u>Ac.</u>	<u>At.</u>	<u>y_0</u>
*0.1414	0.129	1.42	0.0202	0.0544	0.190
0.1160	0.102	1.72	0.0268 ⁸	0.0532	0.186
0.0903	0.0746	2.22	0.0377	0.0561	0.197
0.0736	0.0486	2.72	0.0715	0.0849	0.288
0.0623	0.0526	3.22	0.0330	0.0463	0.163
0.0475	0.0367	4.22	0.0474	0.0644	0.226

c). Variation in Oil / Adsorbent Ratio.

For each experiment, wt. alumina = 100gms., and vol. iso-octane = 200mls. The results are shown in Table 5.3. and Fig 5.8

FIG 5.7

Oil/Solvent Isotherms
at 20°C on Alumina

A_t
 A_c

Expt 14

$$\square A_t (= A_c + (v_p - A_c)x)$$

$$\circ A_c (= \frac{v}{m} \left(\frac{x_0 - x}{1 - x} \right))$$

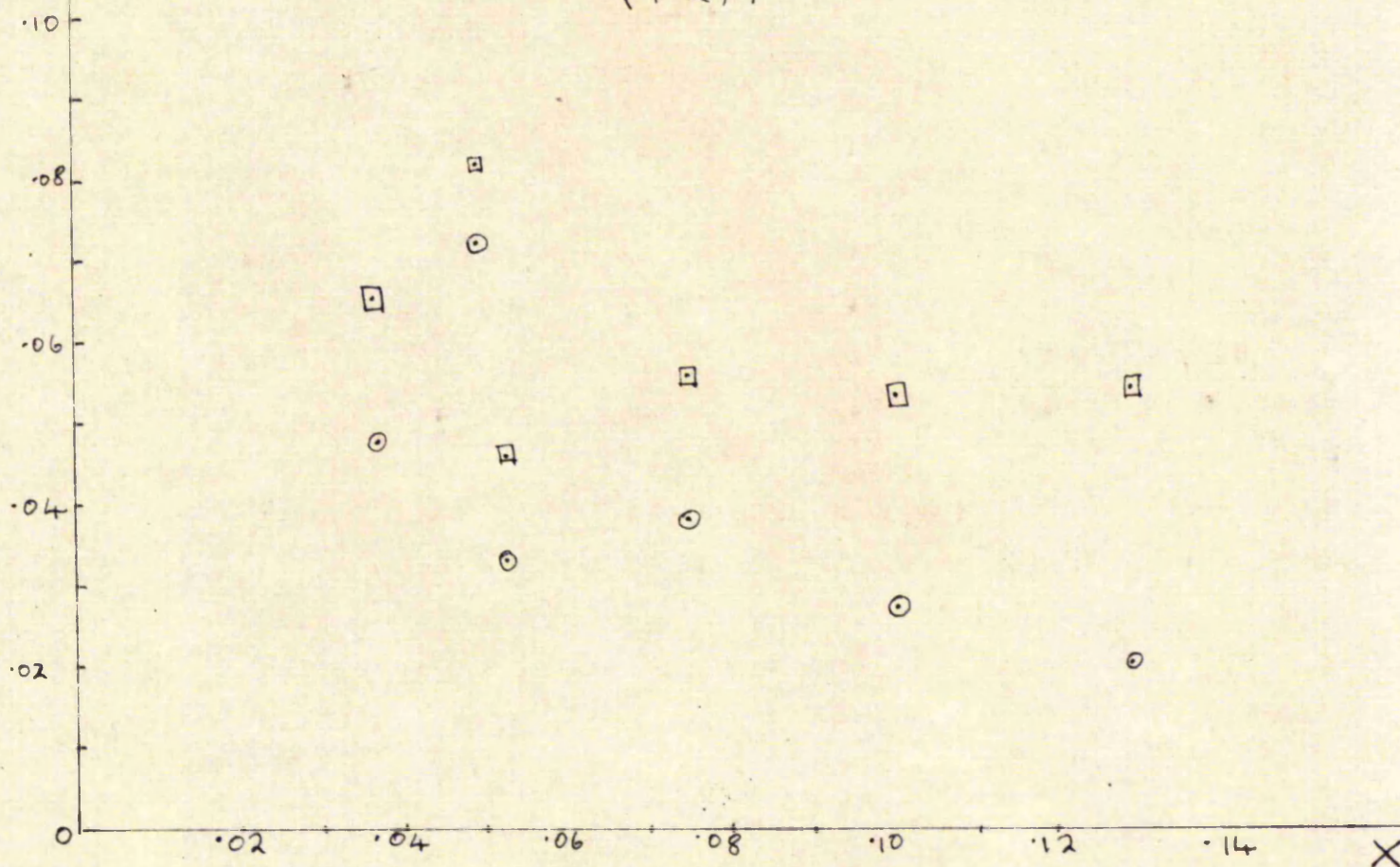


FIG 5.8
Oil/Isd Octane Isotherms at 20°C
on Alumina

Expt 15

□ At

○ Ac

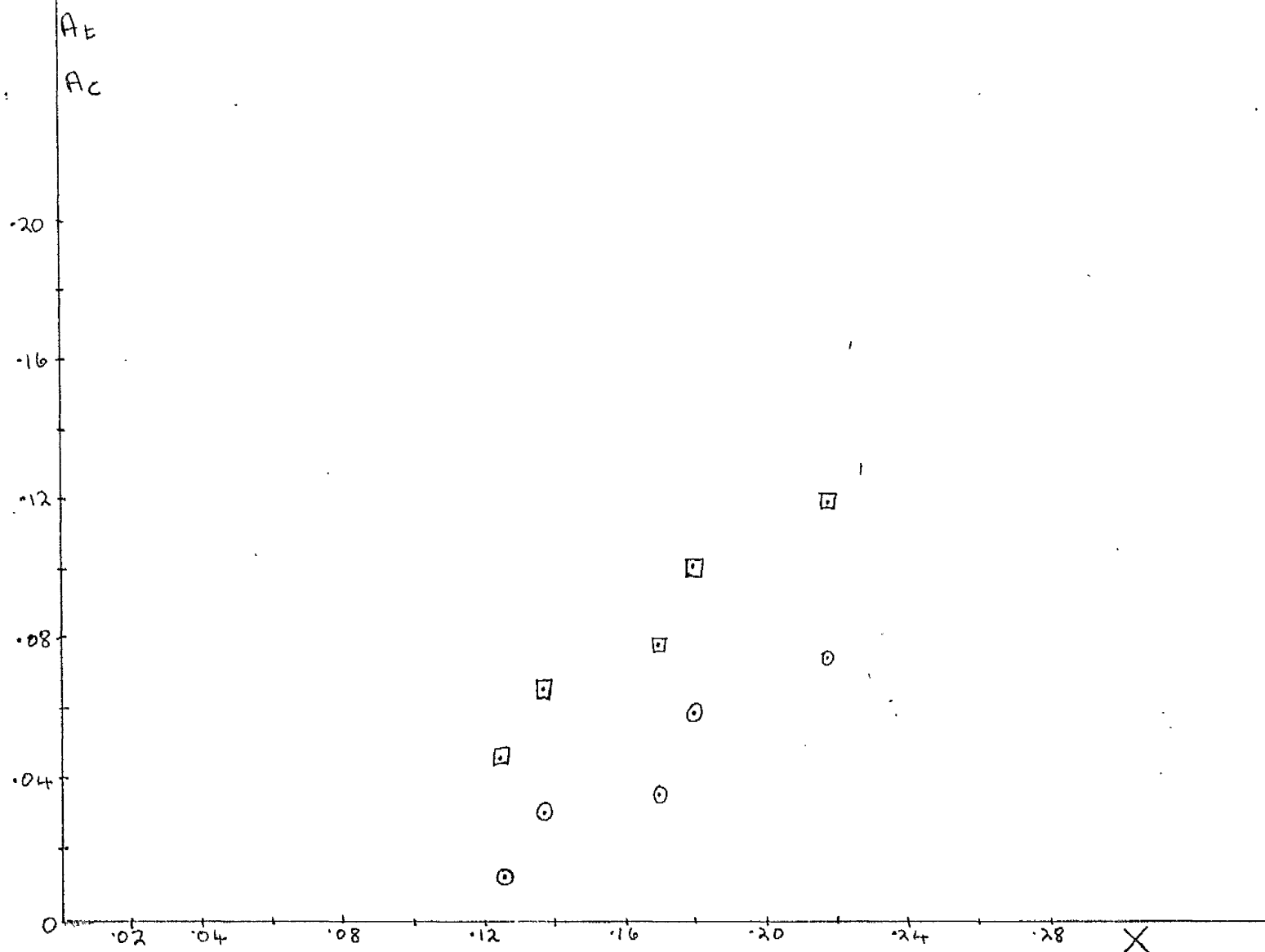


FIG 5.9

$$y (= A \pm / v_p)$$

⊙ Expt 15

□ Expt 14

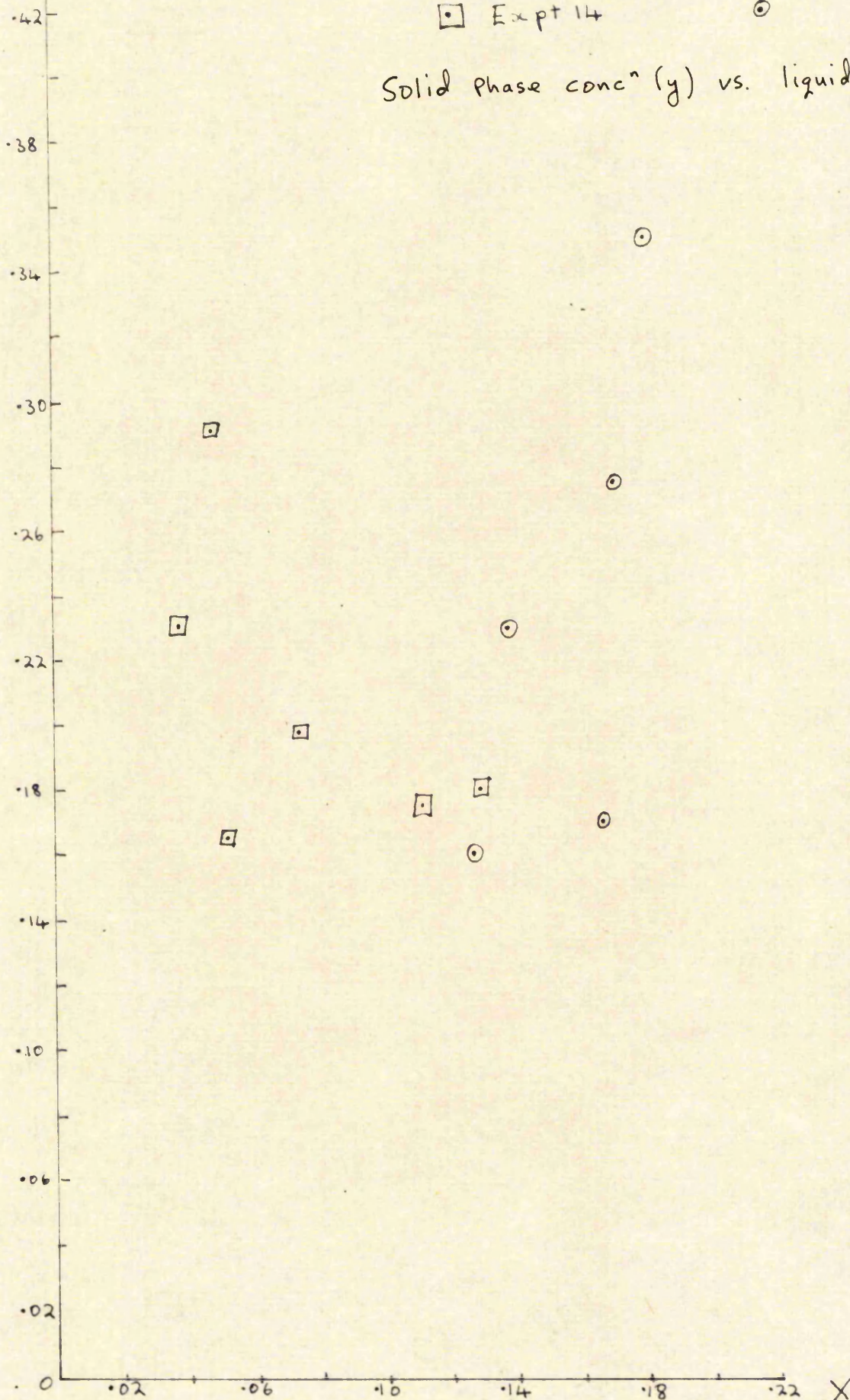
Solid phase concⁿ (y) vs. liquid phase concⁿ (x)

TABLE 5.3.

<u>wt.oil</u> <u>charged.</u>	<u>wt.oil</u> <u>adsorbed.</u>	<u>N²⁵</u> <u>strip-</u> <u>ped oil.</u>	<u>x₀</u>	<u>x</u>	<u>v</u> <u>m</u>	<u>A</u> <u>c</u>	<u>At</u>	<u>y</u>
30gms.	4.5gms.	1.5104	0.130	0.126	2.31	0.0106	0.0452	0.160
35	6.6	1.5270	0.148	0.137	2.36	0.0301	0.0651	0.229
40	4.7	1.5200	0.166	0.166	2.41	0.0000	0.0473	0.166
45	7.6	1.5220	0.182	0.170	2.46	0.0356	0.0780	0.274
50	9.8	1.5280	0.199	0.180	2.51	0.0582	0.1001	0.351
60	9.4	1.5330	0.239	0.217	2.62	0.0736	0.1194	0.420

A comparison of these results with those of b) are shown in Fig. 5.9.

5.5. LARGE SCALE BATCH SLURRY EXPERIMENTS

As about 500mls. of polynuclear aromatic material was required for further chemical analysis at Exeter, and ^{as} this represented between 5% and 10% of the oil, it was decided to separate 20 litres of oil by batch slurring. This would leave enough in each fraction on which to carry out further tests.

The oil used was a Kuwait furfural extract, and was vacuum distilled in five runs into litre cuts. Sample Nos. 30-49 from each of the five runs had an estimated boiling range of 400°C-422°C at atmospheric pressure. Portions of 200mls. of each of these 200 samples were taken to make 20 litres of blended oil. The oil was designated KXII₁₀₋₁₂. It had a refractive index of 1.5532, and a sulphur content of 5.64%wt.

1. Method.

The oil was divided into three portions to enable it to be handled in the laboratory. The same proportions of materials were used as in previous experiments, i.e. numerically five times as much adsorbent and solvent as oil.

The alumina used was 100-200 mesh, used previously on the large columns, and was regenerated at 450°C for eight hours, and stored in polythene lined drums before use. Due to the large amount of material, the adsorbent could not be dried at $115-120^{\circ}\text{C}$ overnight before use. The slurrying vessel was a 20 gallon P.V.C. lined drum, with a $1\frac{1}{2}$ " and 1" dia. hole in its middle and end respectively.

The dry adsorbent (33.33kg.) was charged to the drum and about 20 litres of iso-octane were poured in. The oil followed this, and then the rest of the iso-octane to make up 33.33 litres.

Each stage was in the drum for at least two hours, and in the absence of a drum-roller, the drum was rolled about the laboratory for 5 minutes every 15 minutes during the two hours. The drum was then raised on a bench and a piece of fine wire gauze was fixed over the $1\frac{1}{2}$ " dia. hole with a "Jubilee clip". The slurry was then filtered by rolling the drum over until this hole was underneath, and the liquid drained into a receiver. Air pressure was used to speed the filtering process. The adsorbent remained in the drum all the time, and fresh solvent was added at each stage.

In runs I and II, there were five iso-octane stages, two benzene stages and one methanol stage. Run III had six iso-octane stages, two benzene stages and one methanol. In addition, all the adsorbent was bulked and slurried with approximately 50 litres of methanol to remove any remaining oil in preparation for regenerating the adsorbent. This is referred to as the 2nd MeOH wash.

Each of the samples obtained was analysed by elution chromatography in a $5'\frac{5}{8}"$ column, using 20gms. oil each time. The solvents usually used were as in section 5.2., i.e. 200mls. iso-octane, 80mls. benzene and 200 mls. methanol, but sometimes there were varied if thought necessary for good elution of the sample.

The volumes used will be seen from the refractive index v. volume of effluent graphs, as there are sharp changes in refractive index at each solvent front.

The specific gravities of each sample were determined using a 25mls. standard density bottle at 20°C. The sulphur contents were determined by the Quartz Tube method. (59)

2. Oil Recovery.

Due to the fact that only a limited amount of iso-octane was available (approximately three times that required for one stage), the solvent-oil separation was a limiting factor for each stage. The rotary film evaporator, although it could easily have been made continuous, only had an evaporation rate of about two litres/hr. To improve on this meant that the pressure had to be kept very low. This gave the vapour high velocity, some was not condensed, and the cold-traps were not sufficient to protect the pump from solvent vapours. To overcome this, a climbing-film evaporator was used which had been constructed by King in this department about ten years ago. A sketch of the apparatus is shown in Fig. 5.10. The evaporating section consisted of four tubes of $\frac{1}{4}$ " diameter and about 3' high, through which the solution passed. These tubes were heated externally by steam or a steam/water blend according to the temperature difference required.

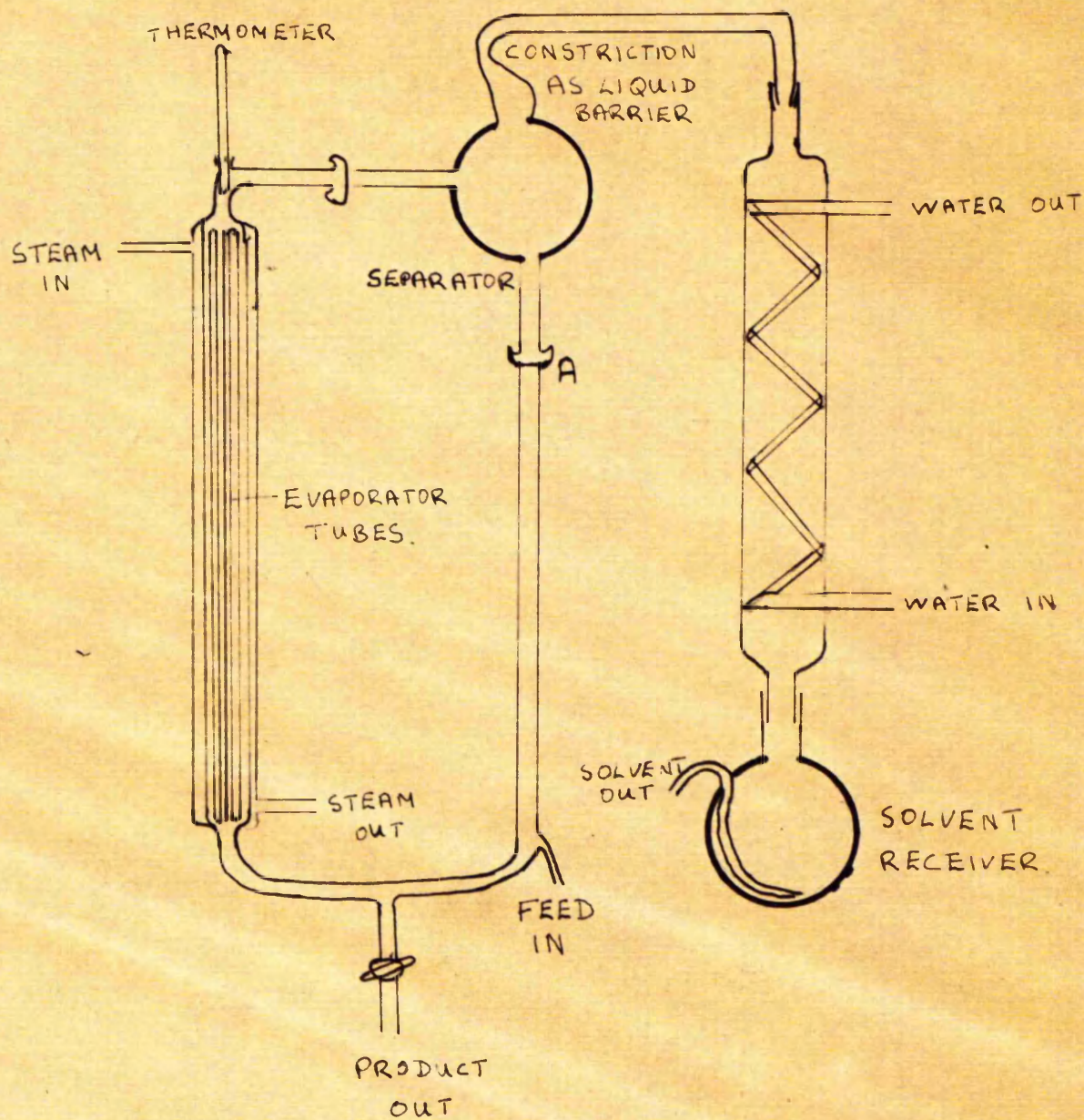
The apparatus was operated at about 30cms.Hg. by means of water vacuum. When the solution reached boiling point, a plug of vapour shot up the tube, and partially condensed on coming into contact with liquid falling down the sides of the tube. Thus some vapour passed right through the apparatus into the condenser, more evaporation took place from the thin liquid film in the upper part of the tube, and much of the liquid was carried over into the separator.

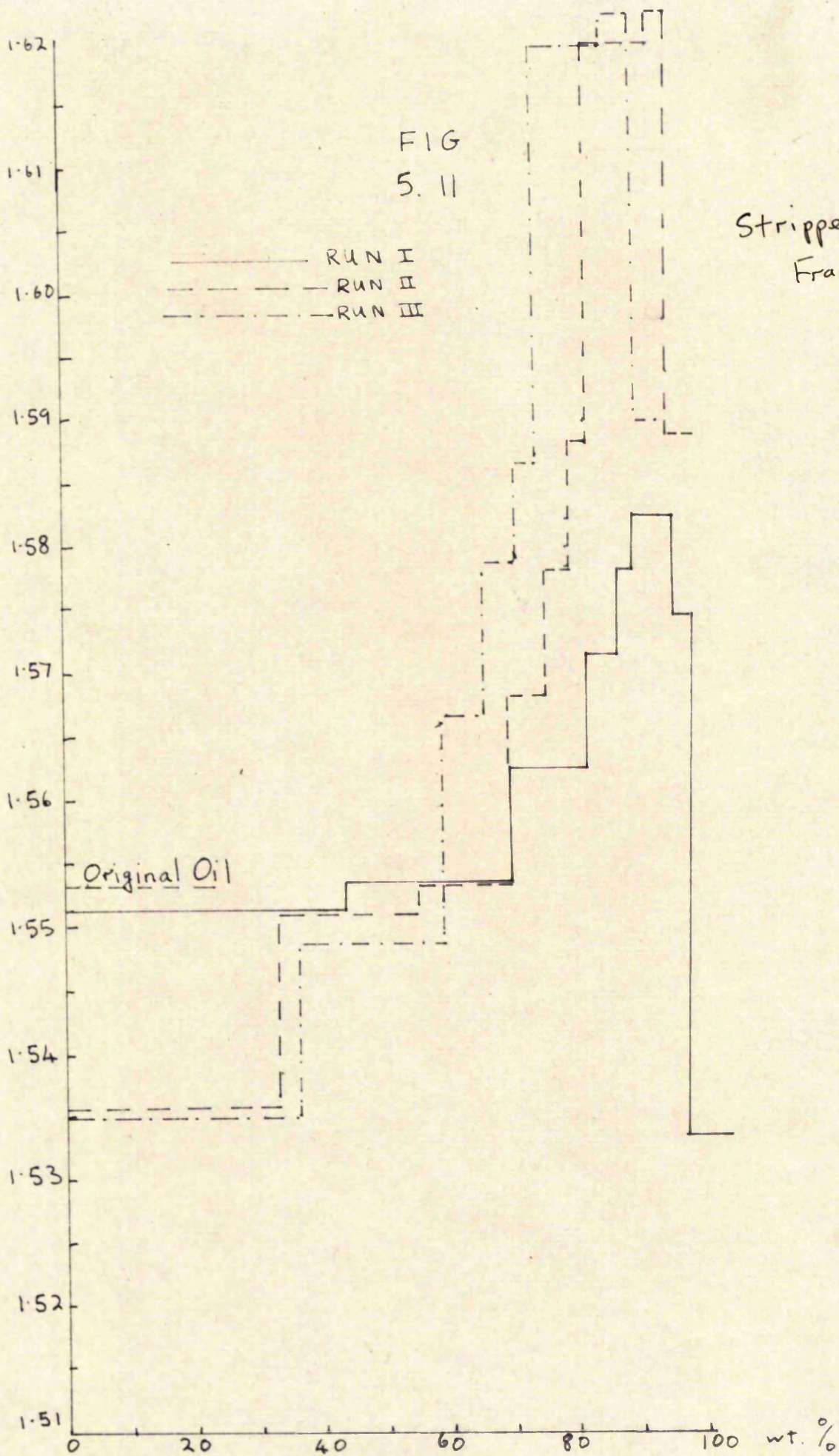
The liquid/vapour mixture, in the form of a foam, was separated, and the liquid recirculated and mixed with fresh feed. A continuous gravity feed of solution was used, and when the column-head temperature showed that the solution was very concentrated (usually 90-95%), it was evacuated from the apparatus by a secondary vacuum system. The recovered solvent was also removed in the same manner, and a throughput in excess of 6 litres/hr. was achieved. The oil solution was then finally stripped in the rotary film evaporator. With volatile solvents, much flashing occurred, and the solution shot up the liquid downcomer and over it into the solvent receiver. To overcome this a roll of wire gauze was inserted in the downcomer at point A to make the pressure drop in this section greater than in the evaporating tubes.

3. Results.

The results of the batch slurry stages are shown in Fig^d. 5.11 ~~=5~~ . The column separation of KX_6 is shown in Fig^d. 5.17 ~~=5~~ . The vertical or diagonal strokes through the N_D^{25} .v.v. graphs show the bulking of samples for solvent evaporation to give the fractions shown in the N_D^{25} .v. wt% of oil recovered graphs. For ease of reference, the sulphur contents of each fraction are shown on the N_D^{25} .v.wt% graphs. The separations of all the fractions, obtained from batch slurry, by adsorption chromatography, are shown in Graphs 5.12 -5.24. The results of all the solvent stripping operations, as well as the sulphur contents and densities are given in Appendix 3. These results will be discussed in Chapter 6.

FIG 5.10
CLIMBING FILM
EVAPORATOR.





25
ND

FIG 5.12

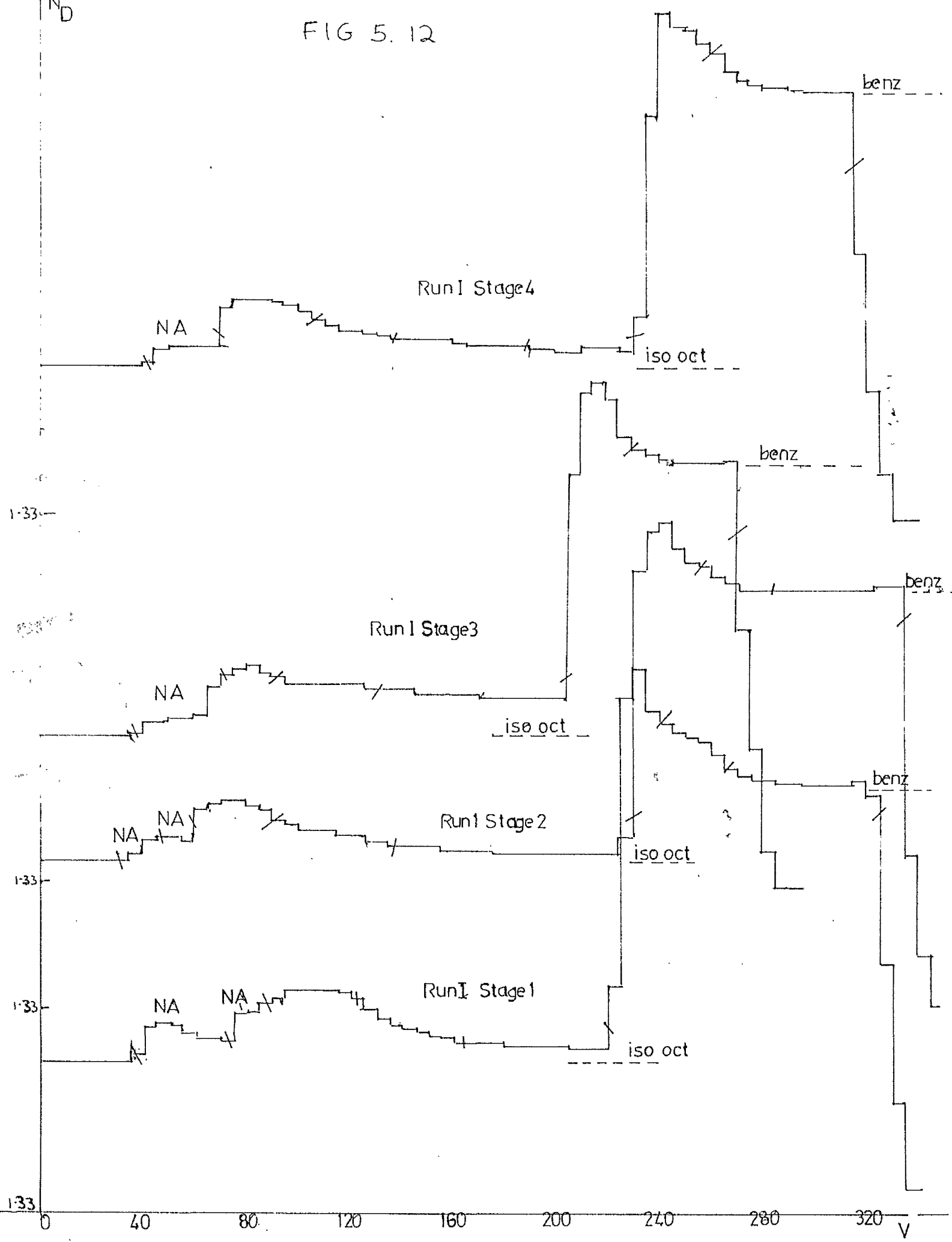
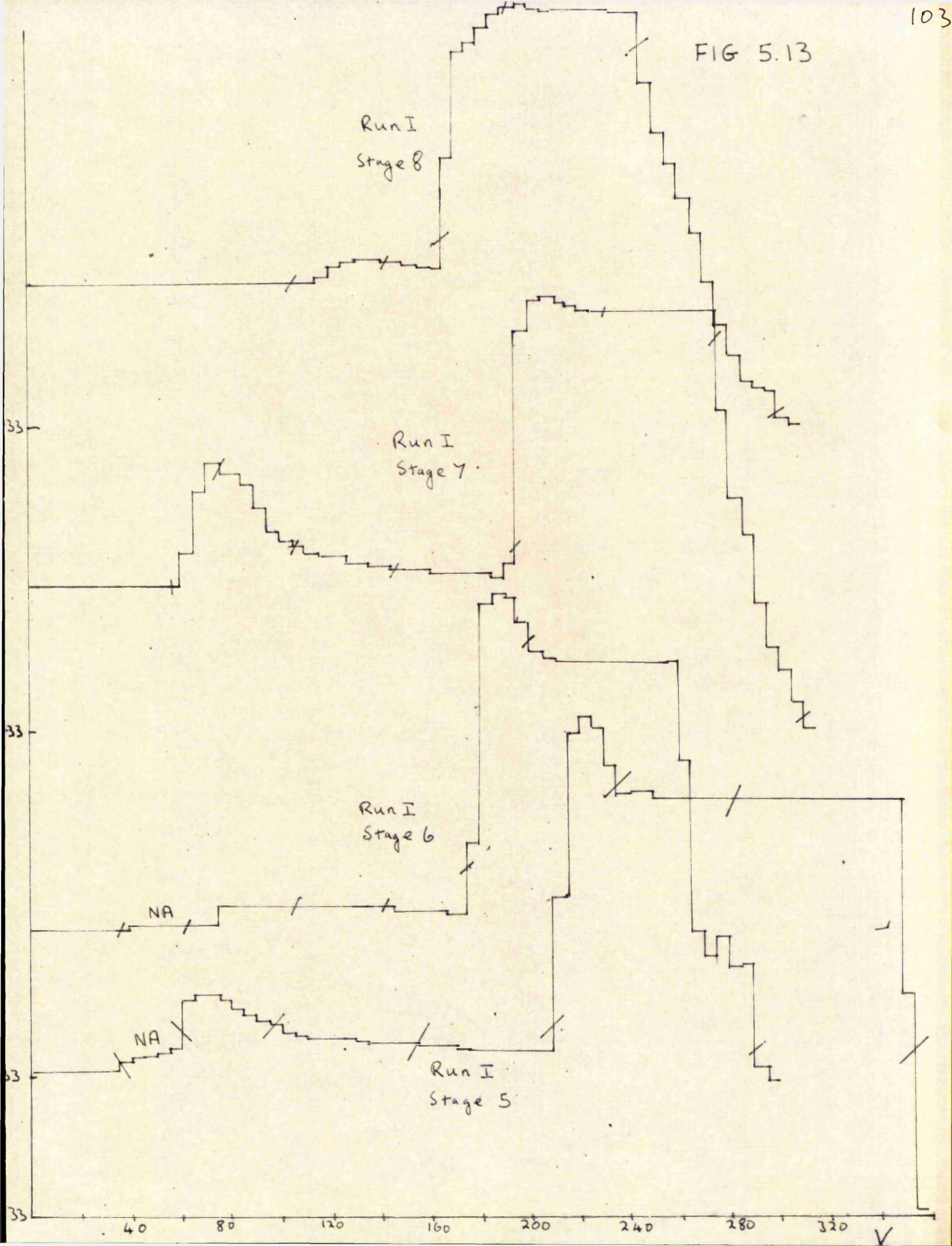
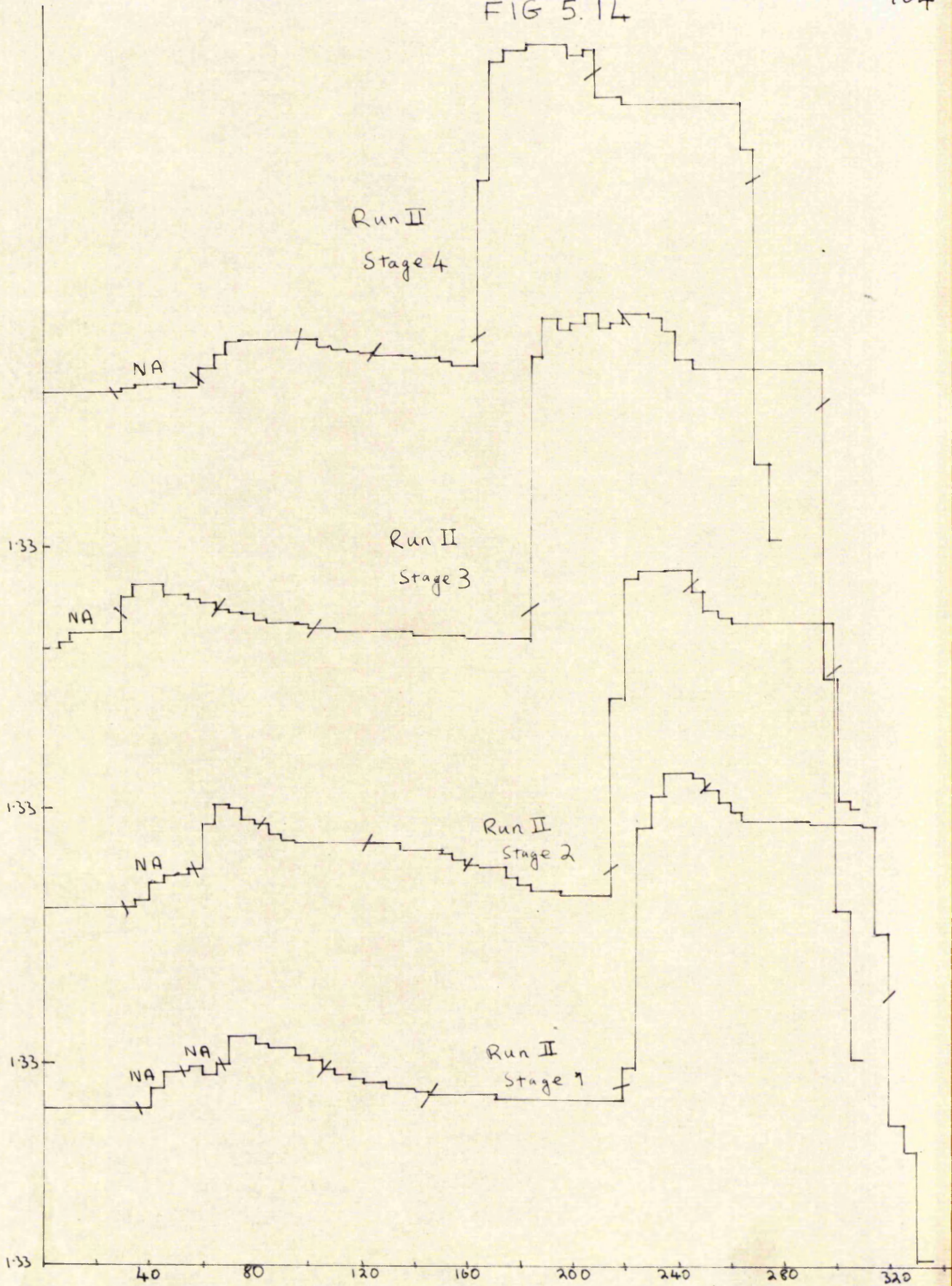
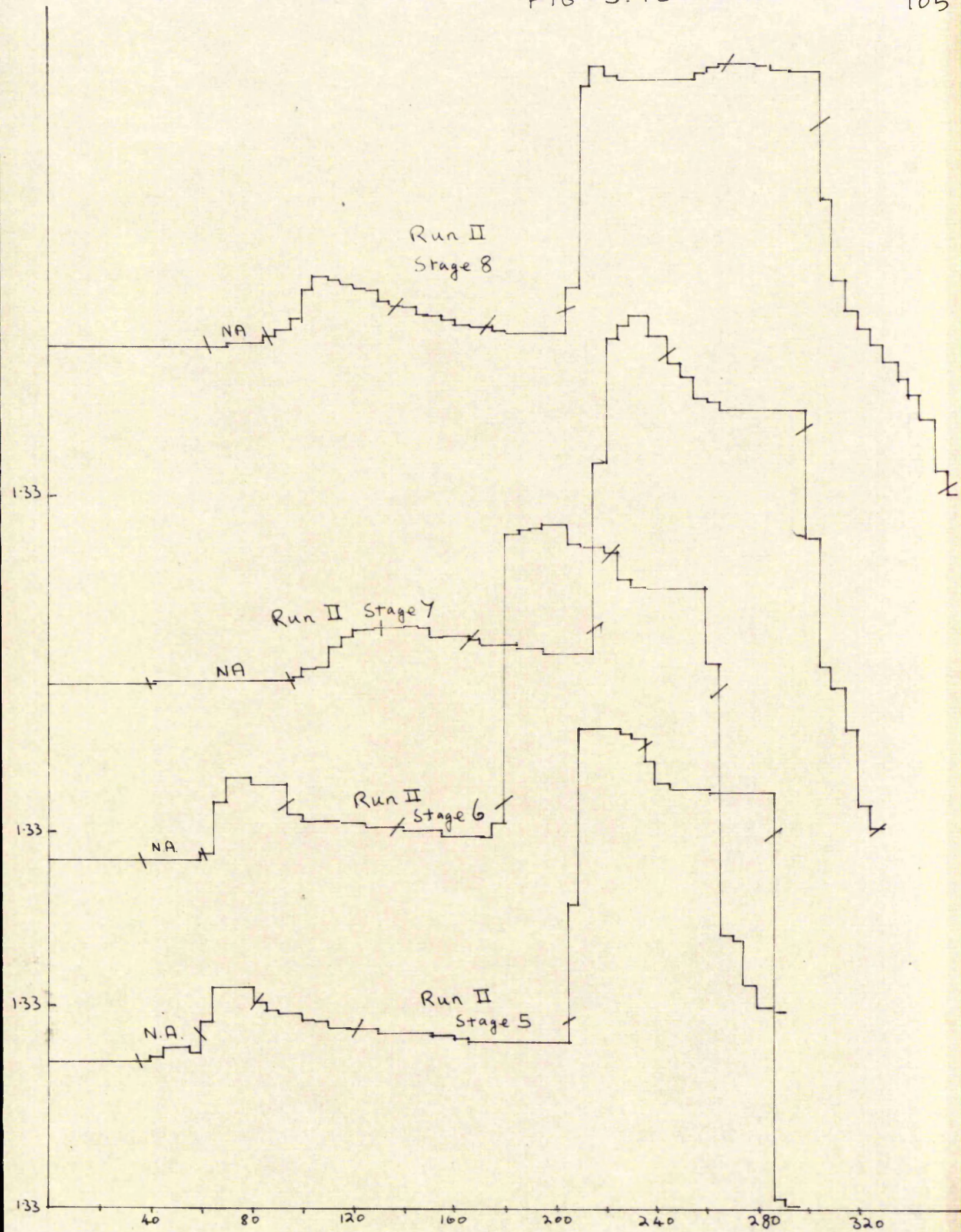


FIG 5.13







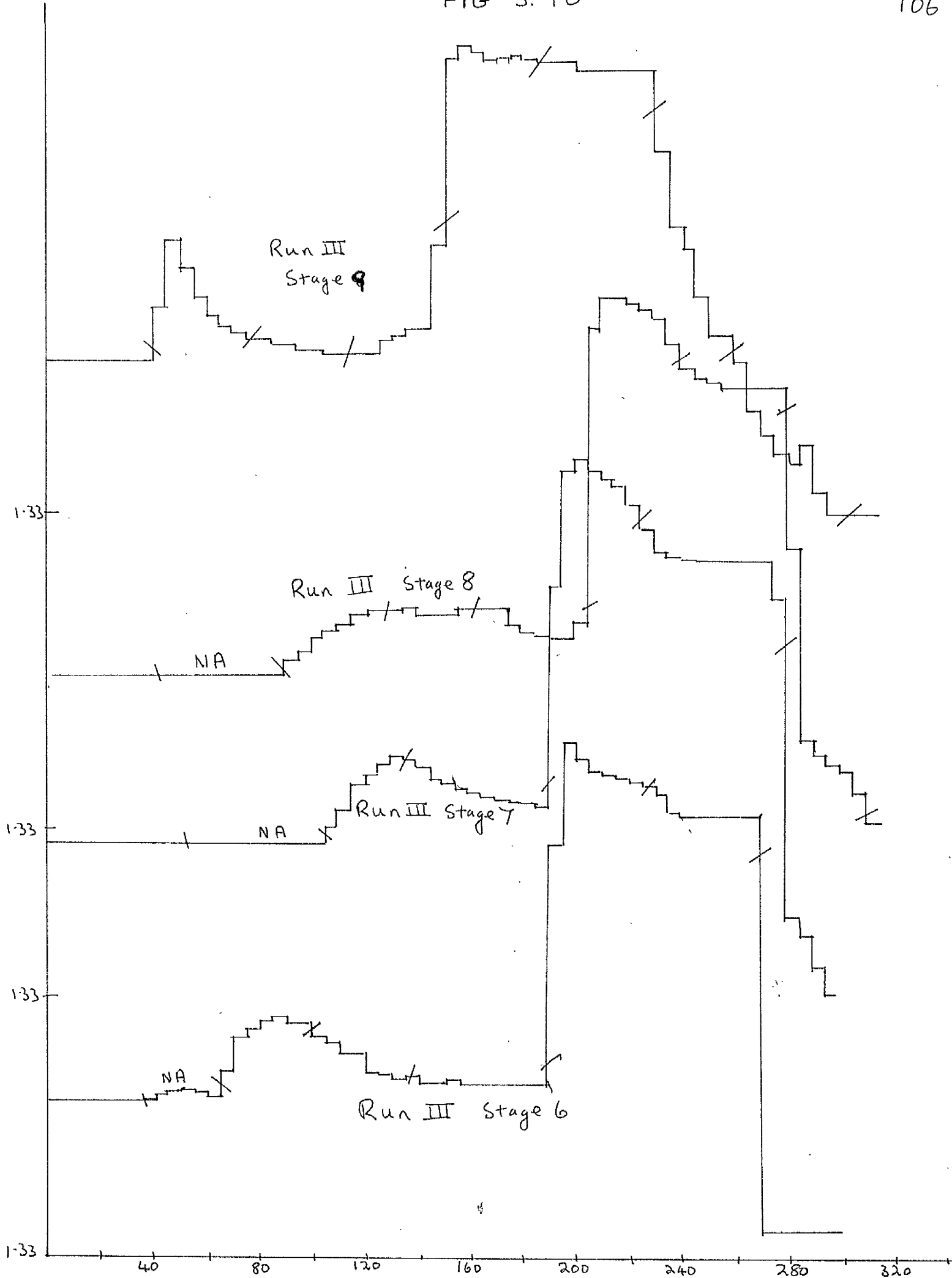
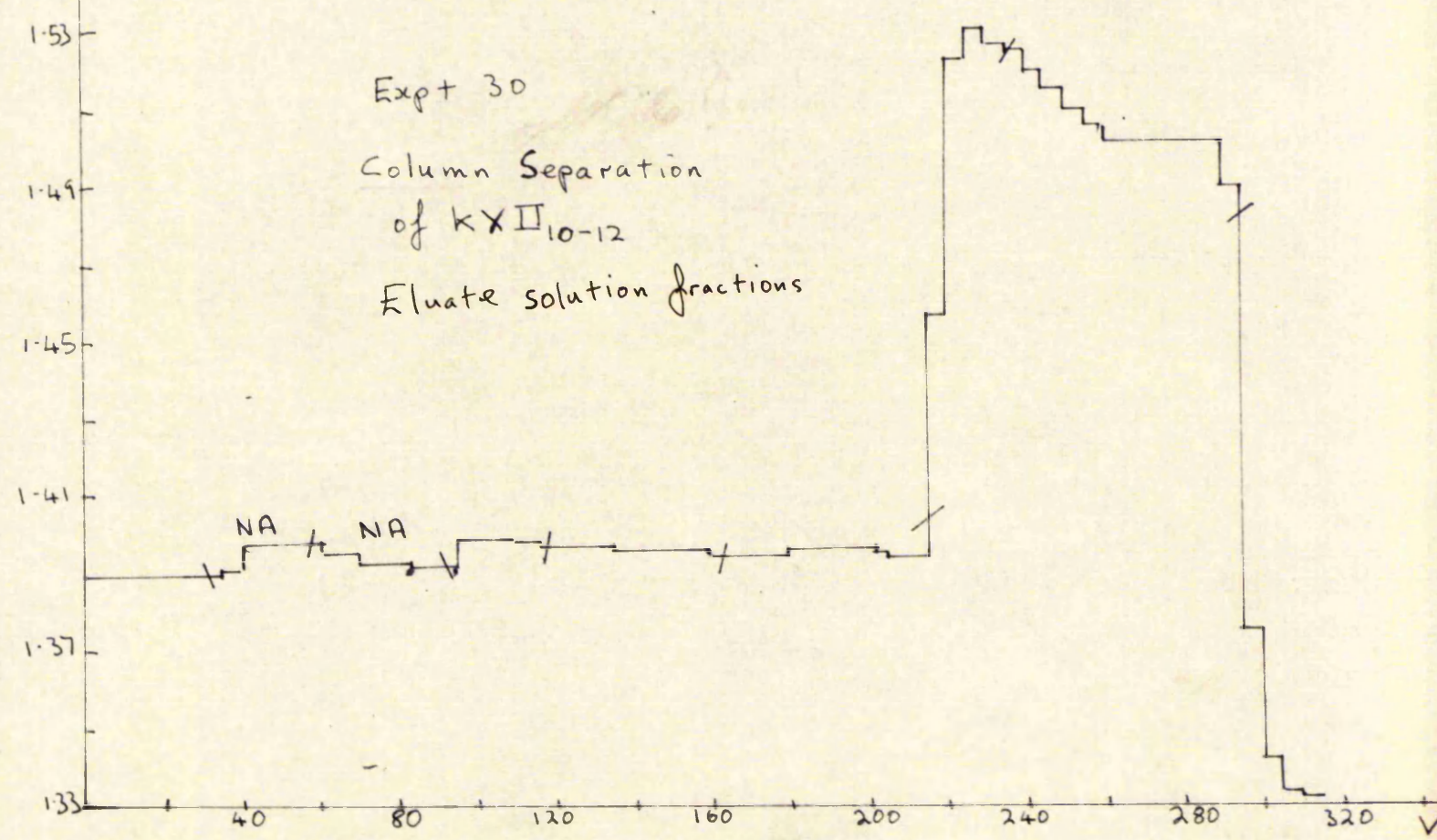
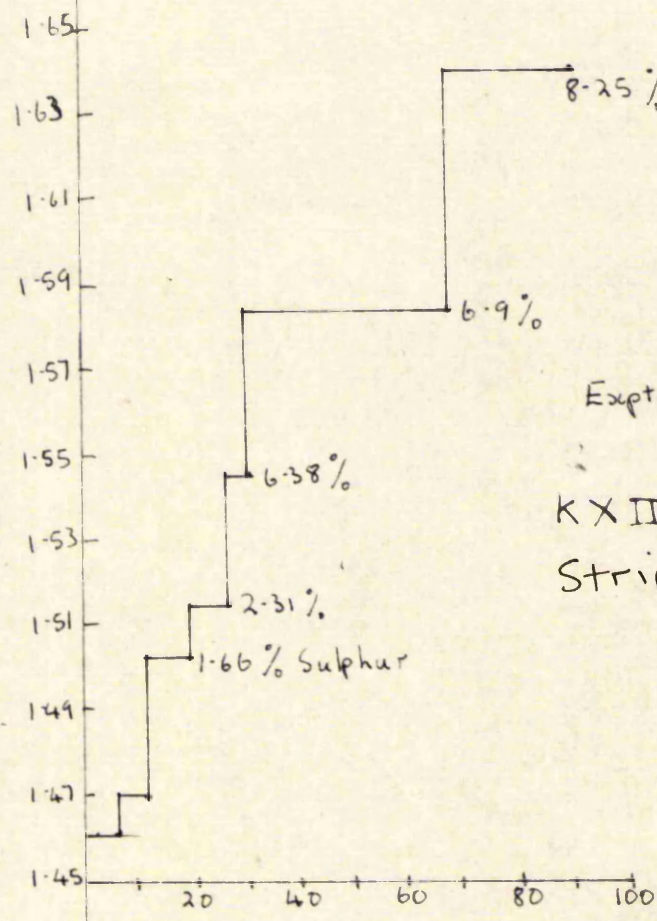
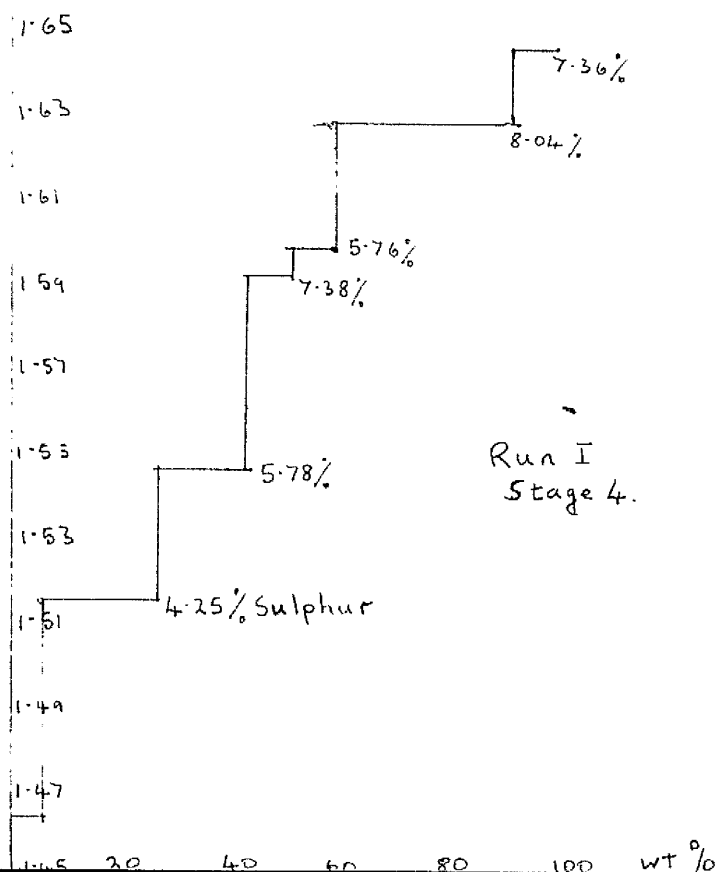
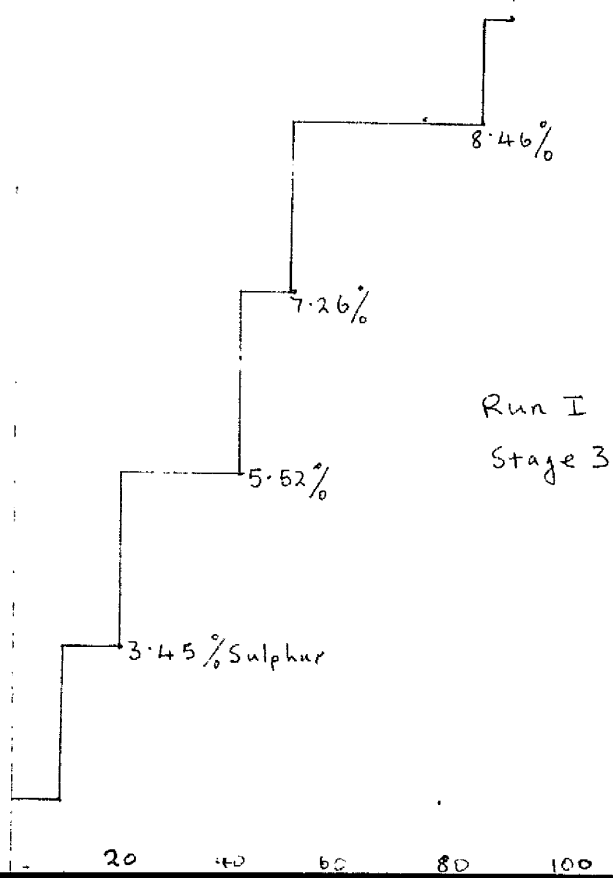
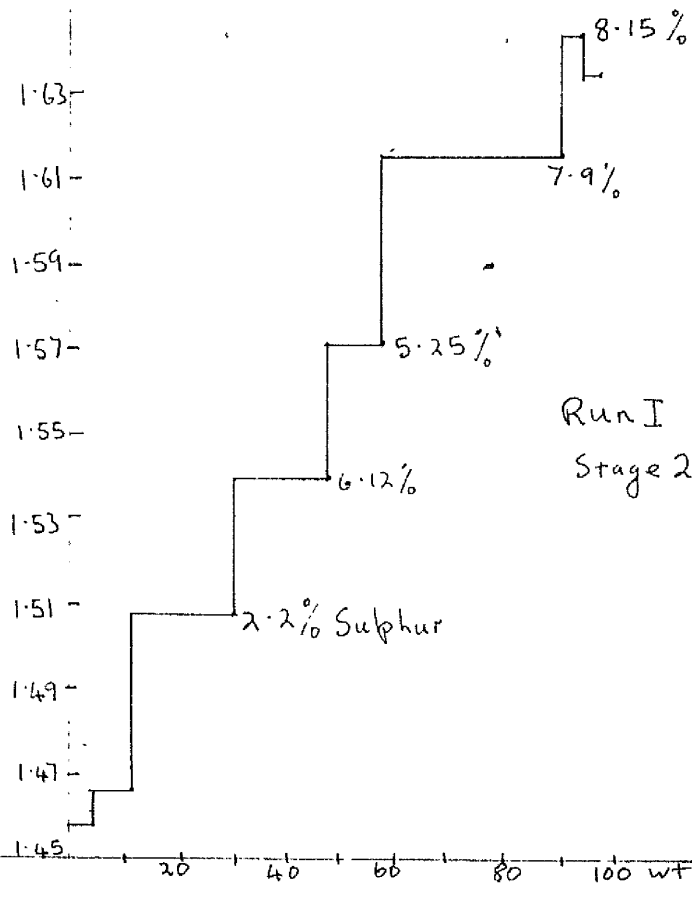
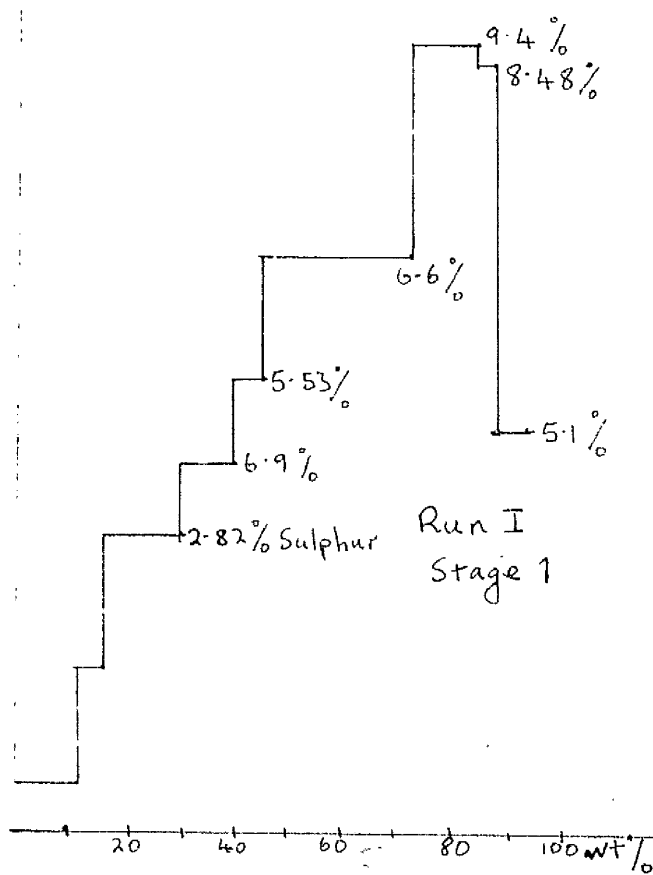


FIG 5. 17



25
ND

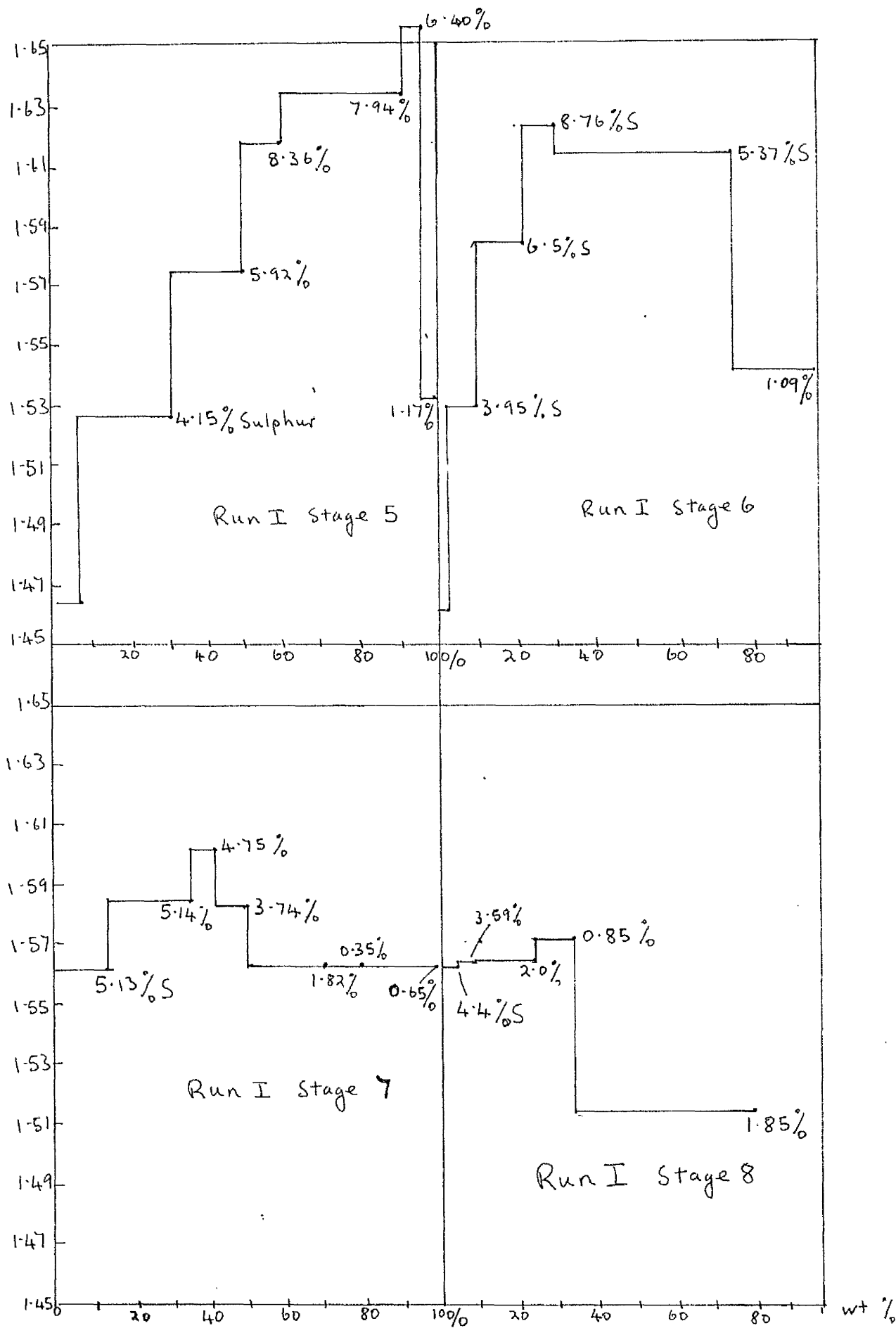


FIG 5. 19

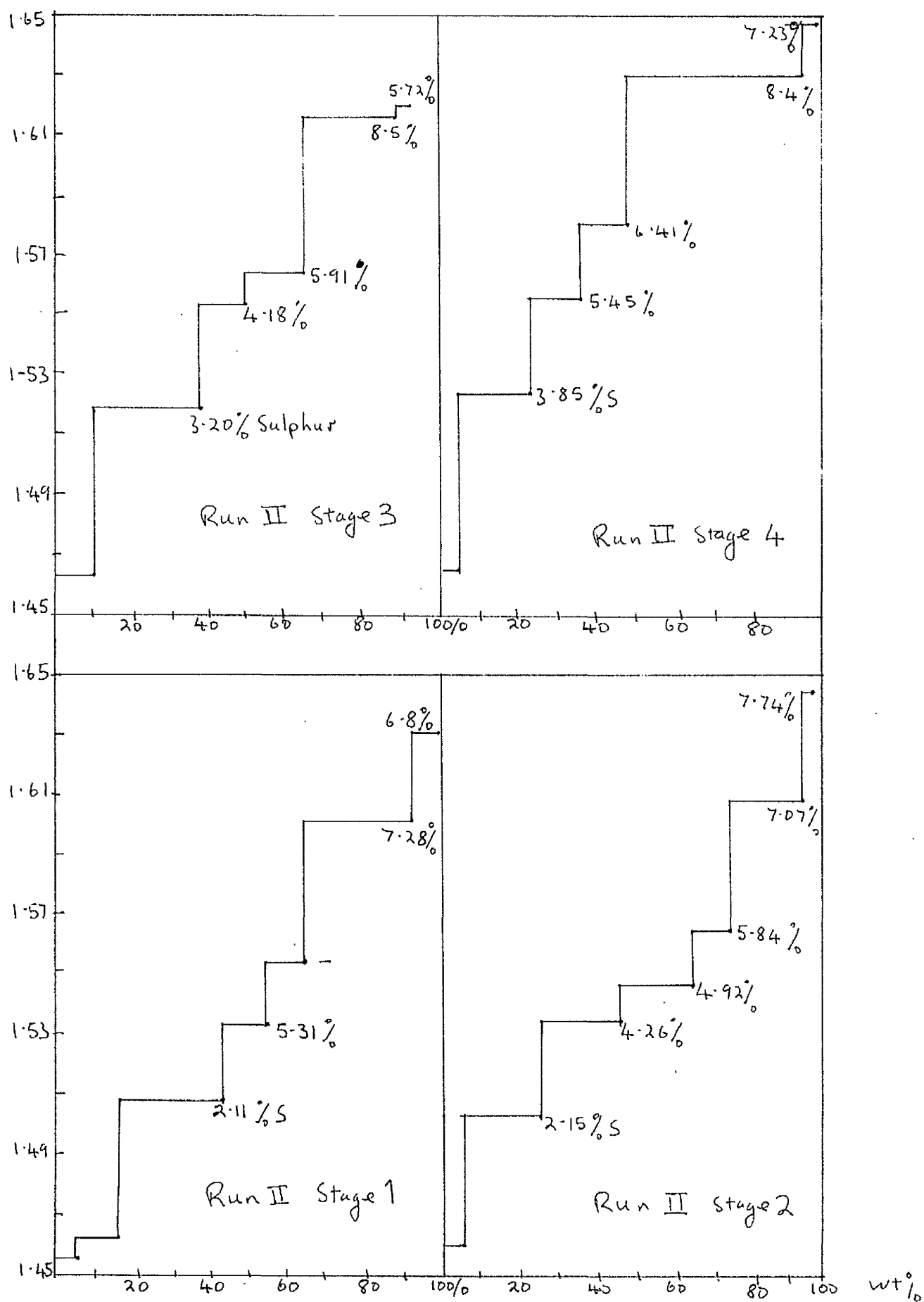
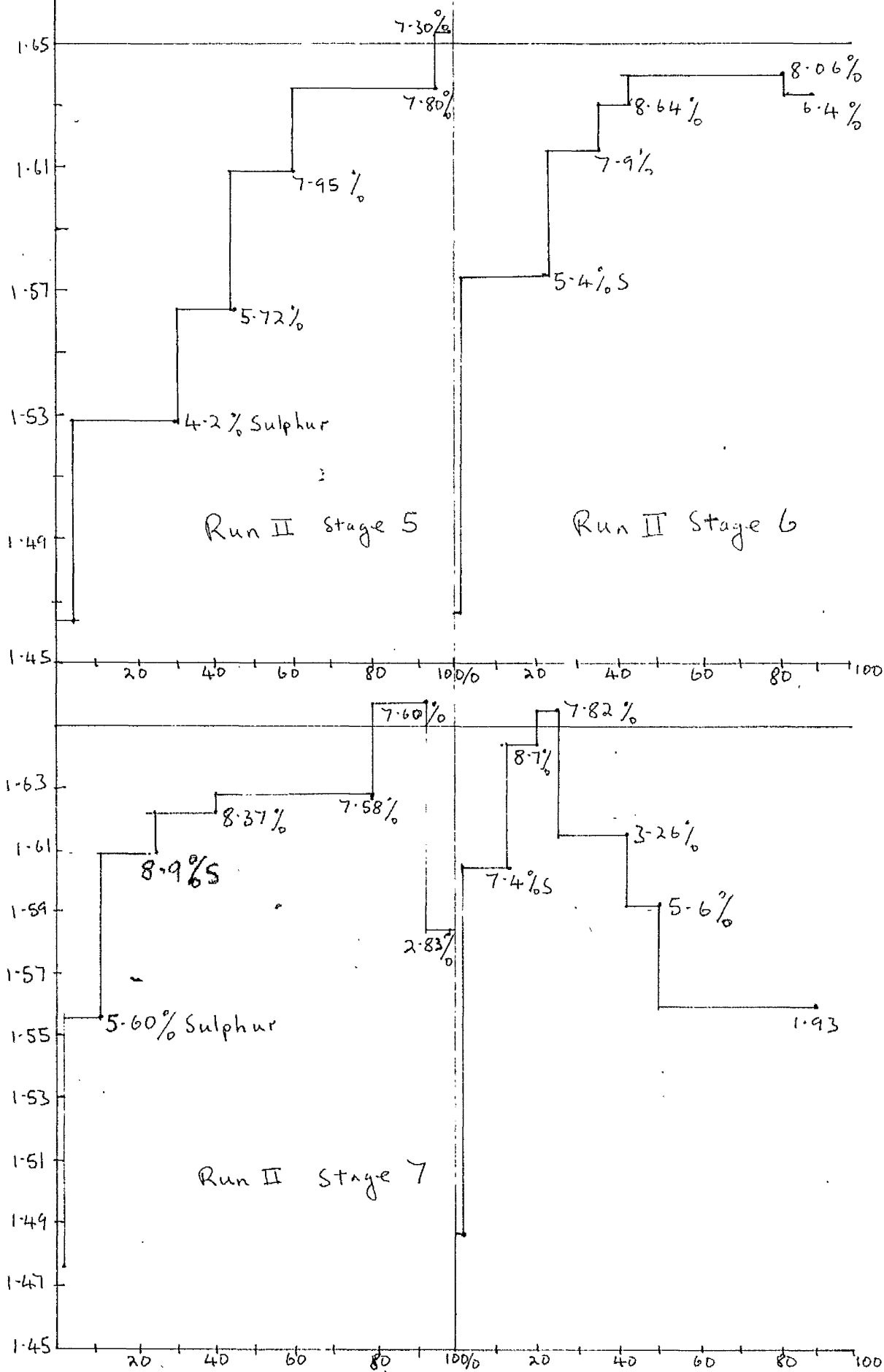


FIG 5.20



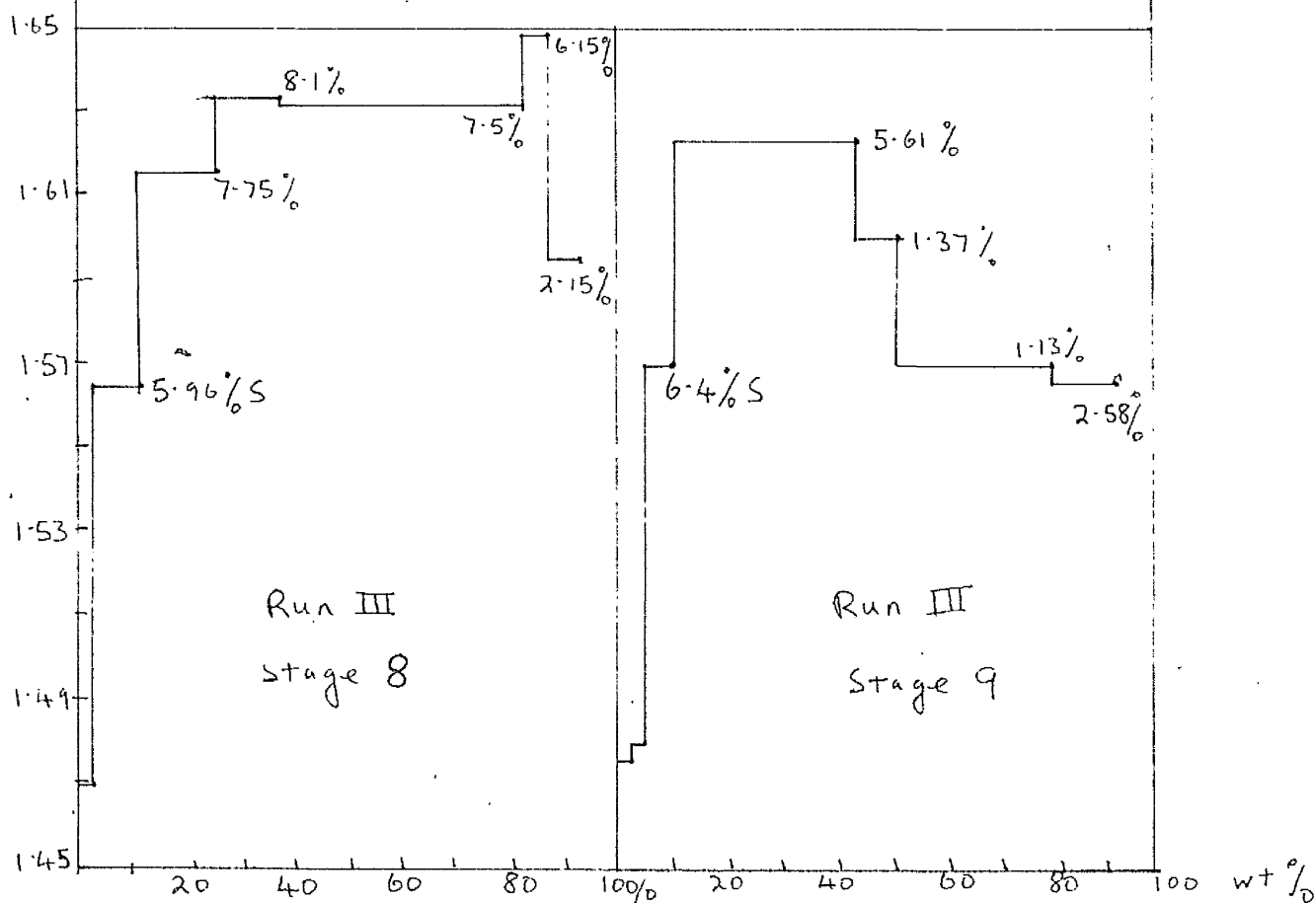
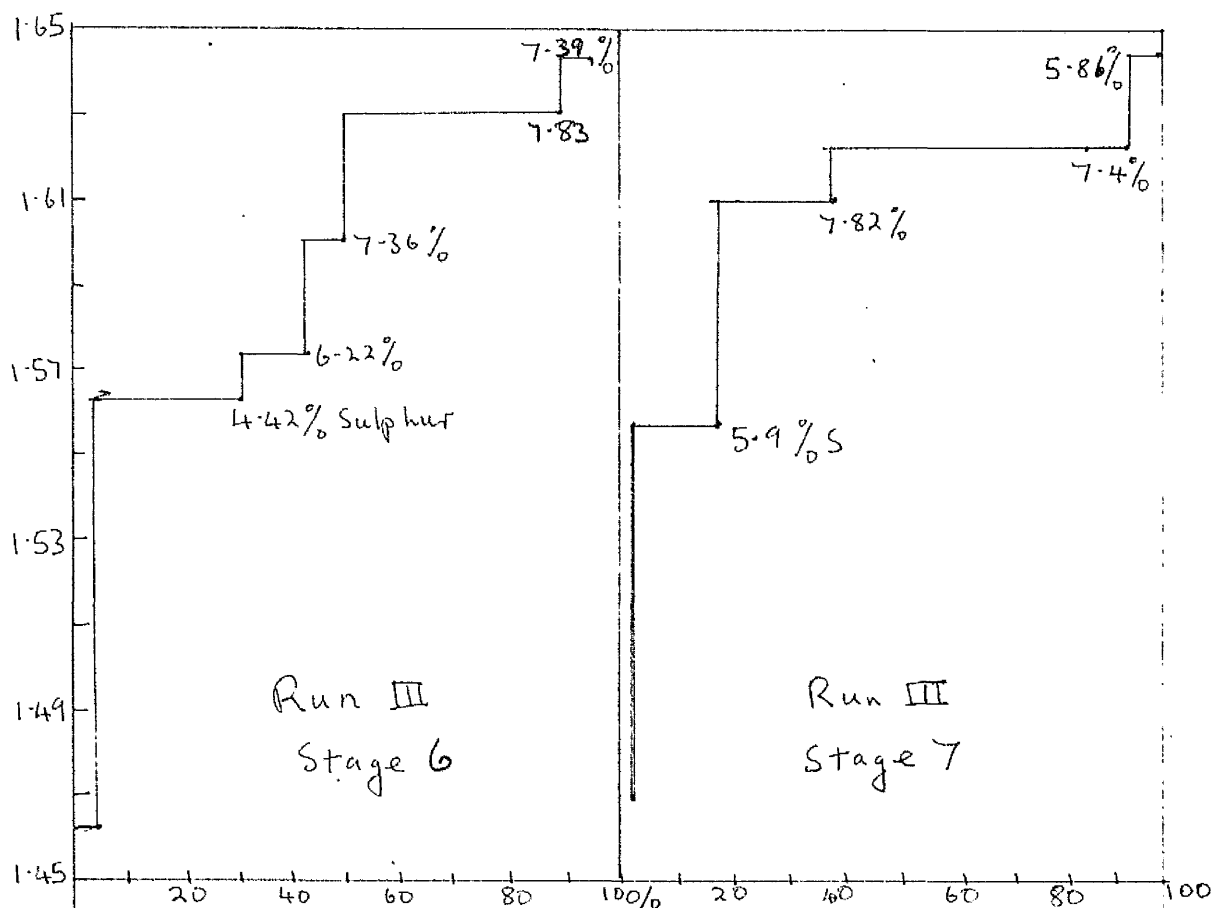


FIG 5.22

Run I 6.66 kg Oil = 100%

Batch Slurry
Stages

1 2 3 4 5 6 7 8

← Iso Octane

Benzene

Methanol

wt%
ND²⁵

44.2	26.0	12.0	4.95	2.4	5.7	2.02	6.25
1.5512	1.5560	1.5624	1.5714	1.5780	1.5824	1.5746	1.5336

Column Chromatography

wt%	7.07	13.25	17.9	2.83	2.8	12.5	9.2	1.08	5.17	4.35	0.28	2.65	2.08	0.16	1.23	1.05	0.13	1.55	4.23	0.99	0.68	0.37	0.56	1.54	2.83
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	D	B	C	D

Fractions A were Saturates, eluted with Iso Octane and combined to give 11.54%
 " B " polar compounds " " 37.92%
 " C " " " " 41.06%
 " D " " " " 5.03%

Run II 6.66 kg Oil = 100% Fig 5.23

Batch Slurry
Stages

Methanol

Benzene

Octane

column chromatography

wt%
N₂ 36.7
1.5350

22.2
1.5486

7.5
1.5666

4.85
1.5790

3.0
1.5866

11.2
1.6196

3.4
1.6224

4.96
1.5900

A B C

A B C

A B C

A B C

A B C

A B C

A B C

A B C

A B C D

wt% 5.02 17.0 12.5

1.47 14.5 6.25

0.61 3.6 2.22 0.295 1.74 2.20 1.2 1.5

1.12 0.11 4.6 5.4

0.035 1.19 1.77 0.26

0.022 1.18

1.24 1.86

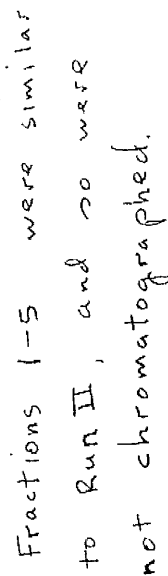
Fractions A were Saturated, eluted with Isooctane, and combined to give 7.88%

" B " polar compounds " " " 45.3%

" C " " benzene " " 32.73%

" D " " methanol " " 2.12%

Run III, 6.66 kg oil = 100%



Fraction	was	Saturates, eluted with	150 Octane	and combined	to give	%
A						0.311
B	"	polar compounds	"	"	"	5.95
C	"	"	"	"	"	9.59
D	"	"	"	"	"	1.83

CHAPTER 6. DISCUSSION OF RESULTS

6.1. INTRODUCTION

The results of the batch slurry separations have been presented in Chapter 5, together with a few observations on the graphs obtained. The main aim of the work was to separate from the oil homogeneous polynuclear aromatics of high refractive index. However these are not readily identifiable by chemical tests, and so the separation obtained in the experiments was determined by the identification of saturate material (paraffins and naphthenes), by the formolite test, and by refractive index. The formolite test did not detect the polar material (aromatic ^{and} sulphur bearing) with sufficient sensitivity, and it was sometimes found that a column effluent sample of oil solution was formolite negative, i.e. contained no polar compounds, while the stripped oil fraction, with solvent-free oil, was formolite positive. Thus it was evident that there was some overlapping of the non-aromatic and mononuclear aromatic zones. The column chromatography was very useful in showing how the batch slurry stages had separated, and gave an insight into equilibrium relationships being established. Due to the overlapping of the zones, it did not give a complete picture, and to obtain this picture, it was necessary to provide a means of estimating the extent of contamination of each zone. Once this had been found, it should have been possible to use the column chromatography results to develop a general method of predicting the equilibrium relationships between the adsorbed and mobile phases by means of some simple physical property. The column chromatography is very time-consuming, and to use this as a means of analysis for batch slurry stages would defeat the object of this new method of separation. As it is known that the

saturate material is much less strongly adsorbed than the polar material, it should be possible to treat the oil as a binary mixture, and use the equilibrium values to analyse the batch slurry results and the isotherm experiments.

6.2. DETERMINATION OF THE ^{Saturate}CONTENT OF KX₆ AND KX II₁₀₋₁₂

A recent paper (62) gives a comprehensive review of all tests applied to lubricating oils. It was deduced that refractive index is a useful measure of oil bulk composition.

The first thing to establish was that refractive indices of KX₆ and KX II₁₀₋₁₂ oil samples were additive. It was known that the benzene-iso-octane refractive index v. composition graph was slightly curved, and concave to the 45° line. A 50/50 volume mixture was found to be $N_D^{25} = 1.4400$, whereas a calculation based on the values of the pure components gave a value of $N_D^{25} = 1.4430$.

A group of oil samples were taken which were obtained from the separation of KX₆ on the 40' column. The polar portions, samples 2-6, were blended in proportion to their weights recovered. This was obtained by dividing the wt.% recovery by 5. The details are given in Appendix 3. The proximity to the original oil was shown by the fact that this experimental reblend was calculated to have a refractive index of $N_D^{25} = 1.5656$, while the original oil polar portion was calculated to have $N_D^{25} = 1.5659$. The actual N_D^{25} of this experimental reblend was 1.5618, showing the same sort of difference as with benzene-iso-octane.

This polar blend was then mixed with varying proportions of the saturate portion, to give a refractive index v. wt.% polar compounds graph. The resulting curve is shown in Fig. 6.1., together with similar experimental curves prepared by Rhodes (63) for KX₁.

Rodes was separating the oil by liquid extraction, and to use triangular diagrams, he required tie-line data which he obtained by chromatographing some of his samples on silica, and blending the polar and saturate portions in various percentages. He then plotted the points for the original sample on each curve, and by joining this points, obtained his experimental correlation. He concluded that for refractive indices above 1.5500, the relationship was not linear, due to a line of different slope being obtained. It is evident that Rhodes' fractions were cross-contaminated and that to extrapolate his correlation beyond his experimental points is not justified, as this would mean a rather low value of refractive index (1.39) for his pure saturate material. The non-linearity over 85% is produced by the wide range of refractive indices of the polar molecules. It is possible that Rhodes' correlation is part of a curve shown by the dotted line in Fig. 6.1. The difficulties in this approach must not be underestimated, and it was thought that the major sources of error would be:

i). the impossibility of defining a refractive index for the pure saturate material;

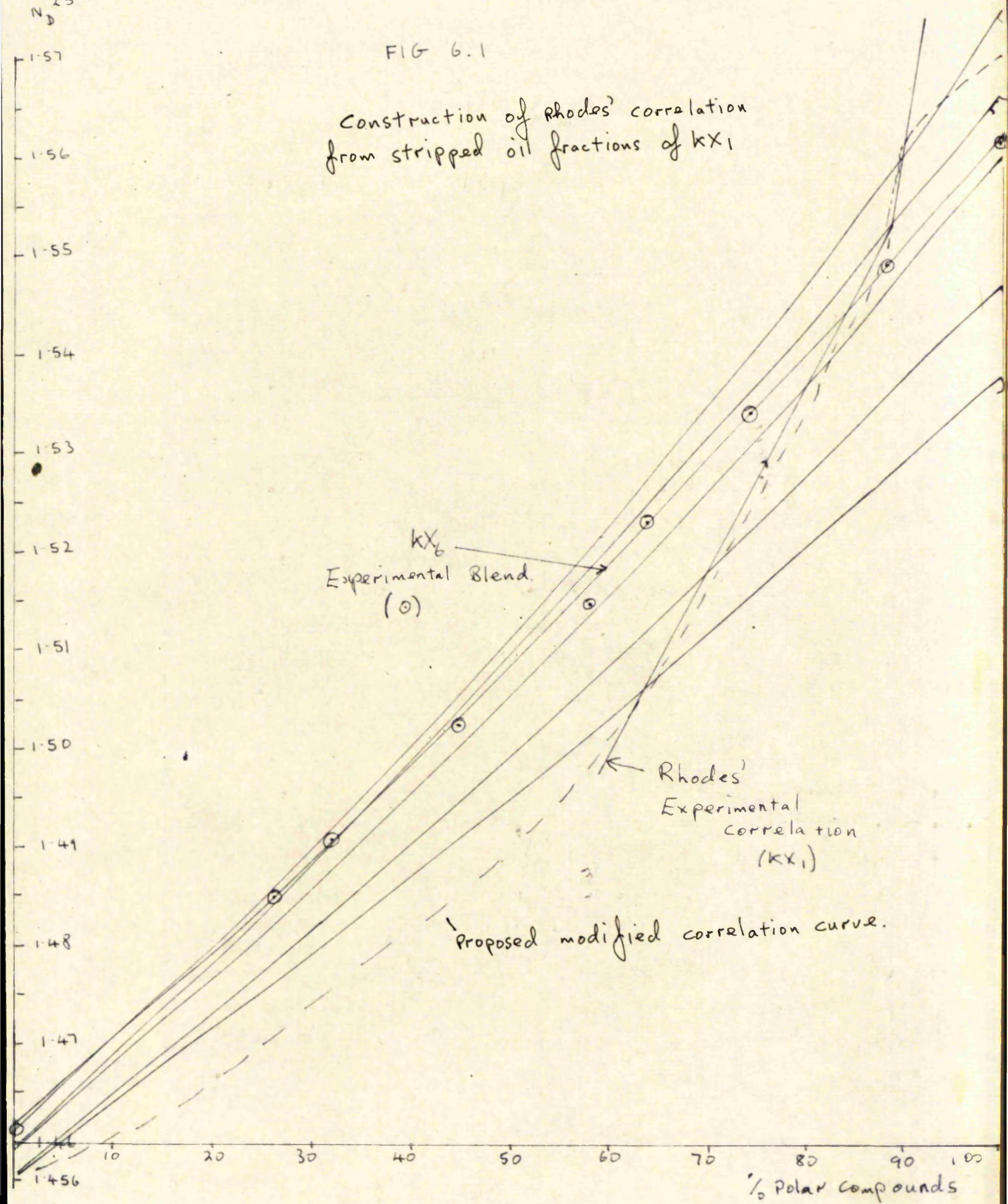
ii). the separation between the polar molecules producing some fractions, where the average refractive index was only 1.52 or 1.53, and other fractions where polar average refractive index was 1.56-1.57. The errors will increase with increased separation of the fractions. The method would be worthwhile, however, if it could predict the saturate content of the oil to within 2-3%.

During this work, it was realised that the methanol eluate, which which had been excluded from the experimental reblend, would make a difference to the average refractive index of the polar portion of the oil.

N_D²⁵

FIG 6.1

Construction of Rhodes' correlation
from stripped oil fractions of KX_1



When a proportional amount of the methanol eluate was then added to the reblend of N_D^{25} 1.5618, the new refractive index was 1.5475, which was very close to Higgins' value for the parent oil (57). This suggested that all the oil had been removed from the alumina, and that no change had occurred in the oil after passing down the column. The refractive index of the methanol eluate was calculated to be approx. 1.5560. The average refractive indices of the KX oils were calculated using the data from Higgins, and shown in Table 6.1. They are based on the actual weights recovered, and exclude the methanol eluate material, as the refractive index of this material had not been determined.

TABLE 6.1.

<u>oil.</u>	<u>N_D^{25} original</u>	<u>Average N_D^{25} after chromat.</u>	<u>N_D^{25} Sats.</u>	<u>N_D^{25} P.</u>
KX 1	1.5355	1.5397	1.4640	1.5637
2	1.5407	1.5438	1.4583	1.5643
3	1.5447	1.5473	1.4741	1.5818
4	1.5465	1.5503	1.4570	1.5616
5	1.5471	1.5509	1.4659	1.5661
6	1.5472	1.5518	1.4612	1.5659
7	1.5470	-----	-----	-----
8	1.5452	1.5615	1.4568	1.5721
9	1.5574	1.5545	1.4732	1.5641
10	1.5601	1.5632	1.4732	1.5688
11	1.5638	1.5656	1.4708	1.5740
12	1.5675	1.5660	1.4703	1.5750

In the case of KX_9 and KX_{11} , a decrease is shown after chromatography, and it is assumed that in this case some high refractive index material has been included in the methanol eluate. It is evident from these values that there is appreciable contamination of the saturate fraction.

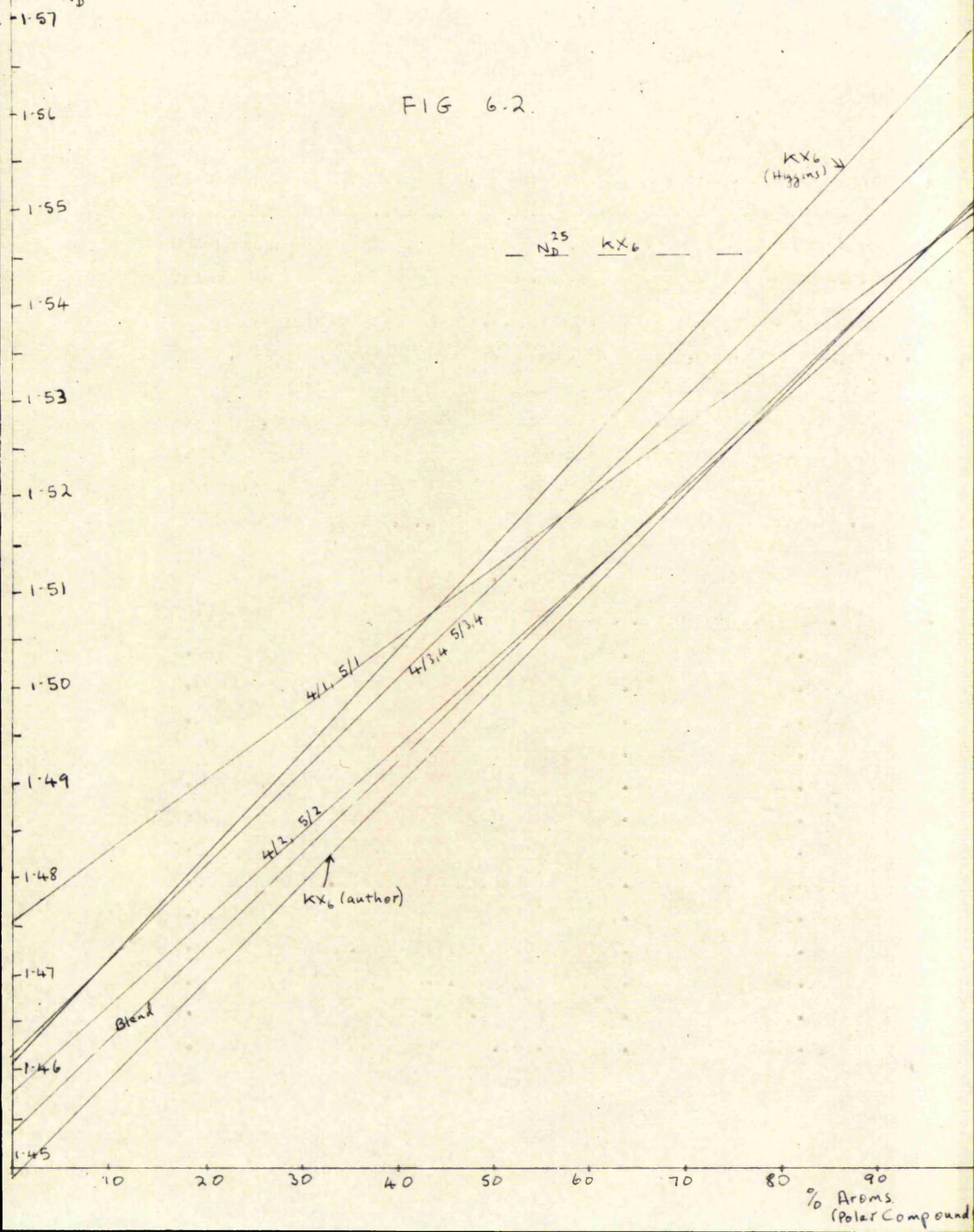
The results of the chromatographic separations of the samples from Expts. 4 and 5 were also treated in this manner, and a graph (Fig. 6.2) was drawn of lines joining the refractive indices of the "saturate" portions, with those of the "polar" portions. The refractive indices of the samples were then used to predict their saturate contents by assuming that these points laid on their respective lines. The results are shown in Table 6.2., compared with the experimental values.

TABLE 6.2.

<u>N_D²⁵</u>	<u>oil</u>	<u>%Sats. from graph.</u>	<u>%Sats. by expt.</u>
1.5472	KX_6 (Higgins)	21.0	13.30
1.5460	KX_6 (author)	5.0	10.55
1.5202	KX_{7-8} (author)	24.5	13.50
"	" "	18.2	8.00
1.5359	KX_1 (Rhodes)	20.8	20.00(on silica)
1.5355	KX_1 (Higgins)	10.5	23.00(on alumina)
1.5465	KX_4 (Higgins)	8.5	10.00
1.4983	St. run Kuwait 357/360°C	59.0	54.94(on silica)
1.5000	" " " 385/388°C	57.0	53.66 " "
1.5250	Expt. 4/5 St. 1.	33.0	27.50
1.5345	" " St. 2.	14.5	17.32
1.5500	" " St. 3/4.	10.0	13.80
1.5335	" " Blend St. 1-4.	19.5	18.65

N_D^{25}

FIG 6.2.



It will be seen that for silica the predictions are very good, suggesting that a more complete separation of saturate material has been obtained than with alumina. The reduction in the oil/adsorbent ratio to as low as to 1/36 in stage 2 did not lead to good agreement by this method.

It was reasoned that a closer approach to the correct line might be to use the lowest refractive index value of the saturates, and the highest value for the polar compounds. These were 1.4490 and 1.5680. This predicted a value for KX_6 of 18.5% Sats. This seemed to be a reasonable value, and so it was checked by using it to predict the % Sats., in stage 2 for example:

$$N_D^{25} \text{ oil, st.2.} = 1.5345$$

$$N_D^{25} \text{ "Sats." fraction} = 1.4580$$

$$N_D^{25} \text{ "Polar" fraction} = 1.5480.$$

To estimate the actual % Sats., two unknowns ~~were~~ introduced:

$$x = \text{wt.\% of Sats. rich fraction}$$

$$y = \text{wt.\% of Polar rich fraction.}$$

Using the graph, and the "lowest and highest line", a mass balance gave $x = 15\%$, whereas it was 17.32% by experiment. Using this low value of 1.4490, a group of lines were drawn passing through 1.5460, the refractive index of KX_6 , at 20%, 25% and 30% saturates as shown in Fig. 6.3. Similar algebraic mass balances using these lines also gave values of 15% Sats. It was obvious that the method was not sensitive enough, as large changes in the lower range of refractive index gave rise to only small changes in P, the polar fraction.

Another approach to this problem was to assume an average value for the N_D^{25} of the saturates and use the N_D^{25} of the polar portion as calculated. These lines are shown in Fig. 6.2.

Using a value of 1.455 for Sats. and 1.5595 for Polar, Rhodes' KX_1 saturate sample is predicted by the line to contain 3.5% polar compounds, and the oil to have 19.2% saturates, compared with the 20% he obtained experimentally.

Using Higgins' values, the saturate portion of N_D^{25} 1.4640 was estimated to contain 12% polar compounds, giving a value of 21.2% for KX_1 . If, however, the remaining stages were also characterised by this line, then the saturate content was estimated to be 34.55%.

Higgins' KX_6 values were then used, and the KX_6 line (1.455-1.5659) gave a value of 17% Sats. The same process was carried out for the batch slurry stages and then for the fractions produced from these samples in Expts. 6,7,8,9,12. The results of these calculations are as follows, using the KX_6 line (1.455-1.5659):

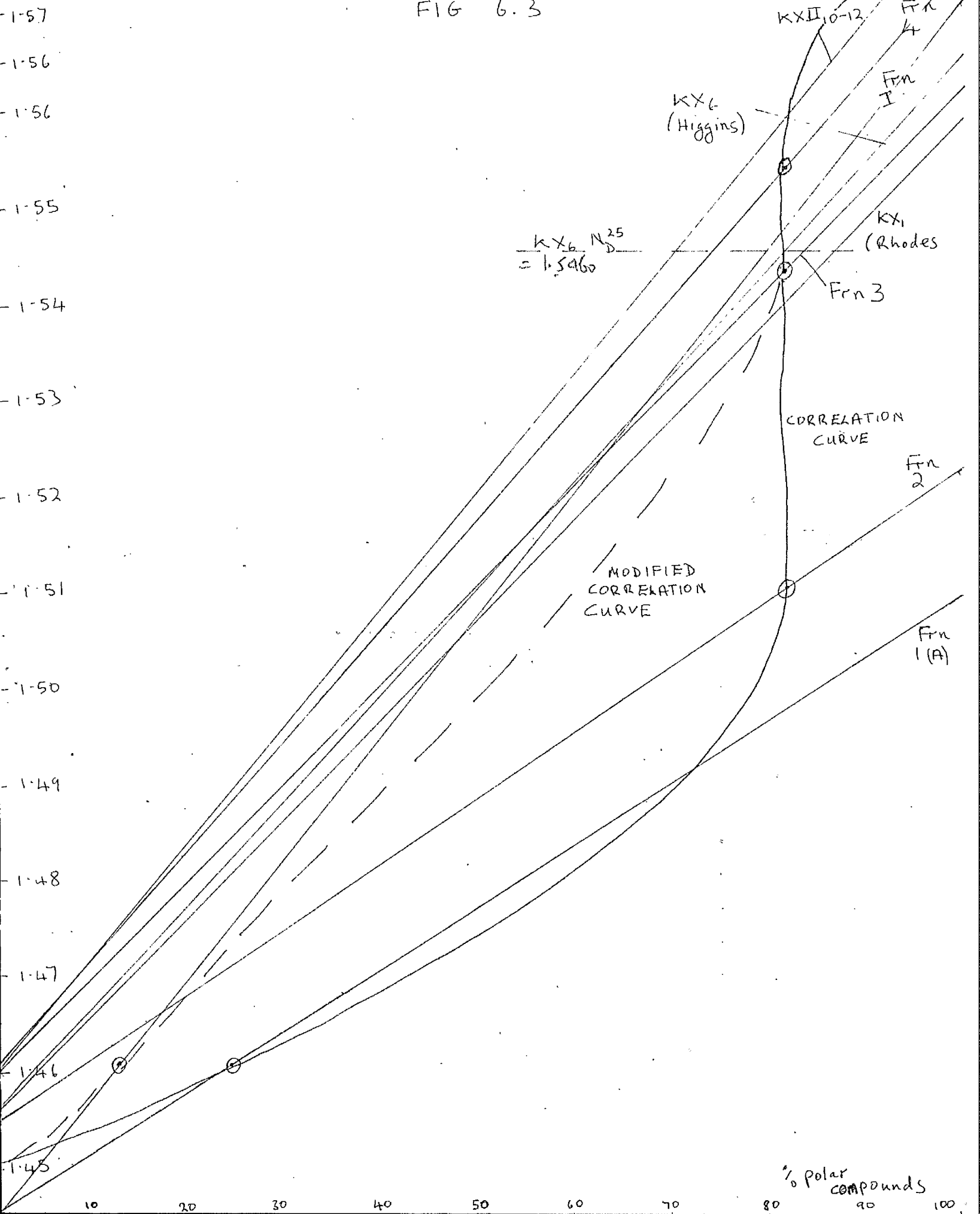
oil.

	estimation using KX_6 line.	using experim. blended curve.
Original oil, 1.5472.	17% Sats.	13% Sats.
After chromatography, 1.5518.	12.5%	9%
Mass balance on Higgins' column fractions	29.8%	
" " " author's " "	38.7%	
" " " " batch slurry stages	24.9%	21.6%
" " column sep. of " " "	31.5%	
By experiment on batch slurry sep.	17.8%	

It is noticeable from the above that the more the separations, the more divergent do the predictions of saturates become. Although the mass balance on the batch slurry stages seems to give a reasonable figure, it is thought that the further separation of polar material renders the values of over 30% unreliable.

58

FIG 6.3



A variation of this approach was to assume a value of the refractive index of the saturate content for KX_6 of 20%. A line was then drawn through these points (1.445, 0% Polar; 1.5460, 80% Polar). This gave the % saturates of the first stage, and a mass balance gave the proportions of Sats. which must be in the other fractions of Higgins' column separation. Lines joining the estimated N_D^{25} of Sats., and the % Sats. in the fraction were drawn, and gave the lines marked Frns. 1-4., on Fig. 6.2. The line used for fraction 1 is obviously too high, as it suggests that the average refractive index of the polar compounds is 1.5715. The slope of the line was modified to a more reasonable value marked frn. 1.(A). This makes little difference to the mass balance, but shows that the fraction will contain polar molecules of the mononuclear aromatic type. The points shown are of the same form as Rhodes' correlation curves, and were used to perform a mass balance over the batch slurry stages. These lines give a value of the polar portion refractive index for each fraction, and from these values, it was possible to calculate an average refractive index of the polar portion of the original oil, which was found to be 1.5766. The line joining 1.455 to 1.5766, i.e. joining the values estimated for pure Polar and Sats., predicts KX_6 to be 22% Sats.

The correlation curve shown in Fig. 6.2. was used for a mass balance over the batch slurry stages, but was modified to give a reasonable value for the first stage, bringing the curve nearer to the straight lines. This was felt to be justified, as the separation was known to be not as great as in column chromatography, and this correlation curve predicted very high saturate contents for low refractive index fractions. As the first stage of the batch slurry separation would contain a large proportion of the saturates, it was important to estimate this stage reasonably accurately. From the experimentally determined saturate content, the curve was modified in the lower refractive index regions.

The mass balance gave:

<u>stage</u>	<u>N_D²⁵</u>	<u>wt. of stage.</u>	<u>%Sats. from graph.</u>	<u>wt. Sats. gms.</u>
1	1.5250	48.8	(30)	14.65
2	1.5345	29.6	23	6.82
3	1.5455	13.2	19	2.51
4	1.5578	7.5	19	1.42
				<hr/> 25.40

The 25.4 gms of saturates are 21.2% of the parent oil.

Using the line 1.455-1.5766, for the batch slurry stages, a mass balance gave 27.5% Sats.

6.3. SUMMARY

It seems that a straight line relationship between the percentage of polar compounds and saturates cannot be used for column-separated fractions, but seems to give reasonable results for batch slurry stages, where separation among the polar molecules is not as great.

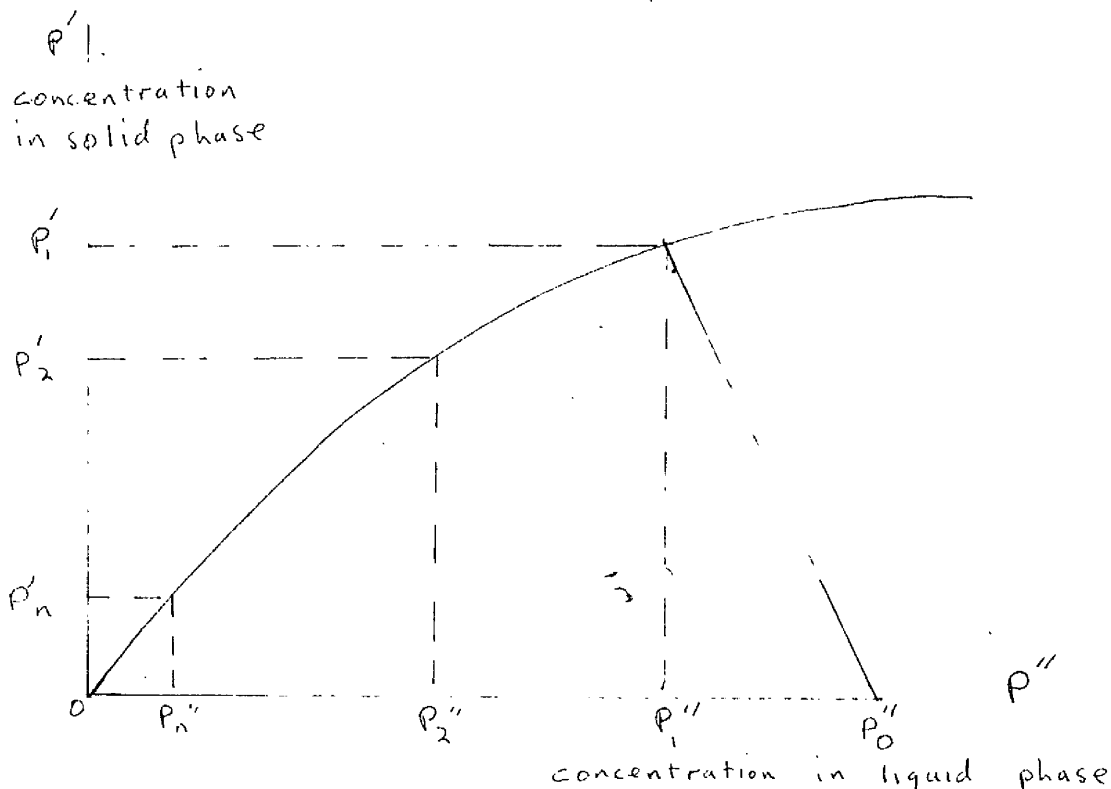
A correlation curve has been shown to be of value in predicting the saturate content of oil samples. It is possible that a family of curves should be used according to the extent of the oil separation. This will take into account the appearance of the naphthenes and mononuclear aromatic molecules of similar refractive indices.

Taking into account the experimental results, and the estimations using correlating lines and curves, it seems that about 25% saturates for KX₆ is a reasonable figure to take, though this may be erring slightly on the high side.

Using Higgins' figures, for KX_{10-12} , a straight line between 1.4600 and 1.5740 predicts 9% Sats. for KX_{10-12} , and a mass balance on the individual fractions gives 23%, using the same line. From the column separation of $KX_{II_{10-12}}$, experiment 30, the average $N_D 25$ of the polar compounds was calculated to be 1.5815. The line 1.5815-1.4600 gives 23% Sats. for $KX_{II_{10-12}}$, where 11.5% was separated experimentally, and a mass balance on the separated batch slurry stages gave 7-9% experimentally. Using the same line for the mass balance on the batch slurry stages gave 19-21%; knowing that these will tend to be too high, it seems that 12% is a reasonable value for the non-aromatic portion of $KX_{II_{10-12}}$.

6.4. THEORETICAL ANALYSIS OF BATCH SLURRY STAGES.

A theoretical treatment was carried out in order to estimate the number of stages required for a given separation. The polar concentrations P were considered, but the same argument follows for the saturate concentrations.



It was assumed that the separation was taking place as in Fig. 6.5. P' is the weight of polar compounds in the solid, and is equal to the amount adsorbed plus the amount in the liquid phase in the pores, per gram of adsorbent. P'' is the weight of polar compounds in the bulk liquid phase, per ml. of solution, excluding that which is in the pores. These expressions were used for the concentrations because in the experimental technique concentration differences were not measured. Filtration gave the weight of oil in the bulk solvent phase at each stage.

Let the weight of polar compounds P , gms/ml. solution, in a solution with V mls. of pure solvent be added to the weight of adsorbent A gms. This oil will be partly adsorbed, along with some of the solvent, and will split up as follows, assuming the oil density is equal to 1, and letting the pore volume be V_p mls/gm.

$$P_o''(V + V_{Po}'') = AP_1' + P_1''(V + V_{P_1}'' - AV_p)$$

Initial conc. = oil in pores + oil in liquid.

To find the equilibrium point on the curve, we require the slope of the line from $(P'', 0)$ to (P_1'', P_1') . This is given by $\frac{P_1' - P_1''}{P_1'' - P_1''}$, which however cannot be expressed exclusively in terms of P_o'' , V , V_p and A . If the volume of oil in the solution is ignored, (i.e. $V_{Po}'' = V_{P_1}'' = 0$), then:

$$P_o''V = AP_1' + P_1''(V - AV_p)$$

In the present case, $A = V$ numerically, $\therefore AV_p = V \cdot V_p$

$$\therefore P_o''V = AP_1' + P_1''V(1 - V_p)$$

For small values of V_p , $\frac{V}{A} = \frac{P_1'}{P_o'' - P_1''}$ approx.

V_p is known to be 0.285 for the alumina used in this work,

$$\therefore \frac{P_1'}{P_o'' - 0.715P_1''} = \frac{V}{A}$$

In stage 2, the oil in the pores now splits up into two phases on addition of Vmls. of fresh solvent. In this case, the volume of solution is V, as the pores are already full, and constant volume displacement is assumed,

$$\therefore AP_1' = AP_2' + VP_2''$$

$$\frac{V}{A} = \frac{P_1' - P_2'}{P_2''}$$

and similarly for succeeding stages.

The case will now be considered where the filtered oil solution is contacted in successive stages with fresh adsorbent.

Stage 1 is similar to stage 1 above.

Stage 2. Assume that the solution for stage 1 is stripped, and the oil is dissolved in fresh solvent:

$$P_1''(V + VP_1'' - AVp) = AP_2' + P_2''(V + VP_2'' - AVp)$$

The volume of the oil in the solution is again ignored, i.e. $VP_1'' = VP_2'' = 0$.

$$\therefore (V - AVp)(P_1'' - P_2'') = AP_2'$$

$$\therefore \frac{P_2'}{P_1'' - P_2''} = \frac{V - AVp}{A}$$

If the adsorbent is added to the filtered solution without any intermediate stripping,

$$\begin{aligned} \text{Stage 2: } P_1''(V - AVp) &= AP_2' + P_2''(V - 2AVp) \\ &= AP_2' + P_2''(V - AVp) - P_2''AVp. \end{aligned}$$

$$\therefore (V - AVp)(P_1'' - P_2'') = AP_2' - P_2''AVp.$$

ignoring $P_2''AVp$,

$$\frac{P_2'}{P_1'' - P_2''} = \frac{V - AVp}{A}$$

$$\begin{aligned}\text{Stage: } P_2''(V - 2AV_p) &= AP_3' + P_3''(V - 3AV_p) \\ &= AP_3' + P_3''(V - 2AV_p) - P_3''AV_p.\end{aligned}$$

$$\therefore \frac{P_3'}{P_2'' - P_3''} = \frac{V - 2AV_p}{A}$$

This process will continue for $\frac{V}{AV_p}$ stages, i.e. when all the solution has been adsorbed. The same equations will also apply to the saturate fractions by replacing P with S.

6.5. EQUILIBRIUM DIAGRAMS FOR BATCH SLURRY STAGES.

From the estimate of the total amount of saturates in the oil, a mass balance was set up to determine the concentrations of S and P at each stage. Only the iso-octane stages were considered, as the benzene stages contained only very small amounts of oil. Details of all the concentrations are given in Appendix 3., but an example is given here, taken from 2 stages of the KX_6 separations in experiments 4/5.

wt.oil charged: 120gms. wt.alumina: 600gms. iso-octane: 600mls. at each stage.

wt.% saturates in oil = 25% = 30gms.

wt. polar compounds = 90gms.

wt. separated by experiment = 24.01gms.

\therefore scale up wts. of saturates obtained by $30/24.01$

Stage 1.

wt. recovered: 48.8gms. wt.Sats. $13.4 \frac{30}{24.01} = 16.7$ gms. in liquid phase.

\therefore 13.3gms. in solid phase.

wt.polar compounds in liquid: $48.8 - 16.7 = 32.1$ gms.

wt.polar compounds in solid; $90 - 32.1 = 57.9$ gms.

volume of solution : $600 + 48.8 - (600.0 \cdot 285) = 477$ mls.

∴ concentrations are:

$$S' = 13.3/600 = 0.0222 \text{ gms/gm. adsorbent;}$$

$$S'' = 16.7/4.77 = 0.350 \text{ gms/gm. } \frac{\text{ml solution}}{\text{gm. adsorbent}};$$

$$P' = 57.9/600 = 0.0967 \text{ gms/gm. adsorbent;}$$

$$P'' = 32.1/4.77 = 0.0674 \text{ gms/gm. } \frac{\text{ml solution}}{\text{gm. adsorbent}}.$$

Stage 2.

wt. oil recovered = 29.6gms;

$$\text{wt. sats. in liquid} = 5.13 \frac{30}{24.01} = 6.42 \text{ gms;}$$

$$\text{wt. sats. in solid} = 13.3 - 6.42 = 6.88 \text{ gms;}$$

$$\text{wt. polar in liquid} = 29.6 - 6.42 = 23.18 \text{ gms;}$$

$$\text{wt. polar in solid} = 57.9 - 23.18 = 34.72 \text{ gms.}$$

∴ concentrations are:

$$S' = 6.88/600 = 0.0115$$

$$S'' = 6.42/600 = 0.0107 \quad (\text{the solution volume is now 600mls.})$$

$$P' = 34.72/600 = 0.0580$$

$$P'' = 23.18/600 = 0.0386$$

N.B. As the batch slurry stages of Runs II and III were very similar, the first five iso-octane stages of Run III were not analysed chromatographically, but the Run II figures were assumed for Run III.

These points for S' and S'' were plotted as isotherm data in Figs. 6.6.-6.8., and combined in Fig. 6.9; the polar concentrations P' and P'' are shown in Figs. 6.10-6.13.

The saturates in Expt. 4/5 and Run III gave an isotherm of the Langmuir type, shown as I in Fig. 6.14B whereas the polar compounds and Run I of the saturates gave an isotherm of type 2. However, both these curves must tend to a maximum, when the amount in the adsorbed phase is equal to the pore volume, and therefore those curves of type II must actually be parts of type IV curves.

FIG 6.7
Saturates Run I

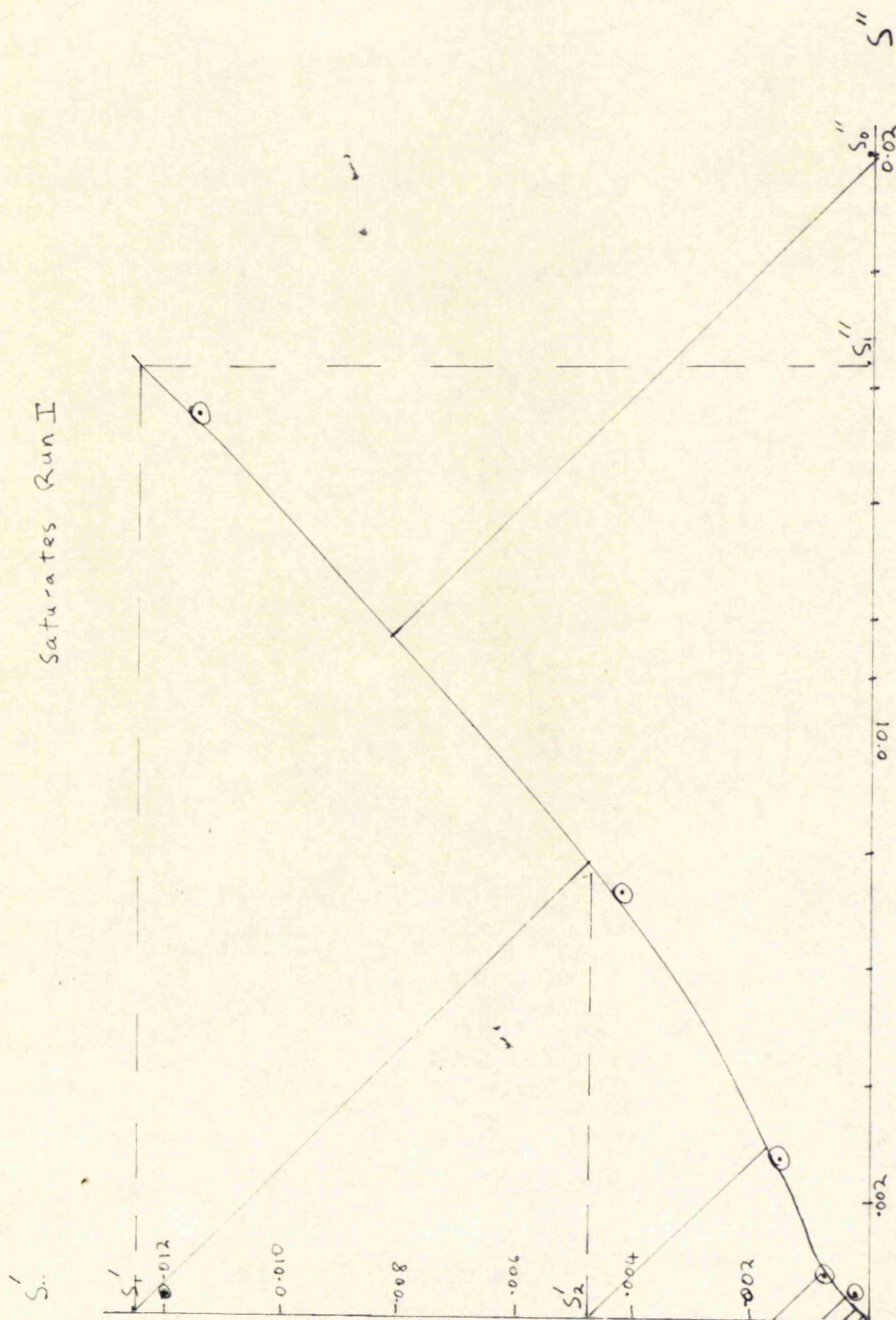


FIG 6.9
Saturates

Run I ○
Run III △
Exp 4/5 □

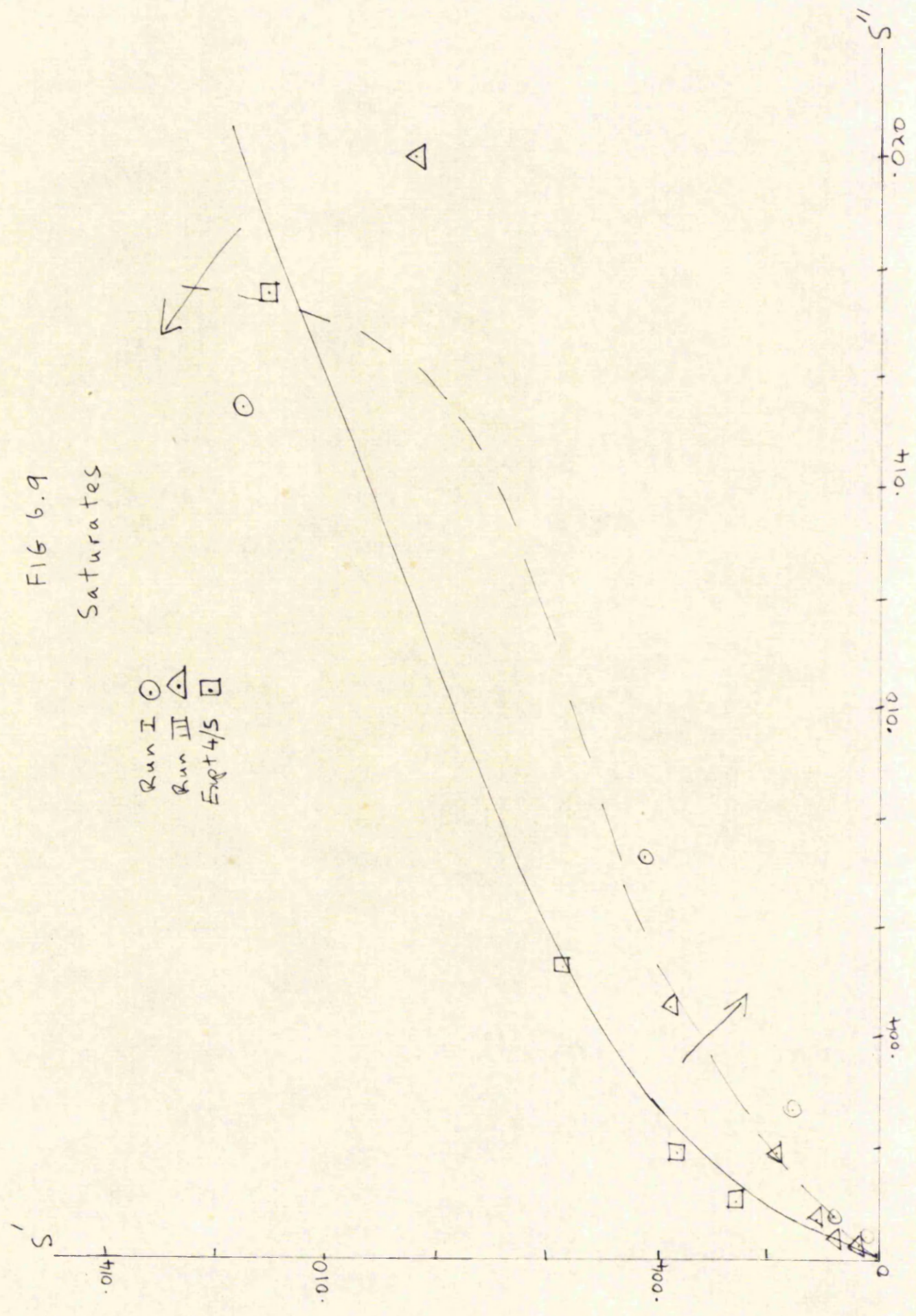


FIG 6-10
Polar compounds
Expt 4/5.

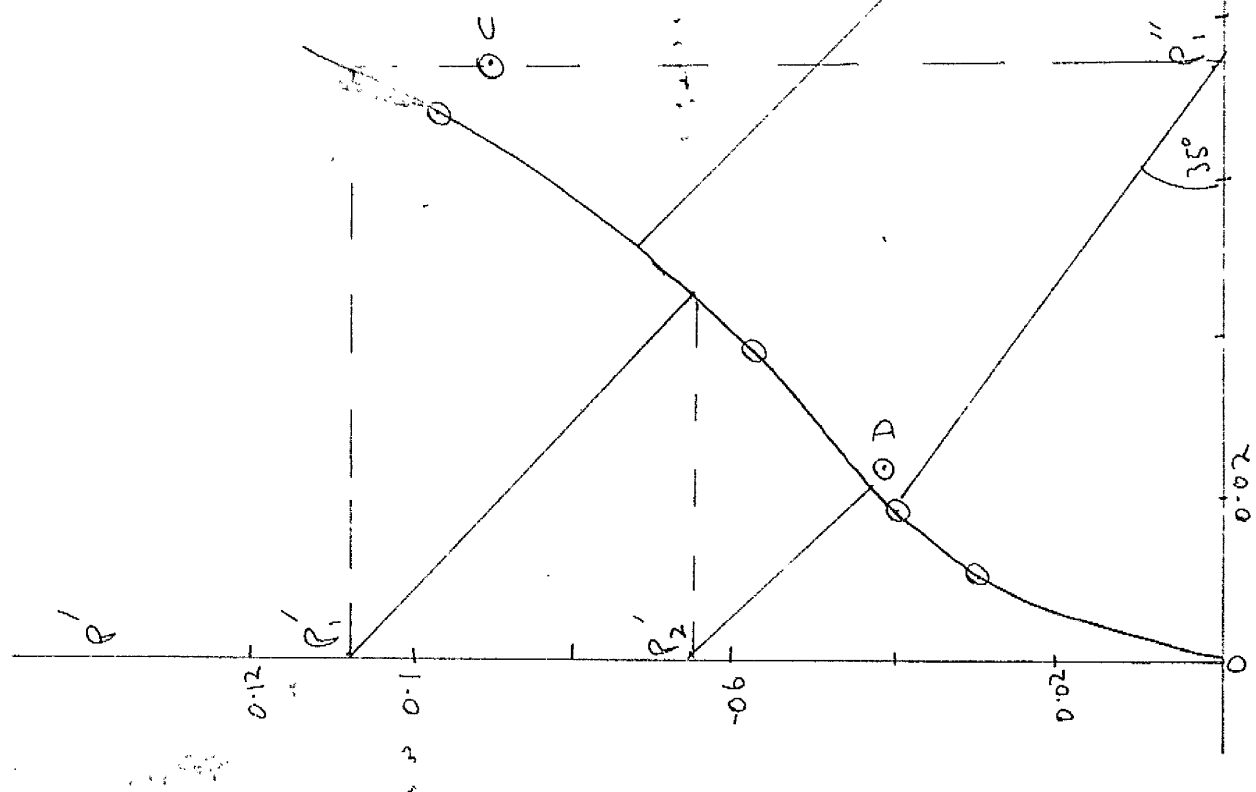


FIG 6.11
Polar Compounds
Run I

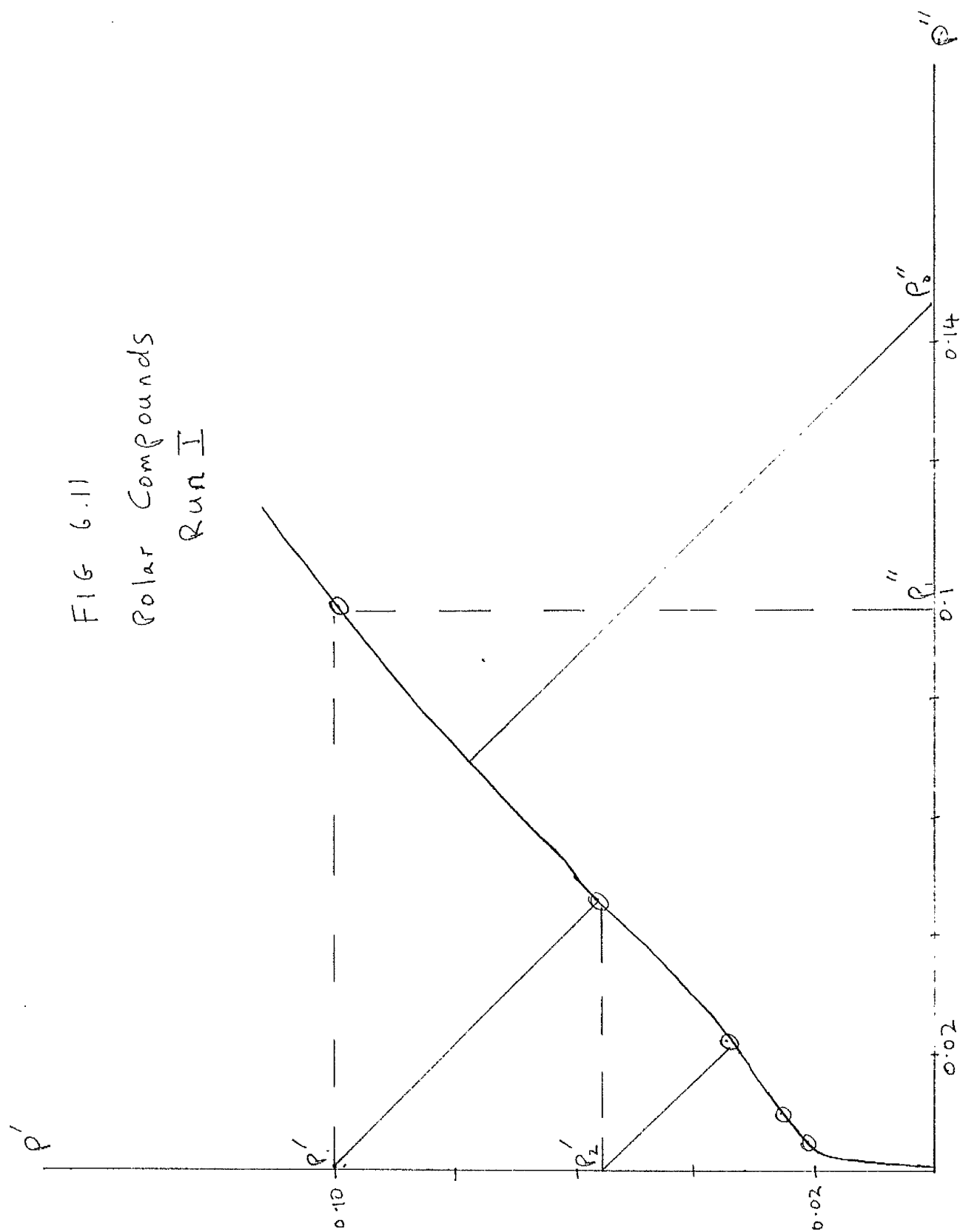


FIG 6.12
Polar Compounds
Run III

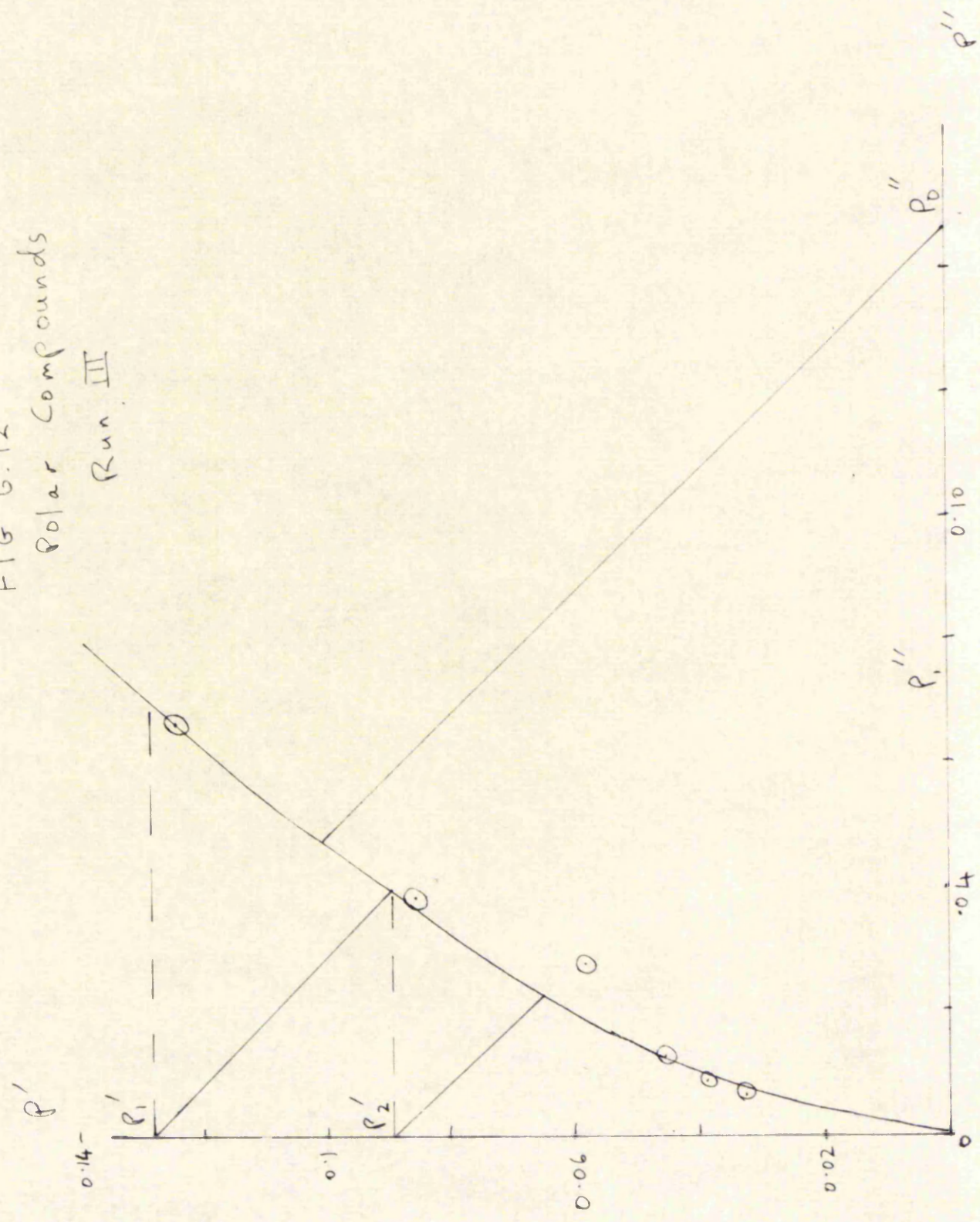
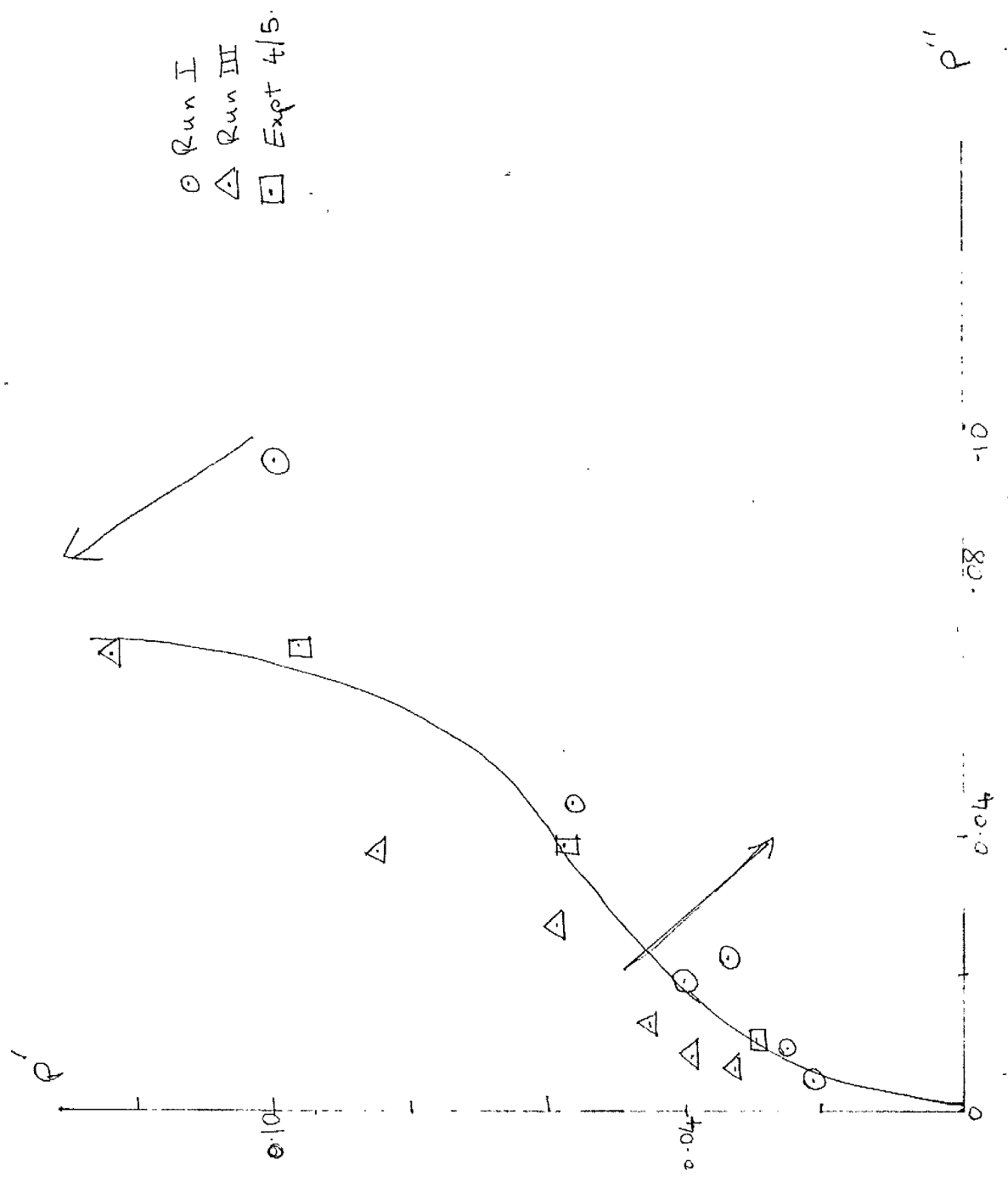
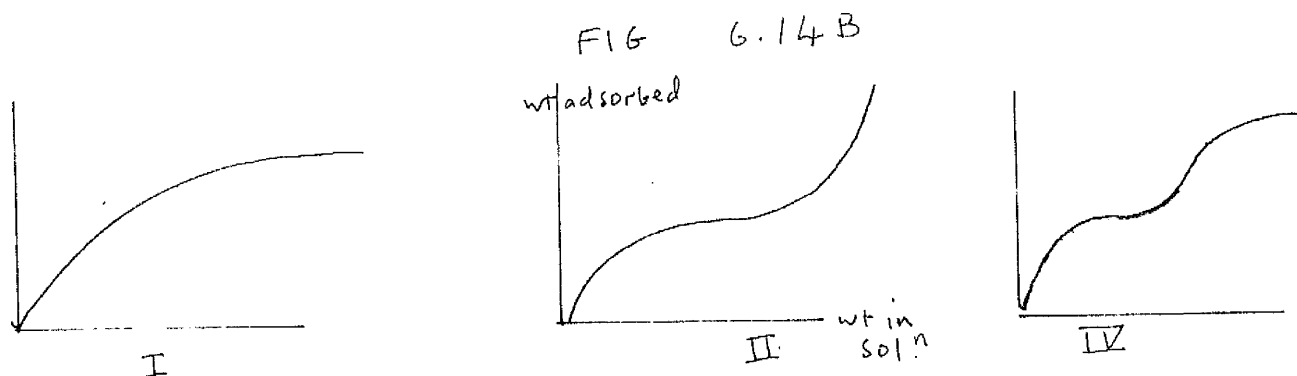


FIG 6.13
Polar Compounds





The combined saturates curve of Fig. 6.9 has been drawn close to the small scale batch slurry stage points of Expts. 4 and 5, as continuous stirring meant that these experiments would be more likely to have attained equilibrium than the drum rolling for Runs I and III. The lower values of these Runs I and III may mean that the saturates are of different composition to those of KX_6 , and a different isotherm has been obtained. If equilibrium had not been obtained, the points would tend to move in the direction of the arrows, and this seems to be a more likely explanation. Thus, at equilibrium, the isotherm would be of the form shown by the dotted curve. The polar compounds curve of Fig. 6.13 shows the same general shape, although much steeper.

The theoretical stages were constructed on the graph by using the relationships derived in section 6.4. Taking Fig. 6.6 as an example, the feed concentration for saturates was 0.0417gms/ml. This is the point So'' .

A line of slope $\frac{V}{A}$ (45°) was drawn through S_0'' , to cut the equilibrium curve at A. This line gives the relationship between the two phases for negligible pore volume. For a larger value of pore volume, which must be taken into account, the slope of the line will be greater than $\frac{V}{A}$. It can only be found by trial and error:

$$\frac{S_1'}{S-S_1''} = \frac{V}{P} + \frac{V \cdot V_p \cdot S_1''}{A(S-S_1'')}$$

In this case, both sides of the equation were equal, when $S_1' = 0.02$ and $S'' = 0.03$. These were taken as the equilibrium points S_1' & S_1'' . From S_1' , the second equilibrium point was found by drawing a line of slope $\frac{V}{A}$ to give:

$$\frac{S_1' - S_2'}{S_2''} . \text{ This gave the point } S_2'.$$

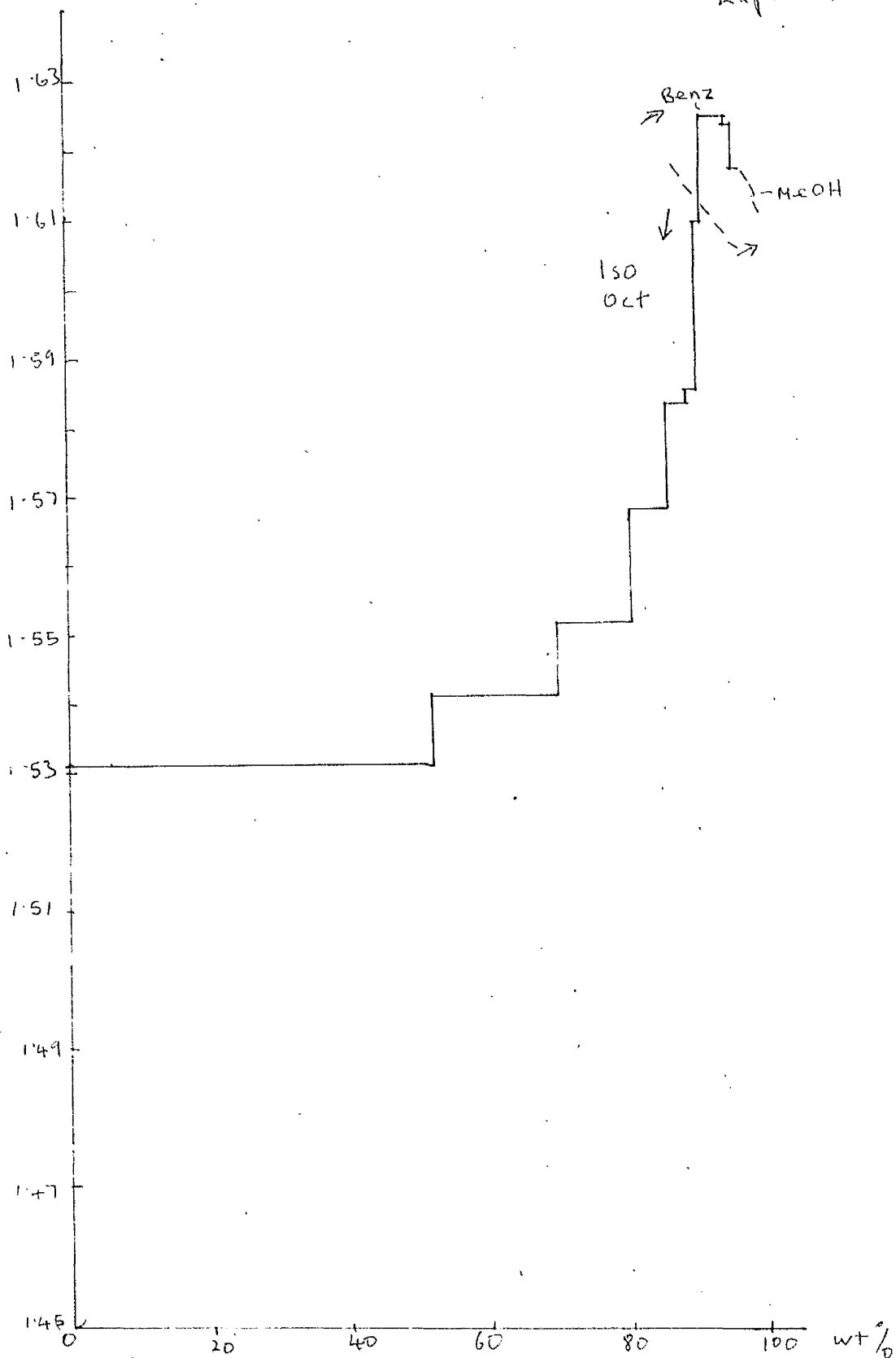
This process was repeated as shown in the diagram, giving a total of 12 stages to reduce the concentration of saturates in the stationary phase to zero. The same procedure was carried out on the other graphs, and the number of stages required to reduce the concentrations to zero by the use of iso-octane were found from the graphs. These were:

	<u>Saturates</u>	<u>Polar compounds</u>
Expt. 4/5	12 stages	13 stages
Run I	7 "	15 "
Run III	8 "	20 "

An experiment (54) was then carried out, similar to Expt. 4, using 300gms. alumina, 300mls. solvent at each stage. However, 80gms. oil were charged to investigate the effect of using a higher oil/adsorbent ratio. Due to the fact that the adsorption capacity of the alumina for the oil seems to have been reached, exactly the same weight of oil remained adsorbed, as in Expt. 4. The results are shown in Fig. 6.14.

FIG 6.14

Expt 54



As the adsorption capacity was exceeded, it is unlikely that there were any saturates in the adsorbed phase, but it can be seen that seven iso-octane stages were required to remove 91% of the polar compounds, whereas only four stages were required according to Fig. 6.14. The final two iso-octane stages only removed 1.5% and 1.4% of the oil respectively, suggesting that the isotherm curve should be steeper (i.e. nearer to the ordinate P'). In Expt. 54 four iso-octane stages removed 86% of the oil, showing the small difference in solid phase concentration produced by successive iso-octane stages after the optimum value had been passed. The 20 stages estimated for the saturates of Expt. 4/5 appears to be too high, which means that the curve should be flatter (i.e. nearer to the abscissa S"), as had been proposed from a consideration of the attainment of equilibrium.

The difference between the number of stages required to reduce the amount of polar compounds and saturates to zero gives the number of stages to separate the saturates from the polar compounds in the adsorbed phase. This is important, as it may be possible to use this as a basis for determining the number of theoretical stages in an adsorption column; the process is not the same, as in a column adsorption and desorption of the oil are taking place continuously, but the same result is obtained, and by determining the contamination of each fraction as quantitative comparison could be used.

On recontacting the filtrate from stage 1 of an experiment similar to Expt. 4., the second stage was represented by point B for the saturates in Fig. 6.6. This point is well below the equilibrium curve, and can be accounted for in a number of ways.

It is possible that with fresh adsorbent the polar compounds are quickly attracted to the active adsorption sites, and the adsorption-desorption process to reach equilibrium would be slow. Inaccuracies may have occurred in the small scale weighings, and the concentrations will similarly be in error. It is also possible that hysteresis is occurring, and that the adsorption isotherm is similar to the dotted curve, while the desorption curve is the equilibrium isotherm already obtained. This effect has been observed by Shull et al (68) and has been justified thermodynamically by Brunauer (69).

For adsorption/desorption on silica, Shull et al. found that above a certain pore diameter (30-100 Angstrom units), hysteresis occurs for large molecules. A slight effect was observed with nitrogen. (Fig 6.14 A)

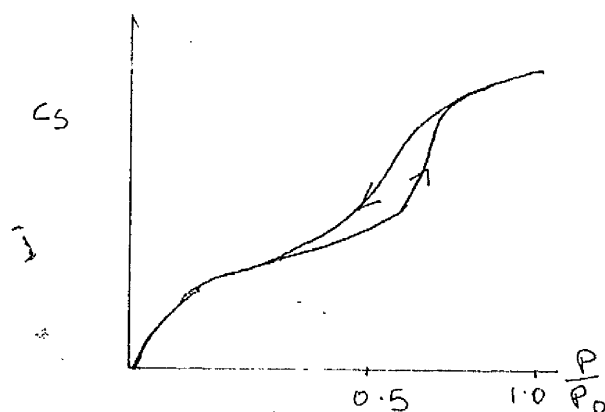


FIG 6.14 A

In the case of oil adsorption, hysteresis could occur, due to the fact that in stage 1 all the very polar molecules, probably oxygen and nitrogen compounds, will remain adsorbed even after many successive desorptions with iso-octane. If, however, the filtrate, containing saturates mono and dinuclear aromatic molecules, is contacted with fresh adsorbent, there are new active sites, and those molecules which would normally be in solution in a desorption process will be in the adsorbent phase.

For the polar molecules, the second stage gave the point D on Fig. 6.10., which is only slightly below the equilibrium curve, and may be due to experimental error, though the possibility of hysteresis cannot be discounted. As the polar molecules are strongly adsorbed, the adsorption-desorption curve would be expected to be much closer.

To estimate the theoretical stages in this process, lines were drawn^W as derived in section 6.4. On the saturates diagram, a line of slope $\frac{V-AV_p}{A}$ was drawn through S_1 " (a), the slope being 35° . This did not coincide with B, but assuming that this curve ~~is~~ to be valid, it gives a total of 11 stages to obtain completely saturate free oil sample. When this point were reached, however, the oil sample obtained would be so small that the value of the separation would be questionable. The line of slope 35° from P_1 " in Fig. 6.10. for the polar fraction almost coincides with D, and four stages are shown to reach zero concentration. If a hysteresis curve, slightly flatter to the abscissa, were being followed, then more theoretical stages would be required. An example taken from Expt. 4/5 will illustrate how the concentrations of saturates are varying with these different treatments.

Addition of fresh solvent,

Initial oil: 25% Sats. Stage 1. Solid phase: 18.5%. Liquid phase: 34.2%.

Addition of fresh adsorbent,

Initial oil: 25% Sats. Stage 1. Solid phase: 9.65%. Liquid phase: 4.7.4%.

If the process is considered similar to distillation, then the two percentages underlined should be compared, as one represents a concentration of the polar compounds on the adsorbent, and the other the concentration of the saturates in the liquid phase. Both these processes take place in an adsorption column.

FIG 6.15

Exp + 53

N_D^{25}

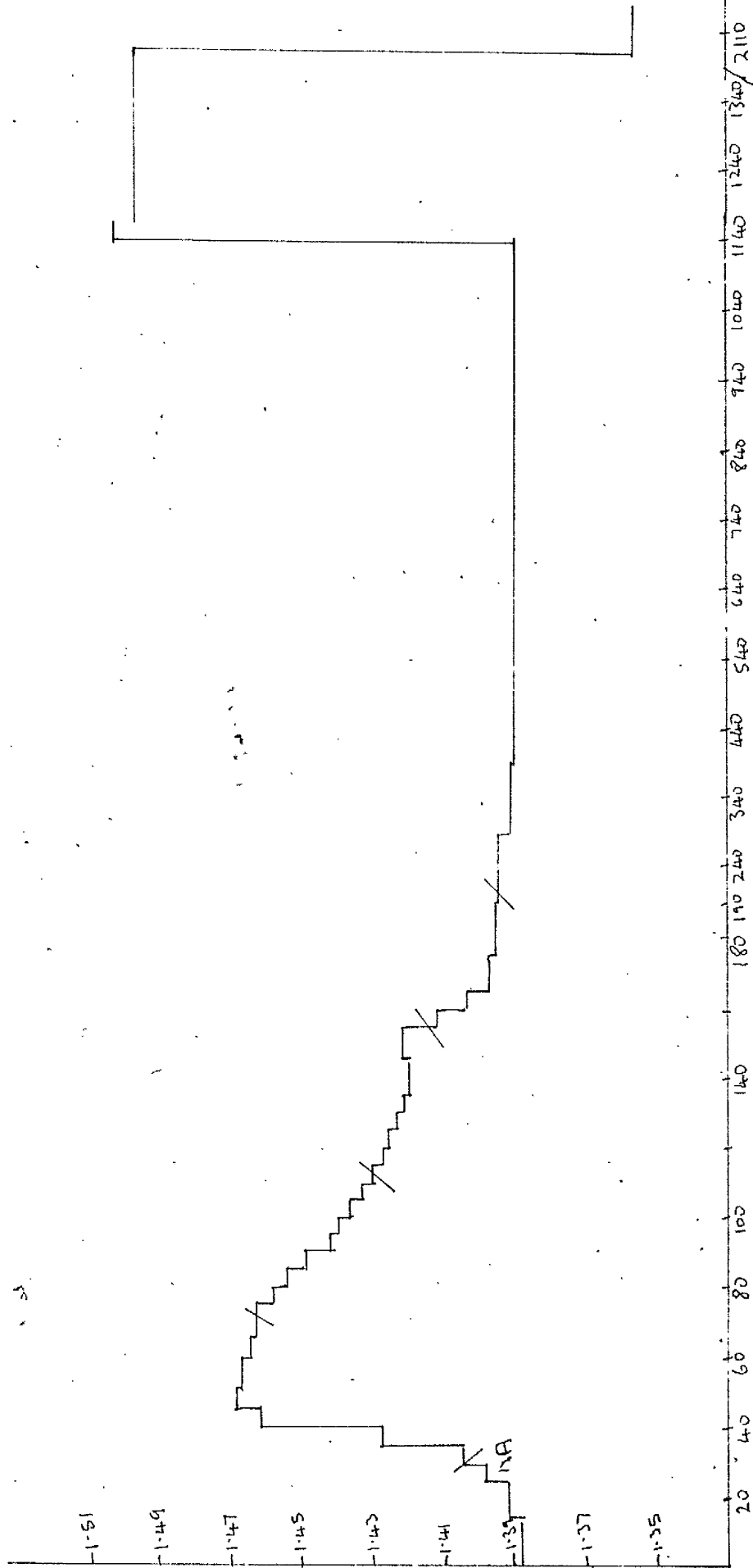
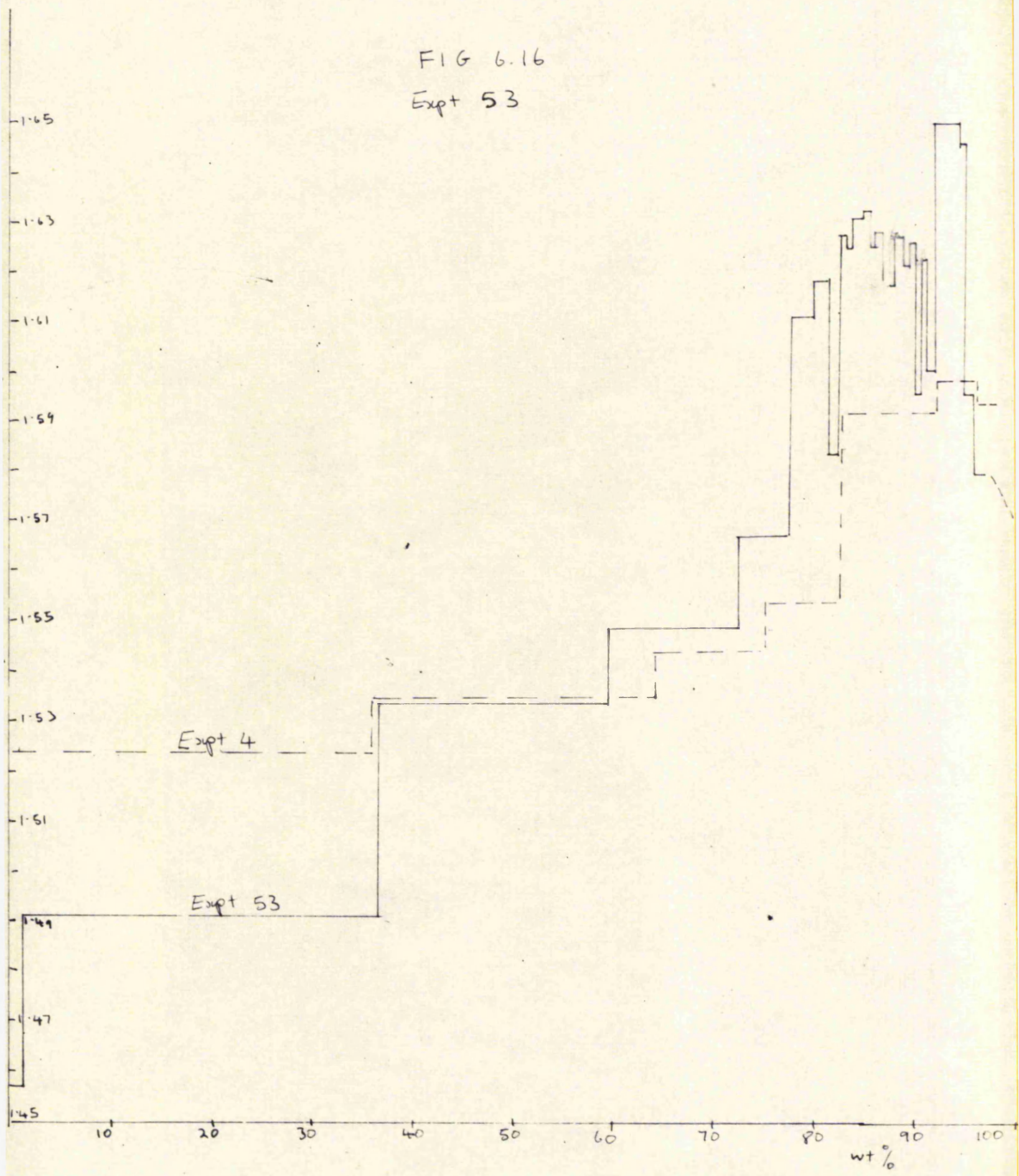


FIG 6.16
Expt 53



As a final comparison between batch slurry process and column separations, Expt. 53 was carried out, using the same amount of material as in Expt. 4. in a 5' x $\frac{5}{8}$ " column. Fig. 6.15. shows the chromatographic separation, and it can be seen that little separation of the oil into zones has taken place, and that almost all the oil has been removed by iso-octane. To remove 80% of the oil required 1200mls. by batch slurrying, compared with only 400 mls. on the column. Although the column was grossly overloaded, a small amount of non-aromatics were isolated.

After the first 190mls, samples were taken every 50mls, and the results after stripping are shown on Fig. 6.16. The fluctuation in the refractive index could mean that small fractions of saturate material were passing over the polar-aromatic material. This could have happened because of the large volume of oil charged, and the necessity to dissolve it in a small amount of iso-octane to facilitate entry of the oils to the column. The first oil solution samples were being collected while the last of the oil was entering the column at the top. Although Expt. 53 has given slightly better separation than the batch slurry, it took 3 days to complete, compared with 1 day for the batch slurry.

6.6. OPTIMUM NUMBER OF STAGES FOR EACH SOLVENT.

It was seen in Fig. 6.14. that successive iso-octane stages were removing less oil each time, although this meant that benzene fraction of high refractive index (1.625) was obtained. A benzene fraction could have been obtained, however, for only half the effort, if the benzene stages had commenced after the fourth iso-octane stage.

wt% of oil remaining at
each stage

FIG 6.17

BATCH SLURRY STAGES

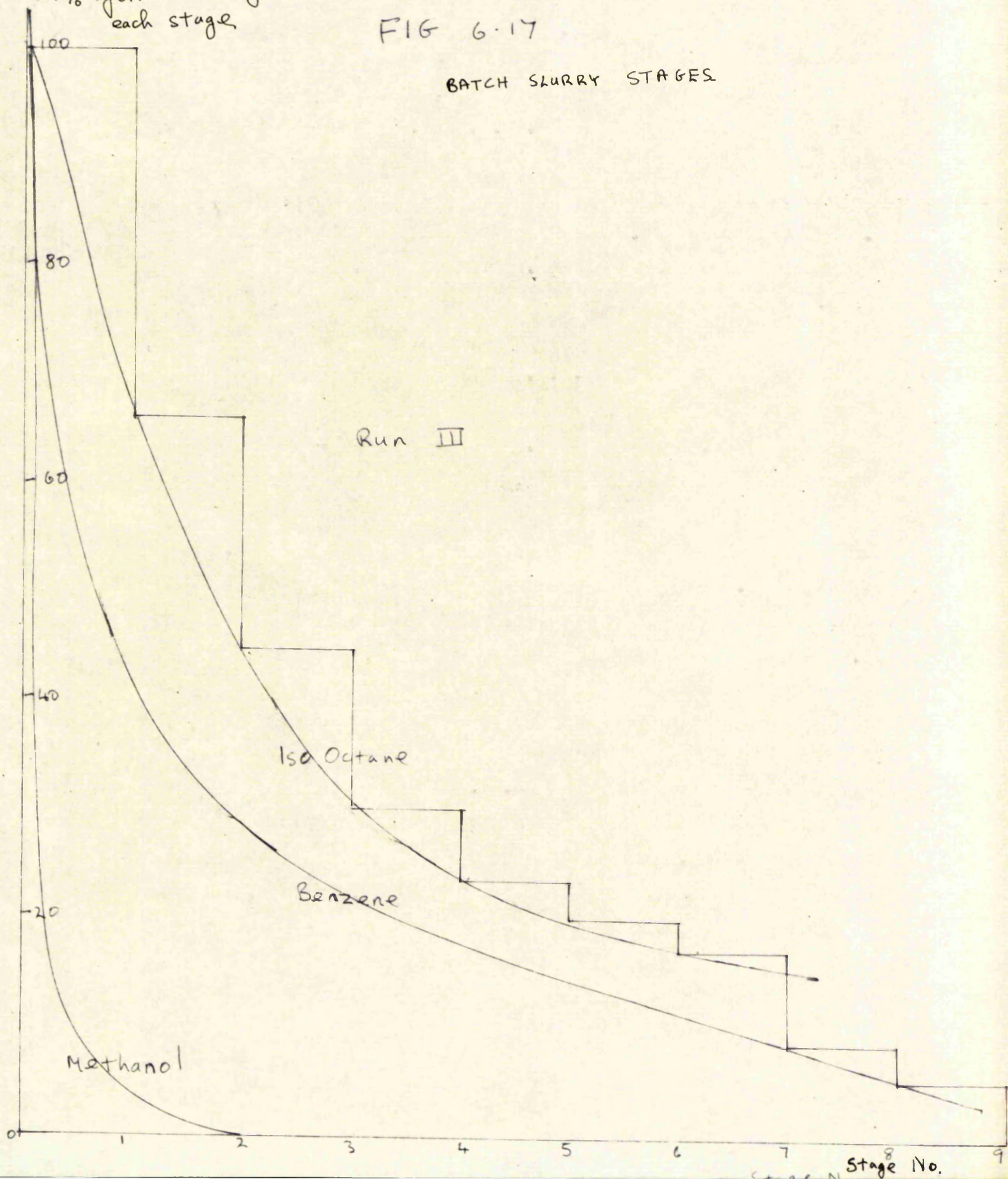


Fig. 6.17. shows the separation of Run III by the wt.% of the oil entering each stage, i.e. the amount adsorbed on the alumina before addition of a fresh solvent. Run III is used as an example because it had the most iso-octane stages. The decrease in weight of oil will tend to become exponential as already seen in Fig. 6.14, and there should be an optimum point to change solvent. The points to be considered are:

- i). the labour and solvents required for many stages;
- ii). the type of material required, and its degree of contamination by other molecular types.

If benzene alone were used, a curve similar to the one shown would be obtained, while methanol would produce a very steep curve, showing almost all the oil displaced in the first stage.

To obtain a reasonable amount of oil at each stage means that the curve must be quite steep. When the amount of oil in any stage is considered to be too small, the next solvent is used. This changeover point may be decided before the experiment, and will depend on the experimental conditions.

6.7. OIL-SOLVENT ISOTHERMS.

The apparently anomalous results obtained, as shown in Chapter 5., are of interest in considering the adsorption capacity of the alumina. The surface area of the alumina used was measured by Harrison (61) by nitrogen adsorption, using the formula $\frac{x_m}{w} = \frac{A}{NA_m}$, where $\frac{x_m}{w}$ = moles adsorbed/gm.

A = surface area of adsorbent, m².

N = Avagadro's Number.

A_m = Area of adsorbed molecule Å².

Assuming a value of 10 Å for the diameter of the adsorbed hydrocarbon molecules,

$$x_m = \frac{140 \cdot 10^4 \cdot 4}{6.024 \cdot 10^{23} \cdot 100 \cdot 10^{-16}}$$

using Harrison's value of 140 m²/gm. for the surface area.

Assuming a molecular weight of 300 for the oil molecules,

$$x = \frac{300 \cdot 140 \cdot 4}{6.024 \cdot 10^3} = 0.089 \text{ gms.}$$

This means that with maximum adsorption, i.e. when the liquid concentration is 1.00, only 8.9gms. of oil could be adsorbed in a monomolecular layer on the surface of 100gms. alumina. If the diameter of the molecules were 12 Å, then the adsorbent capacity would be only 6.2gms/100gms. adsorbent.

This is in very good agreement with the isotherm results.

In Expt. 14., the oil adsorbed was of the order of 2-6gms for a wide variation in solution concentration, but the total oil in the pores did not rise above 8gms. In Expt. 15, the amount of oil in the pores rose to 12gms., at an oil/adsorbent ratio of 60/100, though the amount adsorbed (A_0) remained at 7.36gms,

The findings of Giles (3), mentioned in chapter 1, that hydrocarbons are only adsorbed on 0.1% of the surface would mean that almost all this oil "adsorbed" would be in the pores, but not adsorbed. In the light of the fact that even saturates have been adsorbed by alumina, and in some cases were still present in the adsorbed phase, after several iso-octane stages, it seems doubtful that so little of the surface is used for adsorption. Physical adsorption of a similar order to the conditions assumed above must be taking place.

6.8. SULPHUR CONTENTS.

The sulphur content of each fraction obtained from the chromatographic separation of the large scale batch slurry stages is given in Section D of Appendix 3.

The batch slurry process does not seem to give much separation between sulphur compounds and the rest of the oil. Run I, in which the alumina was suspected of being less active than in the others due to a higher water content, gave no significant separation at all, except in the last two stages. Runs II and III had low sulphur contents in the first stages, rising to a maximum in the benzene stages, and decreasing in the methanol stage.

A mass balance on the sulphur contents of the batch slurry stages compared with the original oil KX II₁₀₋₁₂ gave 99.5%, 93.5% and 97.2% recovery for Runs I-III respectively.

The chromatographic fractions gave good separation of sulphur compounds. After the formolite negative fractions, came fractions with as low as 2-3% sulphur, with the maximum sulphur content in the first benzene fraction. The fact that the last fraction, the methanol eluate, contained so little sulphur suggests that it consists mainly of oxygen and nitrogen compounds. The separation may be even better if one could distinguish between the mercaptans and thiophenes in the oil.

An example will give an idea of the amount of sulphur compounds in the oil. Run II, stage 1, has 4.65% sulphur. An average molecular weight of 300 may be assumed, and it can also be assumed that the 13.68% saturates contain no sulphur.

∴ 83.32% of the oil contains all the sulphur.

-The sulphur compounds so far isolated from the oil have each contained only one sulphur atom per molecule.

∴ if all molecules contained sulphur, the wt.% sulphur would be $\frac{32}{300} \cdot 100 = 10.7\%$.

- The % sulphur of the polar compounds = $\frac{4.65}{83.32} \cdot 100 = 5.57\%$.

∴ Proportion of sulphur-containing molecules = $\frac{5.57}{10.7} = 52.2\%$.

52.2% of 83.32 = 43.5%.

∴ The oil consists of:

13.68% saturates,
39.82% aromatics,
43.5 % sulphur compounds.

As these sulphur compounds will have similar adsorption affinities to many of the hydrocarbons, it is apparent that to separate out the sulphur compounds by chromatography will be very difficult, and it is possible that only chemical methods will ensure a complete removal. It is reasonable to suppose, however, that concentrations of sulphur compounds will also show concentrations of polynuclear aromatic material. An investigation is being carried out at present in this department by Higgins (66) into methods of removing sulphur from lubricating oils.

6.9. SPECIFIC GRAVITIES.

These were measured at 20°C, with two measurements at 25°C, to give an estimation of the temperature coefficient. This is important for the use of specific refractivity correlations to identify molecular types, when the refractive index and density are required at the same temperature. The details are given in Appendix 3, section E.

A steady increase in specific gravity is apparent for each run, with the methanol stage equal to or slightly less than the last benzene stage.

CHAPTER 7. CONCLUSIONS AND

SUGGESTIONS FOR FUTURE WORK

A. CONCLUSIONS

1). A preliminary investigation has been carried out into several variables affecting column efficiency. Using a simple test mixture, the variables studied were:

- wet and dry packing;
- adsorbent activation temperature;
- column diameter;
- particle size;
- direction of flow;
- adsorbate/adsorbent ratio.

It was found that the amount of adsorbent and the column diameter were the only variables to have a marked effect on the separation of the test mixture. Using a fixed amount of adsorbent, the maximum separation could be obtained by using several columns of narrow diameter in series.

2). A comparison has been made between the separating powers of alumina and silica for the test mixture. Silica was found to have a much larger adsorption capacity in this case.

3). Little separation was apparent among the aromatic components of the test mixture, as their refractive indices were very close. The mixture was chosen for analysis by G.L.C., and good separation of peaks was obtained by this means. If refractive index is to be used in future, a different test mixture should be chosen.

4). A number of batch slurry separations of KX_6 have been carried out on alumina (Expts. 1-5). These gave good separation of the high refractive index range, and about 10% of the oil was recovered by benzene and found to have a high refractive index (above 1.60).

5). One of the initial suppositions, that all the saturates would be desorbed from the alumina by one or two iso-octane stages, was found to be invalid. In the large scale runs, small amounts of non-aromatic compounds were detected in the 7th and 8th stages.

6). A Kuwait oil blend known as $KX_{II_{10-12}}$ has been separated by large scale batch slurrying three runs. The separation in Run I was not as good as Runs II-III, and it was concluded that the alumina had been left exposed to the atmosphere and had a higher water content than in the other two runs.

7). The batch slurry technique has been shown to be effective in preparing samples of polynuclear aromatic material of low contamination, similar to samples produced by column chromatographic separation, but in a much shorter time.

8). Small scale chromatography was found to be useful for analysis of the fractions obtained by batch slurrying. It could also be used to give a finer separation of a sample produced by batch slurrying.

9). Several methods were used to estimate the percentage of saturates in the oils. A correlation curve was drawn to estimate the % saturates in each fraction of KX_6 obtained from the 40' column. When this curve was applied to batch slurry stages, it was modified to give the same result as for the column-separated fractions. It seems that a correlation curve can be used to estimate the percentage of saturates in an oil by refractive index only, but the shape of this curve will depend on the history of the fraction to be estimated.

10). Using an estimated value for the percentage of saturates in the two oils under investigation, the concentrations of polar and saturate compounds in the solid and liquid phases were determined for the batch slurry stages. Isotherms were drawn for each type of compound, and using lines, the slopes of which had been derived theoretically, the theoretical number of stages for complete desorption were estimated.

11). On recontacting the filtrate from stage 1 of a batch slurry with fresh adsorbent, concentrations were obtained which did not lie on the isotherm. These could be explained by either the non-attainment of equilibrium, or by hysteresis in the adsorption-desorption curve.

12). It was concluded that the optimum number of stages for a given solvent depended on the separation required, and could be determined before the experiment.

13) The seemingly anomalous results of the isotherm experiments were explained by consideration of the maximum adsorption which could take place. Assuming a monomolecular layer, the results agreed very well with a calculation based on an average molecular diameter.

14). The determination of sulphur contents has been shown to be useful in giving a guide as to the separation being obtained in batch slurries and chromatography,

B. SUGGESTIONS FOR FUTURE WORK.

- 1). Investigation of several variables in batch slurring.
 - a). oil/solvent/adsorbent ratios,
 - b). stirrer speed,
 - c). use of different solvents,
 - d). time to reach equilibrium.

2). The use of apparatus for batch slurring such that the adsorbent need not be transferred to a filter after each stage. Gravity drainage through a porous disc in the bottom of the flask should be sufficient. The use of vacuum may upset the results by sucking oil off the surface or from the pores. (In Expt. 54., the solution in the slurring vessel had a refractive index of 1.4172, while the filtered solution was 1.4183.)

3). The development of a correlation curve, or family of curves, to estimate the percentage of saturates in the oil by means of refractive index. The obtaining of uncontaminated saturate and polar samples will be an essential prelude to this.

4). The use of a test mixture to obtain more information about the equilibrium relationships being established in a batch slurry process, and to investigate the possibility of hysteresis curves.

5). The use of a G.L.C. instrument to analyse all test mixture samples. This will open new possibilities to carry out efficiency studies in a batch slurry process and in column separations.

6). Investigation into the difference in effect that the usual variables have on separation efficiency in frontal and elution analysis.

7). By the use of test mixtures, it should be possible to estimate the number of theoretical stages in an adsorption column by the use of a batch slurry process.

A P P E N D I C E S

+++++

A P P E N D I X 1.

MATERIALS USED IN THIS WORK.

ADSORBENTS.

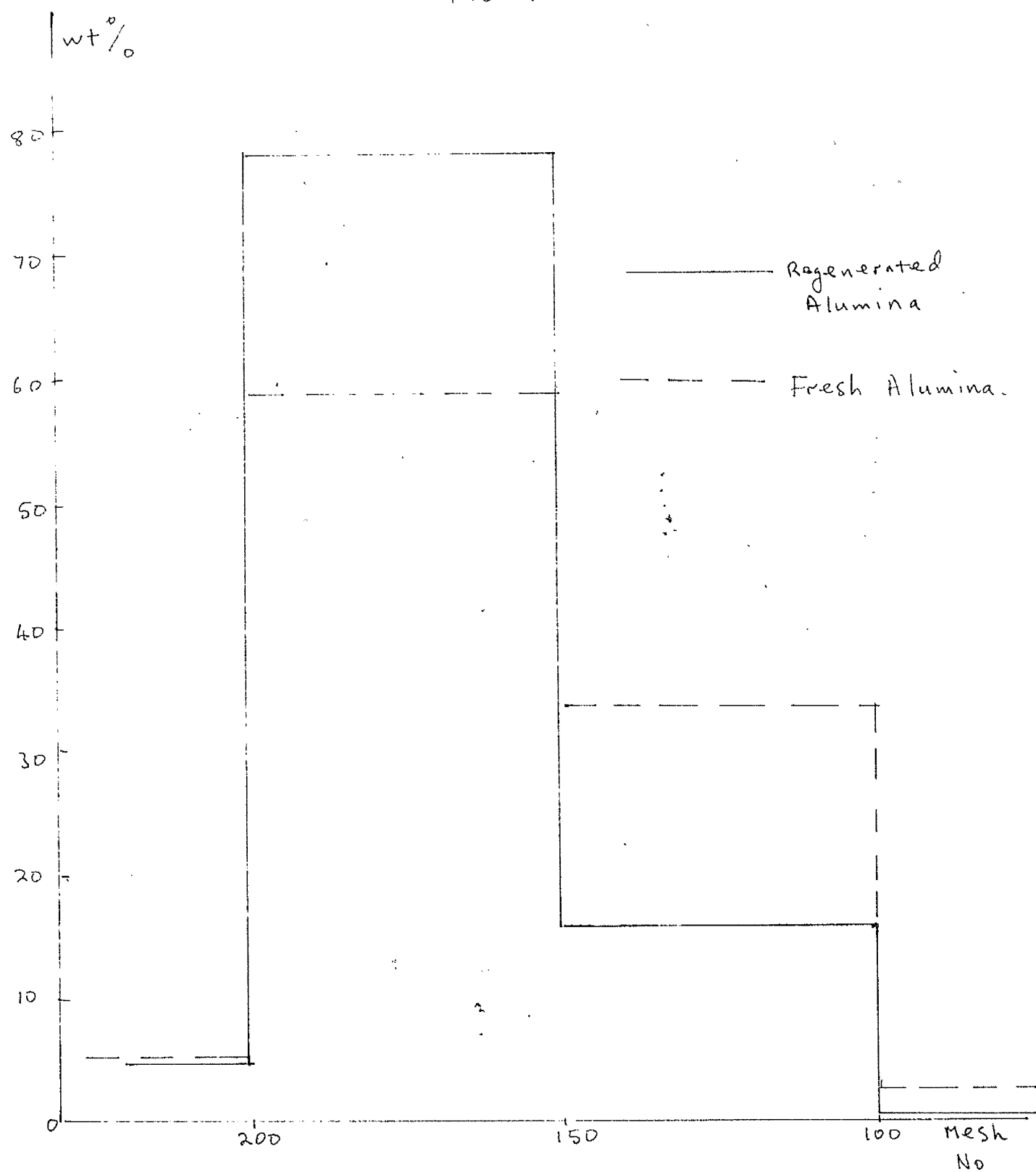
The main adsorbent used was alumina (100-200 B.S.I. mesh) from Peter Spence Ltd. The silica used in Expt.20 was 28-200 B.S.I. mesh, from Crosfields Ltd.

The main physical properties have been determined by Harrison (61) and are as follows:

	<u>Alumina</u> (100-200)	<u>Silica</u> (28-200)
Surface area, m^2/gm ,	140	635
Pore vol. ml/gm.	0.24	0.39
Pore diam. Å	69.8	23.3
% wt.loss at 20° C.	3.2	2.77
Bulk density.	1.035	0.738
Skeletal density.	2.88	1.98

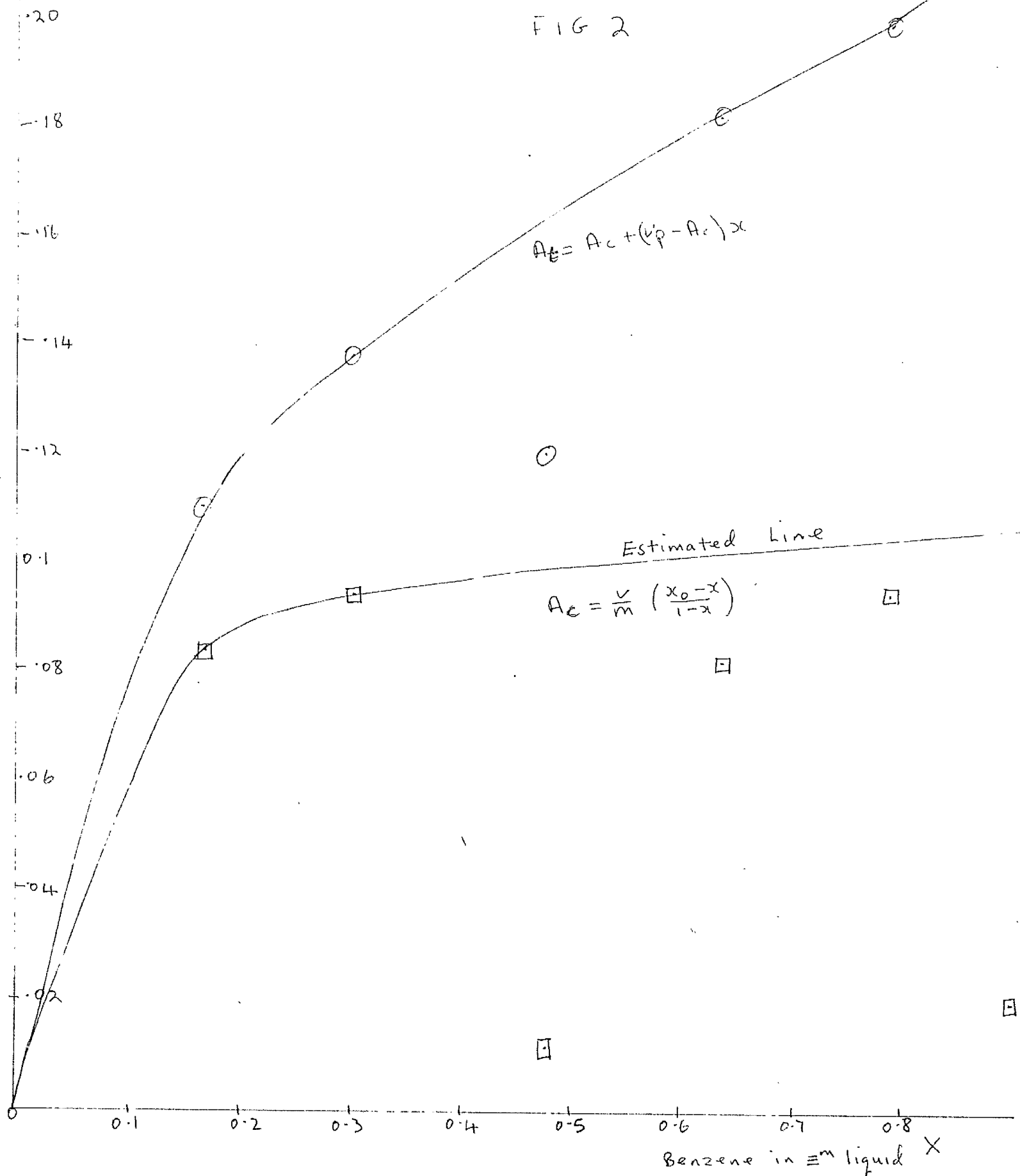
Both adsorbents had been used and regenerated previously, and a sieve analysis was carried out on the alumina. Fig. 1. shows the results compared with those of Ibbotson (14) for fresh alumina. There is a large proportion of fine particles, and this may possibly have been caused by several regenerations. This is a point which must be examined before further work is carried out using this alumina. The pore volume of the alumina was determined using the same method as Harrison, and a consistent value of 0.285 gm/ml. was obtained. This value has been used for calculations in this thesis. The activity of the alumina was checked by isotherm determinations using the benzene/iso-octane system.

FIG 1



A_E Benzene
 A_C adsorbed.

FIG 2



A weighed amount of alumina was placed in a stoppered bottle, and a measured volume of benzene-iso-octane mixture of known concentration was added. The bottle was rotated for two hours and the liquid concentration was determined by refractive index measurement. A refractive index v. volume % benzene graph was used with the following points:

concentration benzene vol. %	N_D^{25}
0	1.3890
10	1.3990
20	1.4082
30	1.4189
40	1.4299
50	1.4400
60	1.4511
70	1.4622
80	1.4736
90	1.4852
100	1.4970

The experimental isotherm data are given below.

No.	N_D^{25} initial	x_0	N_D^{25} final	x	wt. alumina	$x_0 - x$	A_c	A_t
1.	1.4850	0.900	1.4848	0.899	10.0012	0.001	0.0198	0.2178
2.	1.4735	0.800	1.4725	0.790	10.0025	0.01	0.0951	0.2096
3.	1.4568	0.650	1.4550	0.635	10.0018	0.015	0.0822	0.1824
4.	1.4378	0.478	1.4375	0.475	10.0030	0.003	0.0114	0.1204
5.	1.4225	0.335	1.4210	0.302	10.0022	0.033	0.0944	0.1384
6.	1.4086	0.202	1.4053	0.167	10.0007	0.035	0.0844	0.1104

A_c and A_t were calculated according to formulae derived earlier.

$$A_c = \frac{V}{m} \left(\frac{x_0 - x}{1 - x} \right)$$

$$A_t = A_c + (V_p - A_c)x$$

and the results are shown in Fig. 2.

Erratum.

The Ac curve shown in Fig.2. represents the preferential adsorption, i.e. the difference between the amount of benzene adsorbed and the amount of iso-octane adsorbed. This means that it will in fact return to zero at $x = 1$, when no iso-octane is present. The curve shown as "Ac estimated" actually represents the total benzene adsorbed, and at $x = 1$ will be equal to the amount necessary to form a unimolecular layer on the adsorbent.

The wide scatter in the Ac results may be explained by the small concentration differences at high initial benzene concentrations. Point No.4. must have been an experimental error, but point No.6 should not be so low. The Ac curve should tend to a maximum which will be the amount of benzene which can be adsorbed as a monomolecular layer. It should not return to zero at $x = 1.0$, as suggested by Cannon (67) and Ibbotson (14). Some of the scatter in these points is reduced by plotting At. v. x and this should tend to the pore volume at $x = 1$.

After one further regeneration, the alumina was tested again and the results were:

$$\begin{aligned}x &= 0.475 \\Ac &= 0.0722 \\At &= 0.1567\end{aligned}$$

These are a bit below their respective curves, showing a loss in activity after another regeneration.

SOLVENTS.

	<u>N_D</u> ²⁵	<u>B.Pt.</u>
Iso-octane (2,2,4, trimethyl pentane)	1.3890	100.1 °C
Benzene "Analar" redistilled	1.4970	80.1
Methanol redistilled	1.3280	64.0
N.hexane	1.3722	68.7
(actual hexane used contained isomers)	1.3772	
Xylene o. and p. mixture, trace of meta.	1.4925	140.0
Methyl cyclohexane	1.4242	100.9
Toluene "Analar"	1.4938	110.6

OILS.

The KX series of oils were prepared at Birmingham University in a Stedman packed column by vacuum distillation. The oil used was a Kuwait furfural extract, and this was fractionated into 2½° C cuts which were later blended to 5° C cuts and given a KX nomenclature.

The boiling ranges were:

KX ₁	350-355°C	KX ₅	370-375°C
KX ₂	355-360	KX ₆	375-380
KX ₃	360-365	KX ₇	380-385
KX ₄	365-370	KX ₈	385-390

The residue was distilled at a later date, as it was suspected that this residue may contain the most biologically active fractions.

The following boiling ranges are approximate, being estimated from the still temperatures:

KX ₉	390-400°C
KX ₁₀	400-410
KX ₁₁	410-420
KX ₁₂	420-430

KX₆, which was used in the first part of this work, had a refractive index of 1.5460, and a sulphur content of 5.28%.

KX II₁₀₋₁₂. This oil was a blend from a Kuwait furfural extract which had been vacuum distilled into litre cuts at the B.P. Research Centre, Sunbury-on-Thames. The boiling range of this blend was estimated to be: 400-422°C. Its refractive index was 1.5532 and its sulphur content 5.64%.

APPENDIX 2.

THE DENSITY OF SMALL SAMPLES OF OIL.

The density and the refractive index of oil samples are very important as correlations can be used, based on these two properties, and are found in most petroleum reference books. For samples of known molecular type, the number of carbon atoms per molecule can be estimated, and for samples of known molecular weight, the type of molecules present can be discovered. The batch slurry samples were not homogeneous enough for these correlations to be applicable, but it was foreseen that most of the fractions produced by chromatography of the batch slurry samples would contain mainly one molecular type, e.g. n.paraffins, dinuclear aromatics, etc...

As most of the samples produced would be of small volume (some less than 0.5ml.), the conventional methods could not be used.

A. Falling Drop Method.

A method which has been applied to lubricating oil samples is the falling drop method, and as this was the only reference in the literature directly concerned with oil samples, it was tried first. This method has also been used in this department by Walmsley (64) for the determination of the percentage of heavy water in products from a distillation column. The rate of fall of a droplet in a slightly less dense immiscible fluid is governed by Stokes' Law.

$$v = \frac{gD^2(d_1 - d_2)}{18}$$

$d_1 - d_2$ = density difference gm/ml.

D = diameter of droplet cm .

v = falling velocity cm/sec.

= solution viscosity
poises.

$g = 981$ cm/sec.

Hoiberg (65) has determined the densities of oil samples by timing the rate of fall of small droplets in ethanol solution. The concentration of ethanol was varied according to the appropriate density of the oil sample, to give a constant density difference. For oil densities of 0.953 to 0.993, a 45% by volume ethanol solution in water was used, of density 0.923gm/ml.

A tube of approx. 1.3cm. diameter and 50cm. length, was set vertically by plumbline in a constant temperature room. The temperature varied over a period of time from 19.5 to 20°C, but over a few hours, did not vary more than $\pm 0.05^\circ\text{C}$. Two marks were made on the tube 30cms. apart, leaving sufficient space (10cms.) at the top for the drop to achieve constant velocity.

To produce a droplet of constant known size, an "Agla" micrometer syringe was used. This consisted of a precision bore all-glass syringe with a No.76 stainless steel needle. The movement of the plunger was regulated by means of a micrometer, and the whole was set in a stainless steel mounting.

A ethanol solution of approx. 45% by volume was prepared and its refractive index, viscosity and density were determined by the Institute of Petroleum Standard methods (59).

By rotating the micrometer screw, an oil drop was formed under the surface of the solution, and by a sudden upwards movement of the syringe, the drop was released and its velocity measured. One revolution of the screw gave a volume of 0.01ml. $\pm 0.0001\text{ml}$.

The oil used in these tests was Run I, stage I, and its density was checked by Specific Gravity and Westphal Balance methods and found to be 0.9790.

The results obtained by the falling drop method were:

0.9557
0.9564
0.9809
0.9577
0.9549

With one exception the results were of the same order, but consistently too low. The ethanol solution was checked by refractive index, but no change was detected which would indicate dissolution of the oil. It was noticed that a small amount of oil remained on the tip of the needle, and this may have accounted for the low results. Hoilberg overcame this difficulty by applying a small amount of soap to the needle, but this did not make any difference to the results in these experiments.

A further series of tests gave the following results:

0.9441
0.9440
0.9436
0.9439
0.9452

These were remarkably consistent, but much too low, and it seemed obvious that there was one major factor which had been overlooked, but which was not apparent.

B. Direct Weighing.

Small volumes of the liquid were then ejected from the syringe into weighing boats, and the density calculated by direct weighing. This method gave better results:

0.995
0.990
0.974
0.972
0.968
0.981

Although these were not consistent enough to be of value.

C. Water Equivalent.

A small sample of oil (circa 0.5gm.) was added to a 25mls. specific gravity bottle, and weighed. The bottle was then filled up with distilled water and weighed again, giving the water equivalent of the oil, which was defined as the specific gravity. Although the oil was slightly less dense than the water, by careful addition of the water, the oil remained at the bottom of the bottle, possibly due to surface tension effects. The results obtained : 0.9359
0.9578,

were not accurate enough, and it was thought that a larger oil sample must be used for this to be an accurate method.

Four micro pipettes were then made, and calibrated with distilled water. It was not possible to calibrate them with mercury, due to the small size of the tubes (approx. 0.4ml.). The correction to be added to the weight of water in the tube to enable the specific gravity to be quoted "in vacuo" was calculated to be 0.0000522, and the correction was ignored for this work.

The results obtained by this method were:

0.9733
0.9822
0.9554
1.0046
1.0117
0.9751
0.9701

These were still not accurate enough, and so as time was valuable at this point, the investigations were concluded.

Conclusions

It is thought that the reason for the failure to obtain consistent and accurate results were:

- 1). Small amounts of oil remaining on the syringe needle;
- 2). Local fluctuations in temperature in the constant temperature room. The close presence or the breath of the experimenter, or there being more than one person in the room, will lead to errors, especially by the setting up of eddy currents in the ethanol solution;
- 3). Possible inaccuracies in the balance. The balance was zeroed frequently, and the weights and pans dusted, but it is possible that one or more of the weights were not as indicated.

It is recommended that the falling drop method be pursued in the future, with the tube set in a thermostatically controlled water bath to avoid temperature fluctuations. Warmesley observed that small changes in temperature of the order of $\pm 0.001^{\circ}\text{C}$ were enough to give variance in the results.

APPENDIX 3.

RESULTS OF BATCH SLURRY AND COLUMN SEPARATIONS

A. Batch Slurry Results.

(wt.%) (gms.)	wt.%	N _D ²⁵	(wt.%) (gms.)	wt.%	N _D ²⁵	(wt.%) (gms.)	wt.%	N _D ²⁵
<u>Expt.1.</u>			<u>Expt.2.</u>			<u>Expt.3.</u>		
6.5	33.9	1.5298	6.7	36.4	1.5265	8.1	42.4	1.5262
6.6	34.4	1.5425	5.3	28.8	1.5348	4.4	23.0	1.5360
0.9	4.7	1.5565	1.4	7.61	1.5455	2.0	10.5	1.5484
0.5	2.6	1.5630	0.6	3.76	1.5564	0.9	4.72	1.5618
			2.1	11.42	1.5941	1.7	8.9	1.6049
14.5	75.6		0.8	4.35	1.6008	0.7	3.67	1.6097
			0.3	1.63	1.6024	0.3	1.57	1.6096
			0.7	3.81	---	0.5	2.62	---
			17.9	97.4		18.6	97.38	
<u>Expt.4.</u>			<u>Expt.5.</u>			<u>Expt.13.</u> (fresh adsorbent)		
21.9	36.5	1.5244	26.9	48.8	1.5258	26.9	48.8	1.5238
16.4	27.4	1.5322	13.2	22.0	1.5350	9.7		1.5038
6.6	11.0	1.5440	6.6	11.0	1.5474			
4.1	6.83	1.5540	3.4	5.6	1.5612			
5.7	9.5	1.5916	5.0	8.33	1.5980			
2.7	4.5	1.5974	2.5	4.16	1.5995			
1.2	2.0	1.5935	1.3	2.16	1.5994			
2.1	3.5	---	2.4	4.0	---			
60.7	101.23		61.3	102.05				
<u>Run I.</u>			<u>Run II.</u>			<u>Run III.</u>		
2945	44.2	1.5512	2450	37.7	1.5350	2260	33.9	1.5358
1730	26.0	1.5560	1480	22.2	1.5486	1432	21.5	1.5510
800	12.0	1.5624	500	7.5	1.5666	976	14.65	1.5532
330	4.95	1.5714	323	4.85	1.5790	441	6.62	1.5681
161	2.4	1.5780	200	3.0	1.5866	239	3.59	1.5780
381	5.7	1.5824	747	11.2	1.6196	203	3.04	1.5882
135	2.02	1.5746	225	3.4	1.6224	568	8.5	1.6198
417	6.25	1.5336	330	4.96	1.5900	205	3.08	1.6222
6899	103.52		6255	93.81		258	3.86	1.5884
						6582	98.74	

2nd MeOH Wash: 97gms. 1.5710

(wt
(gms.) wt.% N_D²⁵

(wt
(gms.) wt.% N_D²⁵

Expt. 54. (using 300gms. Al₂O₃, 80gms. oil, 300mls. solvent.)

iso-oct. stages.

41.8	52.3	1.5320
14.5	18.1	1.5416
8.7	10.9	1.5524
3.9	4.9	1.5684
2.2	2.75	1.5836
1.2	1.5	1.5860
1.1	1.4	1.6100

benzene stages.

2.3	2.9	1.6253
1.3	1.6	1.6240
0.6	0.75	1.6175
0.1	0.13	--
0.1	(0.1)	--
1.2	1.5	--

(MeOH)

B. Column Separations.

KX₄ on 40' column (Higgins)

267.4	22.9	1.4640
328.2	28.1	1.5120
87.2	7.45	1.5540
90.9	7.78	1.5625
245.9	21.0	1.6117
89.3	7.67	1.6362
41.3	3.54	--

1110.2 98.44

KX₆ on 40' column (Higgins)

158.2	13.3	1.4612
334.6	28.8	1.5109
113.6	9.52	1.5440
149.1	12.51	1.5548
262.4	22.0	1.6133
156.6	13.10	1.6305
51.8	4.35	--

1226.3 103.58

KX₁₁ on 40' column (Higgins)

66.9	5.74	1.4708
228.9	19.63	1.5091
111.1	9.54	1.5350
157.5	13.50	1.5473
267.2	22.90	1.5997
229.2	19.70	1.6374
60.3	5.18	--

1121.1 96.20

KX₆ author. Expt. 11.

2.3	10.55	1.4490
6.1	28	1.4480
3.5	15	1.5306
1.0	5.4	1.5508
0.9	4.13	1.5472
3.7	17.0	1.5999
3.6	16.5	1.6236
0.3	1.38	1.6150

21.4 98.96

(wt
gms.) wt. % N_D²⁵

Frn. 4/1 5/1 Expt. 6.

4.48	27.5	---
2.0	12.2	1.5018
1.5	9.2	1.5170
1.0	6.2	1.5339
5.7	35.0	1.5700
0.8	4.9	1.6184

15.48 95.0

Frn. 4/3,4 5/3,4 Expt. 8.

0.6	8.3	1.4602
0.4	5.5	1.4672
0.4	5.5	1.5052
4.5	61.6	1.5476
1.4	19.1	1.6082

7.3 100.0

Frn. 4/5,6,7 5/5,6,7 Expt. 12.

6.5	35.4	1.5382
3.1	16.8	1.5728
0.7	3.8	1.6048
8.1	44.0	1.6178
0.7	3.8	1.6415

19.1 103.8

(wt
gms.) wt. % N_D²⁵

Frn. 4/2 5/2 Expt. 7.

1.1	11.25	1.4576
0.6	6.07	1.4642
0.7	7.08	1.4960
0.9	9.10	1.4950
6.1	61.70	1.5571
0.4	4.04	1.6268

9.8 99.24

Frn. 4/1,2,3,4 5/1,2,3,4 Expt. 9.

1.7	9.6	1.4496
1.6	9.05	1.4595
2.9	16.4	1.4948
1.4	7.9	1.5110
1.3	7.35	1.5325
6.7	37.8	1.5682
2.1	11.9	1.6082

17.7 99.95

KX II 10-12 Expt. 30.

1.2	6.0	1.4592
1.1	5.5	1.4696
1.2	6.0	1.5028
1.3	6.5	1.5132
1.2	6.0	1.5442
7.6	38.0	1.5830
3.7	18.4	1.6398

17.3 86.4

Run I.

(wt
(gms.) wt.% N_D²⁵

Stage 1.

3.4	10.9	1.4615
1.6	5.1	1.4900
4.0	12.8	1.5198
3.6	11.5	1.5374
1.8	5.8	1.5578
8.3	27.0	1.5865
3.4	10.9	1.6364
0.8	2.6	1.6309
2.0	6.4	1.5455
<hr/>		
28.9	92.9	

Stage 4.

1.2	5.7	1.4638
4.3	20.4	1.5152
3.9	18.4	1.5446
1.6	7.6	1.5918
1.5	7.1	1.6054
7.1	33.8	1.6272
1.7	8.1	1.6456
<hr/>		
21.3	100.8	

Stage 7.

2.9	13.4	1.5620
4.8	22.0	1.5854
1.6	7.4	1.6030
1.3	6.0	1.5838
5.2	24.0	1.5629
2.1	9.7	1.5620
3.9	18.0	1.5626
<hr/>		
21.8	100.5	

(wt
(gms.) wt.% N_D²⁵

Stage 2.

0.9	4.43	1.4594
1.3	6.4	1.4676
3.8	18.7	1.5082
3.6	17.2	1.5409
2.5	12.3	1.5718
6.1	29.6	1.6160
1.1	5.42	1.6452
0.1	0.49	1.6354
<hr/>		
19.3	95.0	

Stage 5.

1.4	6.8	1.4658
4.8	23.4	1.5269
3.9	19.0	1.5750
1.8	8.8	1.6182
6.8	33.2	1.6358
0.7	3.4	1.6579
1.5	7.3	1.5332
<hr/>		
20.9	101.9	

Stage 8.

0.9	4.44	1.5622
0.9	4.44	1.5636
3.2	15.80	1.5644
1.8	8.88	1.5714
9.2	45.40	1.5158
<hr/>		
15.0	78.96	

(wt
(gms.) wt.% N_D²⁵

Stage 3.

1.8	8.96	1.4688
3.6	17.9	1.5050
2.7	13.4	1.5436
2.2	10.9	1.5898
6.6	32.8	1.6288
0.7	3.48	1.6542
<hr/>		
17.6	87.6	

Stage 6.

0.3	2.2	1.4628
1.2	8.13	1.5300
1.8	12.2	1.5862
1.0	6.76	1.6226
6.6	44.6	1.6125
3.9	26.4	1.5432
<hr/>		
14.8	100.0	

Run II.

(wt
(gms.) wt.% N_D²⁵

Stage 1.

1.2	5.66	1.4552
1.7	8.02	1.4619
5.8	27.40	1.5068
2.2	10.40	1.5334
1.8	8.50	1.5526
6.0	28.30	1.6021
1.2	5.66	1.6310

19.9 93.94

Stage 4.

1.0	5.05	1.4650
2.8	14.2	1.5228
2.4	12.1	1.5544
1.9	9.6	1.5809
8.4	42.4	1.6288
0.7	3.54	1.6482

17.2 86.89

Stage 7.

0.2	1.02	1.4740
1.8	9.2	1.5540
2.5	12.8	1.6086
2.5	12.8	1.6218
7.9	40.2	1.6276
2.3	11.7	1.6574
1.5	7.65	1.5834

18.7 95.37

(wt
(gms.) wt.% N_D²⁵

Stage 2.

1.8	6.6	1.4604
5.4	19.6	1.5022
5.5	19.9	1.5340
4.6	16.7	1.5476
2.5	9.1	1.5642
7.0	25.2	1.6086
0.8	2.9	1.6455

27.6 100.0

Stage 5.

0.8	4.04	1.4632
4.5	22.8	1.5280
2.7	13.6	1.5626
2.7	13.6	1.6084
6.5	32.8	1.6364
0.9	4.54	1.6536

18.1 91.38

Stage 8.

0.1	0.45	1.4876
2.5	11.1	1.6042
1.7	7.55	1.6449
1.1	4.0	1.6530
14.0	17.8	1.6150
1.6	7.1	1.5922
8.4	37.4	1.5596

19.4 86.2

(wt
(gms.) wt.% N_D²⁵

Stage 3.

1.7	8.14	1.4625
4.8	23.0	1.5180
2.4	11.5	1.5529
2.8	13.4	1.5660
5.7	27.2	1.6170
0.5	2.4	1.6194

47.9 85.64

Stage 6.

0.2	0.99	1.4662
4.3	21.2	1.5762
2.4	11.8	1.6166
1.7	8.4	1.6306
7.8	38.4	1.6392
2.0	9.85	1.6324

18.4 90.64

Run III.

(wt
(gms.)) wt. % N_D²⁵

Stage 6.

0.8	4.0	1.4618
5.0	25.0	1.5364
2.6	13.0	1.5724
1.7	8.5	1.6011
7.3	36.5	1.6308
1.2	6.0	1.6459
<hr/>		
18.6	93.0	

(wt
(gms.)) wt. % N_D²⁵

Stage 7.

0.2	1.0	1.4689
3.2	16.1	1.5574
4.2	21.1	1.6112
10.9	54.8	1.6225
1.3	6.53	1.6448
<hr/>		
19.8	98.53	

(wt
(gms.)) wt. % N_D²⁵

2nd MeOH Wash.

3.1	17.4	1.6038
4.1	23.0	1.5728
0.5	2.81	1.6004
0.1	0.56	1.6050
2.9	16.3	1.5956
7.1	39.9	1.5374
<hr/>		
17.8	99.97	

Stage 8.

0.1	0.49	1.4688
2.2	11.8	1.5642
2.7	13.2	1.6158
2.4	11.8	1.6318
9.1	44.5	1.6308
0.7	3.43	1.6494
1.7	8.35	1.5942
<hr/>		
18.9	92.57	

Stage 9.

0.5	2.33	1.4765
0.2	0.93	1.4798
1.1	5.12	1.5691
7.2	33.5	1.6224
1.8	8.38	1.5988
5.5	25.6	1.5698
3.3	15.4	1.5648
<hr/>		
19.6	91.2	

Expt. 53. Column sep. of KX₆ using same amounts of materials as in expts. 4 and 5.

iso-octane eluted fractions.

0.9	1.6	1.4568
19.6	34.8	1.4908
14.0	23.3	1.5338
7.1	12.6	1.5488
3.0	5.34	1.5674
1.4	2.5	1.6112
0.8	1.42	1.6184
0.7	1.24	1.5846
0.5	0.89	1.6575
0.3	0.53	1.6246
0.2	0.35	1.6311

0.3	0.53	1.6310
0.2	0.35	1.6326
0.2	0.35	1.6249
0.1	0.18	1.6280
0.1	0.18	1.6248
0.1	0.18	1.6176
0.1	0.18	1.6280
0.1	0.18	1.6274
0.1	0.18	1.6222
<0.1		1.6262
0.1	0.18	1.5956
0.1	0.18	1.6232
<0.1		1.6101

benzene eluted fractions.

2.2	3.9	1.6500
0.2	0.35	1.6460
<0.1		solid
<0.1		solid
0.1	0.18	1.5958
0.3	0.53	1.5796
2.2	3.9	--- (MeOH)

C. Concentrations For Isotherms.

Expt. 4/5.

wt.reco- vered.	N _D ²⁵	wt.Sats. by expt.	wt.Sats. in soln.	wt.Sats. in solid	wt.polars in soln.	wt.polars in solid.
48.8	1.5250	13.4	16.7	13.3	32.1	57.9
29.6	1.5345	5.13	6.42	6.88	23.18	34.72
13.2	1.5455	1.85 estimated	2.32	4.50	10.88	23.83
7.5	1.5578	1.00 "	1.25	3.25	6.25	17.59
10.7	1.5148	2.63 estimated	3.29		10.7	10.18
5.2	1.5984				5.2	5.0
2.5	1.5965				2.5	2.5
4.5					4.5	
		24.01	29.98		95.31	
	S'	S''	P'	P''		
	0.0222	0.0350	0.0967	0.0674		
	0.0115	0.0107	0.0580	0.0386		
	0.0075	0.00387	0.0398	0.0181		
	0.00542	0.00209	0.0293	0.0104		
			0.0170	0.0175		
			0.00834	0.0086		
			0.00417	0.00415		
			0.007	0.00705		

Run I.

wt.reco- vered.	N _D ²⁵	wt.Sats. by expt.	wt.Sats. in soln.	wt.Sats. in solid	wt.polars in soln.	wt.polars in solid.
2940		321	415	385	3342	2525
1730		188	243	142	1855	1487
800		72	92	50	1147	708
329		19	25	25	843	304
159		11	14	9	698	145
379		8	9		328	370
135					202	135
417						417
		619	797			5991

Run I. (continued)

<u>S'</u>	<u>S''</u>	<u>P'</u>	<u>P''</u>
0.01155	0.0155	0.1	0.0946
0.00426	0.0073	0.0557	0.0447
0.0015	0.00276	0.0344	0.0212
0.00075	0.000752	0.0253	0.00914
0.00027	0.000420	0.021	0.00436
		0.00985	0.0011

Run II.

<u>wt. recovered</u>	<u>wt.Sats. by expt.</u>	<u>Wt.Sats. in soln.</u>	<u>wt.Sats. in solid</u>	<u>wt.polars in solid</u>	<u>wt.polars in soln.</u>
2260	335	522	278	4129	1738
1432	98	153	125	2850	1279
976	41	63.9	61.1	1937.9	912.1
441	16	24.9	36.6	1521.8	416.1
239	8	12.5	23.7	1294.3	226.5
203	6	12.5	11.2	1106.8	190.5
568	1	9.4	1.8	548.2	558.6
205		1.6		346.4	203.4
258				88.4	258.0

513

<u>S'</u>	<u>S''</u>	<u>P'</u>	<u>P''</u>
0.00832	0.02	0.124	0.0666
0.00374	0.0046	0.0853	0.0384
0.00183	0.00192	0.058	0.0274
0.00108	0.000748	0.0455	0.0125
0.00071	0.000376	0.0388	0.00680
0.00034	0.000376	0.0331	0.00563
0.00054	0.000277	0.0164	0.00165
	0.0000477	0.0104	0.000607
			0.00077

D. Sulphur Contents.

given as %wt. Sulphur of each fraction, in the same order as the weight recovery and refractive index of the stripped oil samples in Sect. A & B.

<u>KX₁</u> (Higgins)	<u>KX₆</u> (Higgins)	<u>KX₁₁</u> (Higgins)	<u>KX II</u> <u>Expt. 10-12</u>			
<u>orig.oil:</u>	<u>orig.oil:</u>	<u>orig.oil:</u>	<u>orig.oil:</u>	<u>Run:</u>	<u>I</u>	<u>II</u>
<u>4.53</u>	<u>5.02</u>	<u>5.20</u>	<u>5.64</u>	<u>St.No.</u>	<u>wt.%</u>	<u>wt.%</u>
0.0	0.0	0.00	0.0	1	5.39	4.65
2.80	2.46	1.89	0.0	2	5.59	5.17
5.70	6.27	5.37	1.66	3	5.95	6.20
5.16	6.82	5.92	2.31	4	6.00	6.58
8.45	8.26	7.27	6.38	5	6.15	4.35
7.77	8.77	8.25	6.90	6	5.89	8.28
4.00	3.51	2.92	8.25	7	3.06	8.70
				8	1.89	5.54
						3.75
				2 nd	MeOH Wash.	3.16%

Run I.

<u>Stage 1.</u>	<u>Stage 2.</u>	<u>Stage 3.</u>	<u>Stage 4.</u>	<u>Stage 5.</u>	<u>Stage 6.</u>	<u>Stage 7.</u>	<u>Stage 8.</u>
0.0	0.0	0.0	0.0	0.0	0.0	5.17	4.40
0.0	0.0	3.45	4.25	4.15	3.95	5.14	3.59
2.82	2.20	5.52	5.78	5.92	6.50	4.75	2.00
6.90	6.12	7.26	7.38	8.36	8.76	3.74	0.85
5.53	5.25	8.46	5.76	7.94	5.37	1.82	1.85
6.60	7.90	---	8.04	6.40	1.09	0.35	
9.40	8.15		7.36	1.17		0.66	
8.48	---						
5.10							

Run II.

0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	2.15	3.20	3.85	4.20	5.40	5.60	7.40
2.11	4.26	4.18	5.45	5.72	7.90	8.90	8.70
5.31	4.92	5.91	6.41	11.10	8.64	8.37	7.82
---	5.84	8.50	8.40	12.70	8.06	7.58	3.26
7.28	7.07	5.72	7.23	12.45	6.40	7.60	5.60
6.80	7.74					2.83	1.93

Run III.

<u>Stage 6.</u>	<u>Stage 7.</u>	<u>Stage 8.</u>	<u>Stage 9.</u>
0.0	0.0	0.0	0.0
4.42	5.90	5.96	0.0
6.222	7.82	7.75	6.40
7.36	7.40	8.10	5.61
7.83	5.86	7.50	1.37
7.39		6.15	1.13
		2.15	2.58

E. Densities. (Specific Gravity)

	<u>Run I.</u>		<u>Run II.</u>		<u>Run III.</u>
<u>Stage.</u>	<u>20°C</u>	<u>25°C</u>	<u>20°C</u>		<u>20°C</u>
1	0.9789	0.9777	0.9509		0.9548
2	0.9834	0.9814	0.9718		0.9777
3	0.9914		0.9997		0.9813
4	1.0035		1.0163		1.0030
5	1.0122		1.0261		1.0174
6	1.0214		1.0702		1.0317
7	1.0136		1.0774		1.0726
8	1.0134		1.0535		1.0770
9					1.0525

Separations on a 40' column, at 20°C. (Higgins, 57)

<u>KX₁</u>	<u>KX₆</u>	<u>KX₁₁</u>
0.8412	0.8409	0.8640
0.9224	0.9197	0.9210
0.9841	0.9723	0.9609
0.9999	0.9883	0.9791
1.0690	1.0629	1.0469
1.0998	1.0832	1.0917

F. Reblending of KX₆

Aromatic Blend.

<u>Fraction No.</u>	<u>N_D²⁵ rechecked</u>	<u>wt. gms.</u>
1.	1.4618	
2.	1.5111	5.7570
3.	1.5440	1.8953
4.	1.5548	2.5136
5.	1.6133	4.4125
6.	1.6300	2.6279

Refractive index of aromatic blend: 1.5618

Mixing of Aromatic Blend with Saturate Fraction.

<u>wt. aroms.</u>	<u>wt. sats.</u>	<u>wt% aroms.</u>	<u>N_D²⁵</u>
		100	1.5618
4.6232	0.5965	88.57	1.5492
4.6101	1.5603	74.7	1.5341
4.5026	2.5126	64.2	1.5229
4.4738	3.1659	58.5	1.5147
1.7434	2.1143	45.1	1.5022
1.7214	3.6476	32.1	1.4906
1.7144	4.8076	26.3	1.4847
		0	1.4618

The loss in weight due to the sample required for refractive index was accounted for each time, as saturates were added to the same aromatic blend.

Reblend to Make Parent Oil.

wt. aromatic blend = 12.4326 gms.

wt. saturates (frn.1) = 1.9600

wt. MeOh (frn.6) = 0.6116

N_D²⁵ = 1.5475

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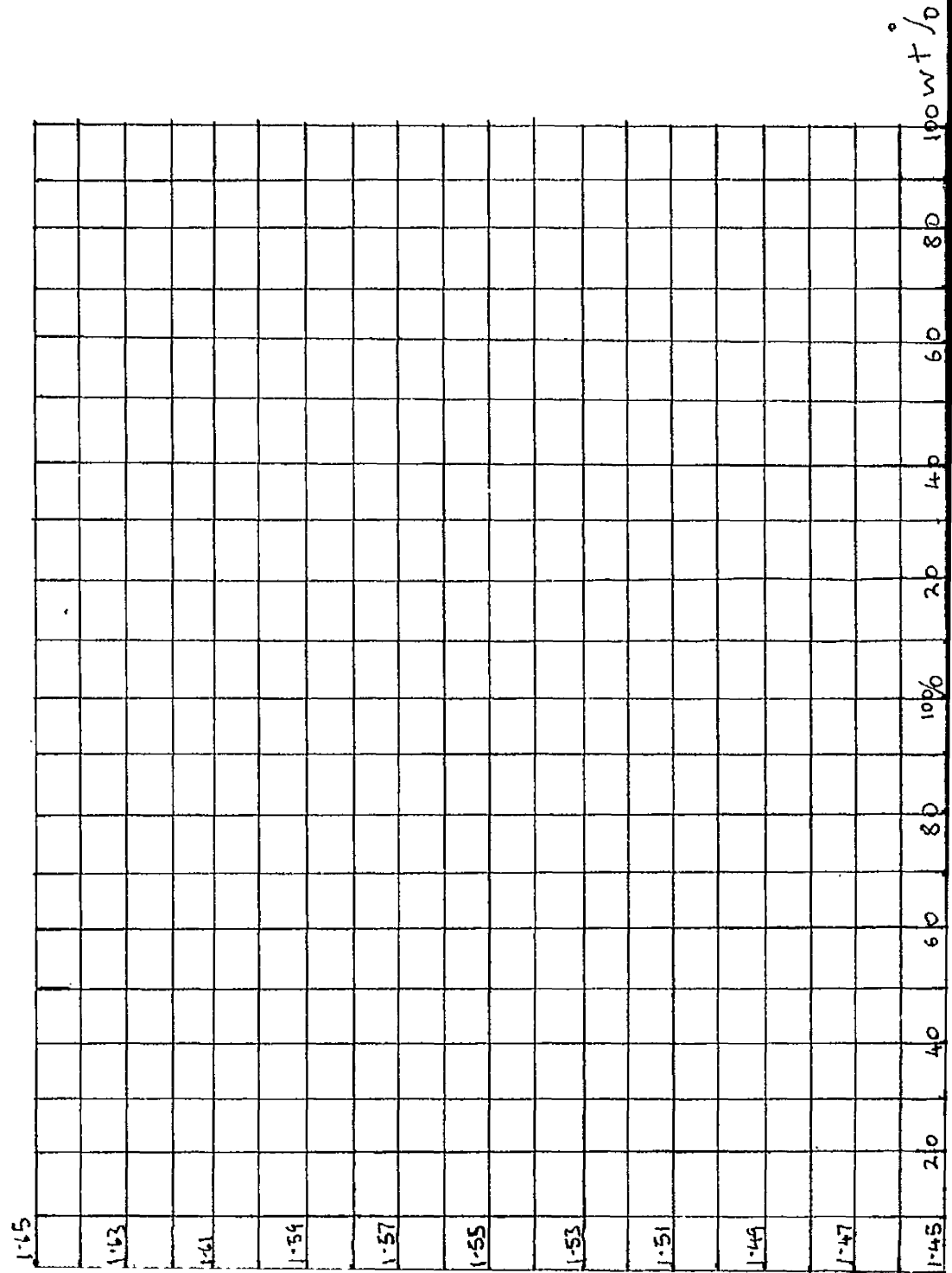
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Scale for use
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