STUDIES IN THE HIGHER

COAL TAR BASES.

by

ALAN MILLAM PRYDE

Thesis presented for the degree of Ph.D.

University of Edinburgh.

October, 1951.

Chemistry Department,
    Heriot-Watt College,
        EDINBURGH.

C O N T E N T S.

INTRODUCTION.

The work to be described in this thesis
takes the form of an investigation of the nitrogenous
bases which can be extracted by sulphuric acid from
the Naphthalene Oil and the Benzol Absorbing Oil
fractions of coal tar, after the tar oils have been
freed from phenols by extraction with caustic soda.

The chief objects of the investigation
were :-

1)   To obtain a weight / temperature of
distillation balance for both fractions of bases,
thus showing the relative abundances of the more
common fractions, and possibly indicating where any
previously unidentified bases were liable to occur.

2)   To make a closer study of the fractions
boiling between 180° and 235°, and over 265°C/760mm.Hg,
as these two fractions have not been exhaustively
studied in the past, and, where possible, to isolate
and identify pure bases.

The nitrogenous bases which can be extrac-
ted by sulphuric acid from coal tar or coal tar oils
consist mainly of pyridine, quinoline, isoquinoline,
and their homologues, together with small quantities
of pyrrole, aniline, toluidines, xylidines, acridine
and naphthylamines.

According to present industrial practice
the only/

the only bases which are extensively utilised are pyridine and its lower homologues, the commercially available products being :-

Pure Pyridine - This is obtained by a close fractionation of the lower tar bases and is used as an intermediate in the production of "sulpha" drugs (sulphapyridine), dyestuffs, vulcanisation accelerators and waterproofing compounds, and as a solvent and catalyst.

"90-140° or 90-160° Bases" - These are obtained by crude fractionation of the lower tar bases and are used as denaturants, solvents, levellers in leather dyeing, insecticides, and also in the production of pattern effects on cotton and rayon, and in lubricating oil refining.

"90-180° Bases" - These are obtained by crude fractionation of tar bases and are used as solvents, in anthracene purification, and as restrainers in metal pickling baths.

In addition to these main industrial products the following are produced in smaller quantities :-

Picolines - These have been produced in small quantities from time to time, but recently, owing to the great demand for nicotinic acid as an accessory dietary factor, an interest has been aroused in β-picoline, and considerable quantities have been produced for oxidation to nicotinic acid.

Lutidines/

Lutidines & Collidines - These have only been produced in semi-commercial and experimental quantities.

It is difficult to ascertain the sources of the above products owing to the differences in works practice throughout the country, especially with respect to the temperature ranges of the oil cuts taken, but it would appear that they are produced for the most part from the lower boiling tar oils, and according to present works practice the bases are seldom removed from the Naphthalene Oil and Benzol Absorbing Oil fractions.

The total United Kingdom production of "pyridine bases" amounted to 166,000 gallons in 1948 and to 167,000 gallons in 1949 (Min. of Fuel & Power), and there are indications that more could be used if it were available. If this is the case, it is possible that the Naphthalene Oil fraction might provide a useful auxiliary source.

Very little work has been carried out on the utilisation of the tar bases boiling above 180°C, such as are obtained from the Benzol Absorbing Oil fraction, although quinoline and isoquinoline have been isolated in semi-commercial and experimental quantities, and during the recent war the xylidines were separated for use as aviation fuel additives. It was considered, therefore, that some quantitative estimate/

estimate of the constitution of the Benzol Absorbing
oil base fraction would be of considerable value.

The Origin of Nitrogen in Coal.

It is generally agreed that the nitrogen
present in coals has come from plant or animal
proteins, or both, which were laid down in earlier
eras of the earth.   The plants which were concerned
with coal formation are now, with few exceptions,
extinct, but it is reasonable to assume that their
chemical composition did not vary substantially from
those of our present day.

The plant proteins, which contain 15 - 19%
nitrogen, are easily attacked by enzymes and con-
verted into amino acids which, being water soluble,
would possibly be partially washed away or might be
attacked by micro-organisms and converted into
ammonia, elementary nitrogen and simpler nitrogen-
free organic compounds.   However, part of these
amino-acids could react with aldehyde or hydroxyl
groups of carbohydrates, thus :-

$$R-\underset{H}{C}-O + H_2N-CH_2-\underset{OH}{C}=O \longrightarrow R-\overset{H}{C}=N-CH_2-\underset{OH}{C}=O + H_2O \qquad (i)$$

$$R-CH_2-OH + H-\overset{H}{N}-CH_2-\underset{OH}{C}=O \longrightarrow \underset{O=C-CH_2}{\overset{R-CH_2}{>}NH} \quad \underset{O=C-CH_2}{\overset{R-CH_2}{|}>NH} + H_2O \qquad (ii)$$
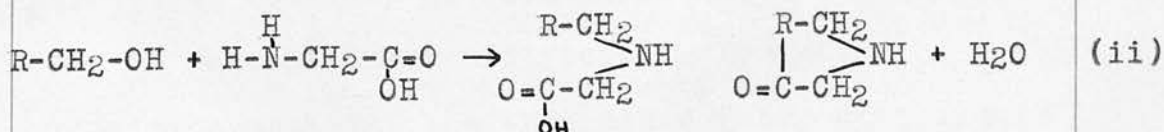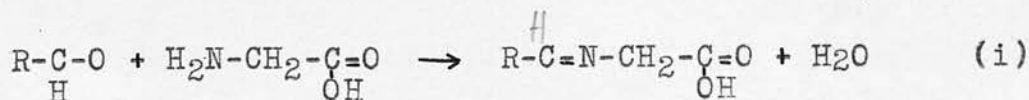
Such reactions can lead to the formation of
complex condensation products (i) with high molecular
weights/

weights and colloidal properties (so-called melanoids),
or to heterocyclic compounds (ii).   Maillard (110)
showed that the heating of these melanoids resulted
in their decomposition with the production of hetero-
cyclic nitrogen compounds.   It is possible by this
mechanism to account for the fact that in an accumu-
lation of plant organisms and their transformation
products (e.g. a peat bed), the nitrogen content does
not decrease with progress in 'turfication', but
sometimes increases.

This does not, however, account for the fact
that the nitrogen present in coal is 10 - 30 times
greater than that in present day wood.   Some
substance high in nitrogen must have been present in
the material from which the coal was formed, and this
substance was obviously protein.   Terres (111) was
able to prepare artificial brown coals, containing
4.16% nitrogen,by pressure-heating peat sludge made
by fermentation of peat moss which contained 1.73%
nitrogen.   The increase in nitrogen content was due
to the protein substances added by micro-organisms.
Terres believed that brown coal is the final product
resulting from the coalification of starting material
consisting entirely of plant substance.   However,
when he fermented and artificially coalified
proteinous material, he obtained a heavy distillable
oil resembling crude petroleum which contained about
5% nitrogen, and a non-volatile bitumen containing
over/

over 6% nitrogen.   Terres claimed that the sludge
formed from protein putrefaction is the essential
material from which coal bitumens are formed, and
that for the formation of bituminous coals it is
neccessary to have protein material present along
with lignin, cellulose, waxes and resins, which come
from plant substance.   This view explains the fact
that bituminous coals generally contain more nitrogen
than brown coals.

Animal remains, doubtless mixed with large
amounts of plant remains, can also furnish proteins
which may be responsible for the major part of nitrogen
in coals.   This has been put forward as an explanation
of the large variations of nitrogen content within the
same seam of coal.   It has been shown that the protein
of animal organisms vanishes completely under normal
decomposition owing to the absence of carbohydrates,
but provided that there were sufficient plant remains,
the nitrogen could be retained in some such manner as
that postulated by Maillard.

Possible additional sources of nitrogen in
coal are - plant alkaloids, chlorophyll and other
porphorins, chitin etc.

It can be seen that as yet there is no
clearly defined view as to the origin of nitrogen in
coal.   It is sufficient, however, for the major part
of this work to state that the nitrogen is combined
in/

in coal as complex organic material which on carboni-
sation yields more simple organic bases which distil
over in the tar.   It is possible that by further
elucidation of the composition of the base mixture
derived from coal tar a more clear idea may be
obtained as to the constitution of this complex
organic material.

LITERATURE SURVEY ON THE BASES DERIVED FROM
COAL TAR AND OTHER RELATED SOURCES.

Dry distillation of nitrogen-containing materials, such as the vegetable alkaloids and animal oils, led to the first recognition of volatile organic basic substances. The "odorin" which was separated from bone oil by Unverdorben in 1827 (1) was not then characterised much beyond its obvious property of possessing a foul odour. In 1846 Anderson (2), in studying naphtha from coal tar, isolated a base by sulphuric acid extraction, neutralising with ammonia and subsequent distillation, which he considered similar to "odorin". A characterisation of the properties of this base caused Anderson to believe that it was a pure compound. He called it picoline and it is very likely that this material was a crude grade of α-picoline. This was the first reported instance of a systematic study of the pyridine molecule.

Concurrently with his discovery of phenol in coal tar, Runge (3), in 1834, also found three bases, one of which he called "leukol". In 1842 Gerhardt (4) obtained "chinolein" by caustic potash distillation of quinine and strychnine. Hofmann (5) showed that "leukol" and "chinolein" were identical. The name quinoline or chinoline was gradually adopted for this compound thereafter, although leucoline still continued to appear in the earlier literature.

It was/

It was not until 1885 that a reasonably
pure grade of pyridine was isolated from coal tar by
Williams (6).   He obtained the compound by fractional
distillation of the crude bases, removal of aniline
with nitric acid, and fractional crystallisation of
the platinum salts of the resultant bases.   The
fraction boiling at 116°C was considered to be
pyridine.   This boiling point approximates the best
value given today.

Since this time a considerable amount of
work has been carried out on the nitrogenous bases
derived from coal tar, and much light has been cast
upon the constitution of the crude base mixture.
It has been shown that the main constituents of this
mixture are tertiary bases of the pyridine, quinoline,
and isoquinoline types, and it is with the isolation
and identification of these types of compounds that
this investigation is mainly concerned.

The following is a list of the homologues
of pyridine, quinoline and isoquinoline which have
been reported as coal tar constituents :-

Pyridine, 2-, 3-, and 4-methylpyridines,
4-ethylpyridine;   2:3, 2:4-, 2:5-, 2;6-, 3:4- and
3:5-dimethylpyridines;   2-methyl-4-ethylpyridine;
2-methyl-6-ethylpyridine;   2:3:4-, 2:3:5-, 2:3:6-
2:4:5- and 2:4:6-trimethylpyridines;   2:3:4:5-
tetramethylpyridine.

Quinoline;   2-, 3-, 4-, 5-, 6-, 7- and
8-methylquinolines/

8-methylquinoline; 2:8-dimethylquinoline; 5:8-dimethylquinoline (Some doubt has been cast on the authenticity of this claim. See Appendix I.); 2:4:6-trimethylquinoline.

Isoquinoline; 1-, 3-, 6-, and 5 or 7-methylisoquinoline; 1:3-dimethylisoquinoline.

The following primary aromatic amines have also been isolated from coal tar :- Aniline; o-, m-, and p-toluidines; 2:3, 2:4-, 2:5- and 3:5-xylidines; α- and β-naphthylamines.

In addition, certain homologues of indole, carbazole and acridine have been isolated, and also three benzcarbazoles, phenanthridine and phenanthridone, but none of these types of compounds are liable to be met with in this investigation.

The physical constants of all the homologues of pyridine, quinoline and isoquinoline mentioned above are listed in Appendix I, together the melting
with
points of three derivatives of each, and references to their isolations from coal tar and other natural sources. It was not neccessary to list the primary bases in this way, as no attempt has been made to isolate primary bases during this investigation.

Shale Oil Bases.

The general character of the nitrogenous

bases/

bases extracted by sulphuric acid from shale oil is
very similar to that of the bases obtained from
coal tar.

In the pyridine series, all the homologues
which have been isolated from coal tar have also been
isolated from shale oil. In addition, Eguchi, in a
very thorough examination of the nitrogenous bases
derived from Fushun bituminous shale (9), has isolated
2:3:4:6-tetramethylpyridine, 2:6-dimethyl-4-ethyl-
pyridine, 2:3-dimethyl-6-ethylpyridine and pyrindane.
Benzie & Milne, in a study of the Scottish shale oil
bases (24), also isolated 2:3:4:6-tetramethylpyridine
and, in addition, isolated a solid base which has now
been proved to be 2:3:5:6-tetramethylpyridine.

In the higher boiling ranges the presence
of quinolines and isoquinolines has been shown, but
very little work has been carried out on these ranges.

In an investigation of the bases obtained
from the "Sapropel" of the Karisino Lake region
(U.S.S.R.), which may be considered as an intermediate
between shale and petroleum, Lanin & Pozhil'tsova (107)
isolated the following compounds :- 3-Methylpyridine,
2-butylpyridine, 2:4- and 2:6-dimethylpyridines,
2:4-diethylpyridine, 2-methyl-6-ethylpyridine,
2-methyl-4-ethylpyridine, 4-methyl-3-ethylpyridine,
2:?-dimethyl-5-ethylpyridine and 2:4:6-trimethyl-
pyridine.

Petroleum/

Petroleum Oil Bases.

The literature dealing with the nitrogenous
bases derived from petroleum is quite extensive, and
it would therefore be outside the scope of this
summary to attempt a complete survey.

Crude undistilled petroleum contains complex
nitrogen compounds which can not be extracted with
acids, but can be concentrated by solvent extraction.
These compounds have not been studied to any great
extent, but according to Pott et al. (108) they may
either consist of pyrrole, indole or carbazole types
of compounds, or may be more complex and contain
combined sulphur and oxygen.

During normal refining slight cracking
takes place and these complex materials are partially
broken down to form nitrogenous bases, the extent to
which this break-down occurs being increased with
rise in temperature of distillation.

Bailey and his co-workers have conducted
an extensive series of researches on the bases
obtained from Californian Petroleum distillates
during the period 1928-1942 (published in the
Journal of the American Chemical Society).   These
researches are of interest because of the novel
methods of separation used, as well as for the
isolation and identification of the following alkyl-
quinolines ;-/

alkylquinolines :-   2:3-, 2:4- and 2:8-Dimethyl-
quinolines;   2:3:8- and 2:4:6-trimethylquinolines;
2:3:4:8-tetramethylquinoline;   2-methyl-8-ethyl-
quinoline;   2:3-dimethyl-8-ethylquinoline;   2:4-
dimethyl-8-ethylquinoline;   2:3:4-trimethyl-8-ethyl-
quinoline;   2:3-dimethyl-4:8-diethylquinoline;
2:3-dimethyl-8-n-propylquinoline; 2:4-dimethyl-8-n-
propylquinoline;   2:3:8-trimethyl-4-ethylquinoline;
2:3:4-trimethyl-8-n-propylquinoline;   2:3:4-trimethyl-
8-isopropylquinoline;   2:3-dimethyl-4-ethyl-8-n-
propylquinoline; 2:4-dimethyl-8-sec-butylquinoline;
2:3- and 2:4-dimethylbenzo(h)quinoline.

A few non-aromatic bases have also been
isolated from straight-run petroleum, but the
elucidation of the structure of these bases has
presented considerable difficulty.

Bailey and Bratton examined the bases
derived from cracked petroleum and isolated the
following compounds :- 2-, and 4-methylpyridines;
2:4-, 2:5-, 2:6- and 3:5-dimethylpyridines; 2:4:6-
trimethylpyridine; quinoline; 2-methylquinoline.
These, they believed, accounted for the total amount
of bases present.

Hackmann and Wibaut (25), on the other
hand, examined the bases from a Californian Oil,
cracked at 500°C. and 30 atmospheres pressure, and
presumably of different origin to that used by
Bailey/

Bailey, and obtained, in addition to all the compounds found by Bailey, the following :- 3-methylpyridine; the remainder of the possible dimethylpyridines; 2:3:6-trimethylpyridine; 4-ethylpyridine; 2:4-, 2:5- and 2:6-methylethylpyridines; 2-ethyl-4-methyl-pyridine; 3-, 4-, 7- and 8-methylquinolines; 2:8-dimethylquinoline; isoquinoline; 1- and 3-methylisoquinolines. Several unidentified bases were also obtained.

The very noticeable differences in results obtained in these two investigations may, however, be explained by differences in the origin of the starting material and in cracking conditions.

From a study of the results obtained from these investigations on the bases derived from coal tar, shale oil and cracked and straight-run petroleum, certain noteable points stand out.

1) The general character of the bases obtained in all cases is similar (i.e. they consist mainly of pyridine, quinoline and isoquinoline homologues), with the exception that aromatic primary amines appear to be more abundant in coal tar than in either shale oil or petroleum.

2) The individual components increase in complexity in the order - coal tar, cracked petroleum, shale oil, sapropel tar, straight-run petroleum./

petroleum.   This fact indicates that the composition
of the basic material derived from these natural
sources depends more on the temperature attained in
the processing of the starting material than on any
other single factor, including even the origin of the
starting material.

3)   In the quinoline ranges the poly-
substituted quinolines which have been isolated from
any of these sources have all been substituted in the
2-position, with the exception of a claim made by
Ganguli and Guha to the isolation of 5:8-dimethyl-
quinoline about which there is some doubt (See note
in Appendix I.).   This phenomenon could be explained
either by some peculiarity in the constitution of the
complex organic material from which the bases are
derived, or by the possibility that the poly-
substituted quinolines which are substituted in the
2-position are more stable to heat.

Figure 1.

WILTON PATENT PIPE STILL.
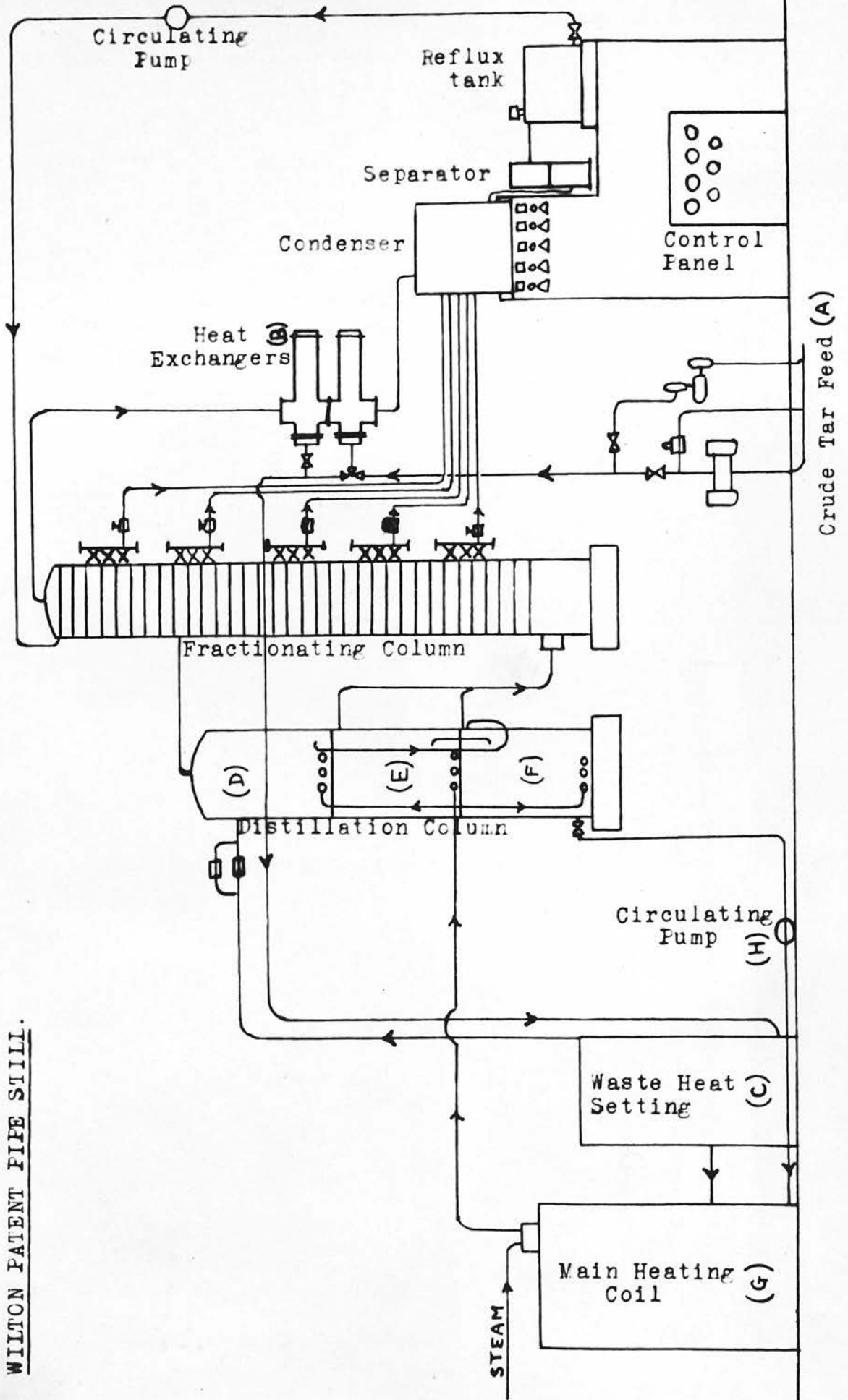
ORIGIN OF THE STARTING MATERIAL.

The coal tar oil fractions, from which the bases were extracted for this investigation, were obtained by fractional distillation of vertical retort tar derived mainly from Granton Gas Works. The distillation was carried out in a continuous pipe still of the Wilton type which is described below, and the conditions were those of normal working.

Wilton Patent Pipe Still

At the Falkirk Works of Messrs. Scottish Tar Distillers Ltd. there are two sizes of Wilton Plants, one of which has a throughput of 150 tons/day and the other 75 tons/day. These do not, however, differ in fundamentals, and the sketch shown in Figure 1 applies to both sizes, as does the following description :-

The crude tar, which is usually pre-heated to some extent, is pumped in at the point A in Fig. 1 and thence through the vapour-tar heat exchangers,(B) in which the temperature is raised to 50-60°C, to the waste-heat setting (C), which utilises waste from the main furnace to raise the temperature of the tar to 110°C.

The hot tar then travels to the primary flash chamber (D) where the water and light oil are flashed off, their vapours being led in at about the middle/

middle of the fractionating column.

The remaining liquid runs over into the mixing vessel (F) and is thence pumped to the coils of the main furnace (G) which may be heated with either liquid or solid fuel. The tar attains a temperature of 270-370°C in this furnace and then travels to the secondary flash chamber (E) where the volatile oils are flashed off leaving a pitch whose nature depends on the temperature to which the tar has been raised.

The hot pitch runs over into the mixing vessel where it mixes with the tar from D (in the ratio of about 1:7), and some volatile oils from the tar are vaporised. These vapours, along with the vapours from the secondary flash chamber, are led in at the foot of the fractionating column. The pitch/tar mixture is circulated through the main furnace again.

The pitch level in the mixing chamber is indicated by a mechanical float and pointer mechanism, and is controlled by a relay system to the control panel and thence to a motorised valve on the pitch off-take on the secondary flash chamber.

All three chambers in the distilling column are kept hot by means of steam which is super-heated in the furnace and which passes through "pokers" in the chambers.

The input of tar is dependant on the size of the plant. In the 150 ton/day plant the pitch/ tar mixture/

pitch/tar mixture passes through the circulating
pump (H) at about 9,200 gals/hour.

The fractionating column has 35 crocodile
bubble-cap and down-pipe trays.   The over-heads from
the column are passed through the vapour/tar heat
exchangers, condensed, the water separated and part
of the separated crude benzol returned to the column
as reflux, in sufficient quantity to keep the column-
head temperature at about 84°C.

The fractions are drawn off continuously
from the five sidestreams on the side of the column,
condensed and run to storage.   Each side-stream can
be drawn from three adjacent sections of the column
as desired.   The boiling range of any cut may be
varied by collecting from a different section, or by
varying the take-off rate at the cock.

Naphthalene Oil

The Naphthalene Oil from which the bases
were derived for this investigation was obtained in
a yield of 20 gallons/ton of the crude tar of 5%
water content.   On analysis it showed the following
characteristics ;-

Specific Gravity of the oil 0.960

Phenols present............ 5.0%

Bases present.............. 2.0%

Water present.............. trace

Distillation Test/

Distillation Test :-

3%	@	190°C;	10%	@	200°C;
30%	@	210°C;	43%	@	220°C;
65%	@	230°C;	78%	@	240°C;
83%	@	250°C;	87%	@	260°C;
91%	@	270°C;	94%	@	280°C;
95%	@	290°C.			

Benzol Absorbing Oil

The Benzol Absorbing Oil from which the bases were derived for this investigation was obtained in a yield of 18 gals/ton of the crude tar of 5% water content. On analysis it showed the following characteristics :-

Specific Gravity of the oil 0.990

Phenols present............ trace

Bases present............. 2.4%

Water present............. trace

Distillation Test :-

6%	@	230°C;	10%	@	240°C;
20%	@	250°C;	32%	@	260°C;
49%	@	270°C;	66%	@	280°C;
78%	@	290°C;	90%	@	300°C;
95%	@	304°C;.			

Both fractions of tar oils were separately freed from phenols by extraction with 10% caustic soda in a packed tower. The bases were then extracted from each of the phenol-free oils by stirring/

stirring the oils with 30% sulphuric acid in a lead-lined conical washer.   The mixture was then run down into settling pans where a considerable amount of dirt and sludge separated.   The aqueous "pyridine acid" was separated from the oil and pumped to a lead-lined beaker where the bases were liberated by means of soda ash.   The free bases were then separated and dried over solid caustic soda.

Naphthalene Oil Bases.

Quantity of oil washed for bases   3000galls

Strength of sulphuric acid used   30%

Quantity of sulphuric acid used   100galls

Yield of crude bases...........   1.8% on oil.

Specific Gravity of crude bases   1.024 (5% water)

Distillation test on dry bases:-

Drop	@	136°C;	4%	@	140°C;
15%	@	160°C;	23%	@	170°C;
35%	@	180°C;	45%	@	190°C;
53%	@	200°C;	58%	@	210°C;
63%	@	220°C;	66%	@	230°C;
70%	@	240°C;	80%	@	250°C;
87%	@	260°C;	90%	@	270°C.

Benzol Absorbing Oil Bases.

Quantity of oil washed for bases   5,500galls

Strength of sulphuric used......   30%

Quantity of sulphuric acid used   150galls

Yield of crude bases...........   2.0% on oil

Specific Gravity of crude bases   1.078 (5% water)

Distillation test/

Distillation test on dry bases :-

Drop	@	140°C;	0.5%	@	160°C;
1%	@	180°C;	1.5%	@	190°C;
4%	@	200°C;	9%	@	210°C;
15%	@	220°C;	21%	@	230°C;
32%	@	240°C;	50%	@	250°C;
70%	@	260°C;	80%	@	270°C;
84%	@	280°C;	87%	@	300°C.

SEPARATION METHODS.

a) Fractional Distillation.

In the study of complex organic liquid mixtures fractional distillation has for many years proved of great importance. Until recent years, however, the methods used have been crude, and efficient laboratory-scale fractionation as known today has been developed mainly within the past two decades. Tribute for this advance is due in the main to the petroleum industry.

A number of excellent reviews of the literature dealing with distillation have been published from time to time, of which those of Ward (112) and Fay (113) are particularly useful. The bibliography of Stage and Schultze (114) covers the years 1920-1944, while that of Rose and Rose (115) covers the years 1941-1945 and includes abstracts of all papers on distillation. Developments during the years 1946-1948 have also been reviewed by Rose (116). The extensive literature on the design and testing of fractionating columns has been summarised by Underwood (117).

It would be impracticable in a work of this nature to attempt to summarise the literature on laboratory type fractionating equipment. The following, however, is a brief description of the main types of columns which find a use in the laboratory/

laboratory.

Unpacked Columns :- Provided that the column is of small enough diameter, a fair degree of fractionation can be obtained from an unpacked column. High efficiencies, however, are obtained only when the boil-up rate and through-put are very low.

Bubble-cap Columns :- Although this type of column is of the greatest industrial importance, their use in the laboratory is limited by the difficulty of manufacture, high liquid hold-up and high pressure drop.   The "pear" type of column, which has been in use in laboratories for many years, is very similar to the bubble-cap column but is of little practical value.

Packed Columns :- This type of column has found the most wide-spread use in the laboratory and many different packing materials have been used.

Prior to 1936, the most common random packings used in laboratory stills were glass and metal beads (118), "Lessing Rings" of metal or ceramic materials (119), metal eyelets, carding teeth (120) and jack chain (121).   The fractionating efficiency of these packings was low, being only equivalent to about four theoretical plates per foot of height.

Notable increases in efficiency were obtained by Fenske (122) using single turn wire or glass helices, by Stedman (123) who used a regular packing in the form of conical wire gauzes, and by Leckey/

Leckey and Ewell (124) who produced a spiral packing made from wire gauze. These last two types of packing, however, possess the disadvantage of difficulty of fabrication.

A much greater advance in the efficiency of laboratory type fractionating columns was made by Dixon (125) who used a random packing of gauze rings. This packing consisted of small open- ended cylinders of wire gauze, and the column was operated in such a manner that a thin film of liquid was maintained over the entire surface of the cylinders. This film was produced by flooding the packing before commencing distillation. The packing showed a high fractionating efficiency, a performance of 84 theoretical plates per foot of height having been obtained by Dixon with some columns. It had also a low hold-up per theoretical plate, a low pressure drop and was easily fabricated.

It was shown by Dixon that the efficiency of gauze ring packed columns was dependant on the following factors :-

    1. Degree of wetting of the packing.

    2. Boil-up rate during flooding. It was found that the best results were obtained by flooding at the same boil-up rate as that required during the fractionation itself.

    3. Vapour velocity. It was shown that, provided a correct flooding treatment had been given, the efficiency/

the efficiency of the packing was approximately
proportional to the reciprocal of the vapour velocity
over the packing over a wide range.

4.   Ring dimensions.   It was shown that
the efficiency decreased with increasing ring size
and was roughly proportional to the area of gauze
surface in a given column.

5.   Gauze mesh.   It was shown that a
coarser mesh than 60x60 gave poor efficiency, and it
appeared that this was due to the inability to
support a film.

6.   Column height and diameter.   It was
shown that the performance of a column was propor-
tional to the height but diminished as the diameter
decreased.

7.   Gauze material.   Steel and phosphor-
bronze gave the same efficiency after flooding except
at low vapour velocities, where unsealing of apertures
appeared to be more pronounced in the case of the
"Staybrite".

8.   Inclination of the column from the
vertical.   It was shown that there was a gradual
reduction in efficiency with increasing degree of tilt.

Gauze ring packed columns have been employed
exclusively in the laboratory type fractionating
equipment used in this investigation, and their
efficiency has been shown to justify the claims made
by Dixon.

The main/

The main disadvantage with gauze ring
packed columns is that, when working at low pressures,
the pressure drop is too great.   For this type of
work the recently developed spinning band (126), and
rotary concentric tube (127) columns are very
suitable.

The technique of fractional distillation
has provided the main basis for this investigation.
A high degree of separation has been obtained by this
means alone, and in several cases where the pure bases
were solid at room temperature, they have been
isolated merely by cooling the appropriate finely cut
fractions.

b)   Separation by means of the Base Salts.

In the majority of the earlier researches
on the separation and isolation of the tar bases,
the separation and purification of the individual
bases were carried out by means of their salts after
an initial crude fractional distillation of the base
mixture.   Several salts have been used for this,
including the picrates and the calcium chloride,
mercuric chloride and zinc chloride double salts,
and the methods have consisted mainly of fractional
salting and fractional crystallisation.

In this investigation the method of
fractional treatment with picric acid has been
employed/

employed in cases where a narrow boiling range cut
has been obtained, which has been thought to consist
essentially of one component.   The method employed
consisted of treating a portion of the cut, in
solution in ethyl alcohol, with the theoretical amount
of picric acid, also dissolved in ethyl alcohol, in
three or more separate portions, allowing the salt
to crystallise out and filtering after each addition.
In this way three or more fractions of picrate were
obtained, and it was usually found that the impurities
were concentrated in either the first or the last
fraction.   The purer picrate fractions were then
recrystallised to constant melting point from a
suitable solvent and finally recrystallised from a
different solvent to ensure that a pure picrate of
constant melting point had been obtained.

This method was found to be quite suitable
for the isolation of the major constituents of most
of the cuts examined, without resort to the tedious
process of fractional crystallisation, and in the
examination of the more complex cuts it was considered
that the method of fractional acid extraction would
be more efficient than fractional crystallisation
of picrates.

c)   Fractional Acid Extraction.

Processes of extraction are in some respects
akin to those of distillation.   In the latter case,
two/

two components are separated by fractionation on a
volatility basis, each "plate" growing progressively
richer in the one or the other component.   Likewise
in multiple extraction of a solution of two substances
there will be a progressive separation determined by
relative solubilities.   Hunter and Nash (129) have
reviewed such methods of fractional extraction, but
these methods would be laborious and inefficient
when applied to the homologues of pyridine or
quinoline owing to the similarity of their distribu-
tion coefficients.

Jantzen (78), however, devised a method of
fractional acid extraction which he applied most
successfully to the separation of quinoline and iso-
quinoline homologues in a most thorough investigation
of certain higher coal tar base fractions.   The
theory of the process has been discussed in detail
by Jantzen, and it is sufficient here to describe
merely the mode of carrying out such a separation,
as follows ;-

A portion of the mixed bases is neutralised
with N. HCl to the end point as indicated by methyl
red.   Caustic soda solution (10N) is then added in
portions equivalent to one tenth of the acid required
for neutralisation, and the solution extracted with
equal volumes of solvent after each addition, to
give ten extracts, S.1 to S.10, containing equivalent
amounts/

amounts of bases.   The completion of the fractional acid extraction from this point is represented diagramatically in Fig.2.

Figure 2.
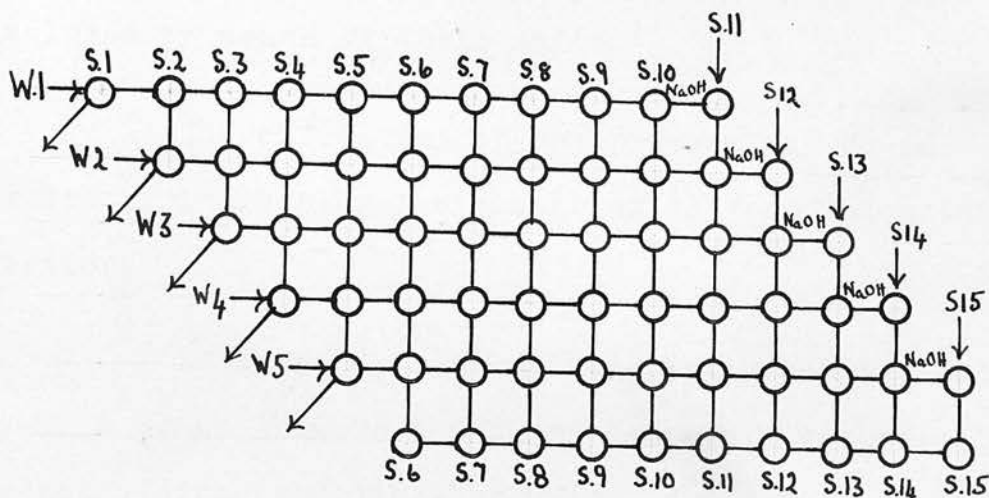
Five portions of normal acid, W.1 -W.5, each portion being equivalent to one tenth of the acid required for the neutralisation of the bases, are prepared.   W.1 is shaken with the solvent layer S.1, the acid layer drawn off and the solvent layer run to waste.   The acid layer W.1 is then succes- sively contacted with S.2 to S.10, thereby giving an acid layer containing a high proportion of the stronger bases, which is made alkaline with caustic soda and extracted with solvent to give S.11.

The whole process is then repeated a further four times with the remaining portions of acid, and finally the bases are obtained as ten solutions ranging in order of basicity.

The bases/

The bases are finally recovered from these
solutions, and refractive index measurements of each
fraction taken to give an indication of the degree
of separation attained.   Provided that sufficient
separation is attained the pure bases may then be
isolated by means of their salts.

The efficiency of the process may be im-
proved by increasing the number of solvent and acid
portions.

If many separations were being carried out
by this means, however, the process would become
rather tedious and time-consuming, and for this
reason Jantzen (loc. cit.) has designed various
columns etc. by means of which the process may be
carried out more easily.   For the purpose of this
investigation it has not been found neccessary to
construct any such column.

d)   Miscellaneous Methods.

Pyridine homologues which are substituted
in the α- or γ-positions react with cyclic aldehydes
to yield condensation products which are solid and
non-volatile in steam.   This reaction, which usually
leads to an equilibrium mixture, has been found to
proceed to completion when applied to a mixture of
3- and 4-picolines and 2:6-lutidine.   The 3-picoline
does not itself react, but acts as a catalyst to the
reaction/

reaction (46).. This has provided a means of
isolation of 3-picoline from the "β-picoline" fraction
of coal tar, but no means has been found for
regenerating the free bases from the condensation
products of the α- and γ- substituted pyridines.

Cyclic aldehydes also react with 2- and 4-
substituted quinolines to yield similar condensation
products. It was thought that this might provide
a convenient method for the identification and semi-
quantitative estimation of the 2- and 4- substituted
quinoline homologues, provided that the melting
points of the various pure condensation products
were known. This method, however, did not seem so
promising when it was found that the great bulk of
the poly-substituted quinolines present in the coal
tar base mixture was substituted in the 2- position,
and that even in close-cut fractions the occurrence
of more than one quinoline homologue substituted in
the 2- position was very probable.

Another possible application of this con-
densation reaction is as a means of getting rid of
the quinolines substituted in the 2- and 4-positions,
thereby either proving the absence of quinoline
homologues not substituted in these positions, or else
obtaining a mixture richer in the homologues not
substituted in these positions, from which the pure
components might then be isolated more easily.
Unfortunately, insufficient time was available to
explore/

explore this possibility.

Chromatographic absorption is another mode
of separation which might find application in the
study of the coal tar bases, although very little
work appears to have been carried out so far.

Kondo (130) describes the separation of
pyridine and 2-methylpyridine by adsorption on an
alumina column, and it is possible that this method
might be applicable to the higher homologues also.

Walker (131), using the more modern method
of paper chromatography in the study of the coal tar
bases, revealed the presence of pyridine, 2-methyl-
pyridine, 2:6-dimethylpyridine and 2:4:6-trimethyl-
pyridine.   The method of separation was by ascending
development, using a solvent prepared by shaking
together equal volumes of butyl alcohol and 2N.HCl,
discarding the aqueous layer and adding a small
amount of methyl red.

It is felt, however, that the method of
ion-exchange chromatography would afford a better
means of separation than either of the above
chromatographic techniques, as it would take advantage
of the differences in the relative strengths of the
bases.   This method would, in effect, be very
similar to Jantzen's method of fractional acid
extraction.   J. Idris Jones, in a study of the by-
products/

by-products from the hydrogenation of pyridine with
Raney Nickel (132), was able to separate N-n-amyl-
piperidine from a mixture containing similar bases
by means of a selective elution from an ion-exchange
column, the resin being of the sulphonated cross-
linked polystyrene type.   It is possible that a good
separation of pyridine or quinoline homologues might
be achieved by a method similar to this, but
insufficient time was available to explore this
possibility.

C R U D E   C O A L   T A R   (1000 parts by weight)

Other Oil Fractions ————————————————————— Other Tar Oil Fractions

Naphthalene Oil (85.7)   Benzol Absorbing Oil (79.5)

(Acid Extraction)   (Acid Extraction)

Naphthalene Oil Bases (1.54)   Benzol Absorbing Oil Bases (1.59)

DISTILLATION   IN   THE   20-GALLON   STILL

A-Fractions (5°C Cuts)   B-Fractions (5°C Cuts)

DISTILLATION   IN   THE   30-PLATE   COLUMN

C-Fractions (25 Shortrange Cuts)   D-Fractions (50 Shortrange Cuts)

C2-C7   C21(0.031)   D19(0.028) D20&21(0.033) D27&28(0.032) D44&45(0.027) D46(0.025) D47(0.026) D48-50(0.044)

DISTILLATION   IN   THE   100-PLATE   COLUMN

Quantitative estimates   1E Fractions   2E Fractions   3E Fractions   4E Fractions   5E Fractions   6E Fractions   7E Fractions   8E Fractions
of the lower pyridine
homologues

2:4:5-   2:3:4-   2:3:4:6-   3-Methyl-   2:7-Dimethyl-   2:3-, 2:4
Trimethyl-   Trimethyl-   Tetramethyl-   isoquinoline   quinoline   and 2:6-
pyridine   pyridine   pyridine   Dimethyl-
                                                                                                                     quinolines.

2:3:5:6-
Tetramethyl-
pyridine

PROCEDURE. (See Flow Sheet)

The procedure adopted for this investigation
may be summarised by the following five stages :-

1)   Fractionation of both the Naphthalene
Oil crude bases and the Benzol Absorbing Oil crude
bases, separately, in the 20 gallon still made available
by Messrs. Midland Tar Distillers Ltd.   The purpose
of these distillations was to free the volatile bases
from water and pitch, and to provide suitable charges
for the "30-plate" column by taking $5^{\circ}C$. cuts.

2)   Fractionation of each of these $5^{\circ}C$ cuts
in the "30-plate" column, thus obtaining weight dis-
tribution balances for both the Naphthalene Oil Bases
and the Benzol Absorbing Oil Bases, and reasonably
close-cut fractions of the bases.

3)   Subjection of several of the higher of
these fractions to further fractionation in the "100-
plate" column, thereby obtaining cuts suitable for
the isolation of pure bases.

4)   Separation and purification of the
individual components from these close-cut fractions
by methods referred to before.

5)   Identification of the individual bases
isolated.   This was generally accomplished by com-
parison of their physical properties and the melting
points of their derivatives with recorded data, and
where possible by mixed melting points and comparison
of infra-red absorption spectrograms.

FIGURE 3.

20 GALLON BATCH STILL.

To Buffer Vessel & Pump.
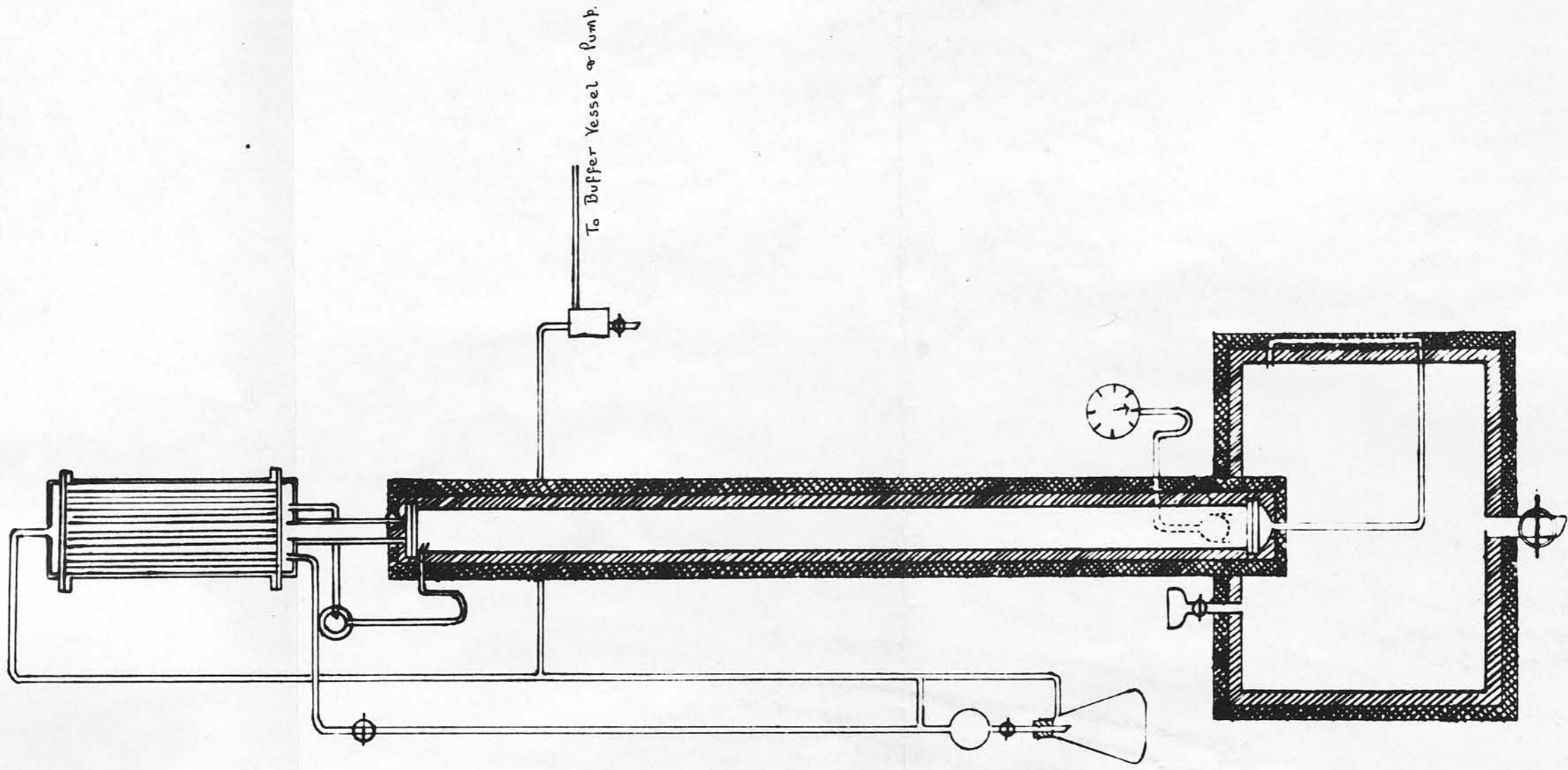
APPARATUS.

20-Gallon Still.

The author is indebted to Messrs. Midland Tar Distillers Ltd. for permission to use the 20-gallon still in their works at Oldbury.   This still was used for the initial fractionation of the crude tar bases, and was operated either at atmospheric pressure or under reduced pressure as required.

The following is a brief description of the plant and a sketch is shown in Figure 3.

The boiler consists of a cylindrical steel vessel (18" x 2') with six steel tubes running through the lower half, heating of the charge being carried out by six 2Kw. electrical heaters which are contained in these tubes.   To the top of the boiler are fitted a filling funnel and a vapour up-riser pipe.   This pipe, to which a manometer is fitted for use when operating at reduced pressures, is in the form of a right-angled curve which joins the foot of the fractionating column at the side.

The fractionating column is in the form of a steel tube, 3 inches in diameter and approximately 6 feet in length, and is packed with 1/4 inch diameter Raschig rings.   To the dished bottom of this column is/

is fitted ~~with~~ a liquid return tube which returns the reflux liquid to the boiler. To the top of the column is fitted a pipe through which the hot vapours rise to the condenser.

The condenser is of the tubular water-cooled type with a weir at the bottom. Into this weir two tubes are fitted. The first tube, which protrudes a little distance into the weir, is the liquid return line and contains a sight glass for the purpose of obtainigg an approximation to the reflux rate. The second tube, which is the take-off line, is fitted flush with the foot of the weir and has a steel needle-type valve for controlling the take-off rate. To the top of the condenser is fitted a tube which connects up with the receiver assembly and with the vacuum line.

The boiler, column and vapour and return lines are lagged with a casing of 1 inch of magnesia and 1 inch of "Stellite".

The receiver assembly consists of a steel vessel, in the line, and a Buchner flask with appropriate connections to the take-off, vacuum line and overhead. These connections are shown clearly in Figure 3.

When working under reduced pressure, the vacuum is maintained by a "Speedivac" pump and is variable through an air bleed. The vacuum line also contains/

contains a stainless steel buffer-vessel and a small catch-pot.

The column-head temperature is read by means of a simple mercury in glass thermometer which is situated in a pocket at the top of the fractionating column.   Three further thermometers are situated in pockets spaced regularly along the length of the column, their purpose being to measure the temperature gradient in the column.

This still proved quite satisfactory for the task which it was called upon to perform, but it possessed the disadvantage of having no reliable means of measuring the rate of reflux, the sight-glass providing only a rough guide.   Thus it was possible that the still was not always running at a constant reflux ratio and, consequently, the fractionating efficiency of the column may have varied slightly during the distillations.

No figures were available as to the fractionating efficiency of this column but it was thought that this would be equivalent to between 5 and 10 theoretical plates.

30-Plate, I.C.I. Gauze-Ring Packed, Column.

This column, based on similar ones in use

in/
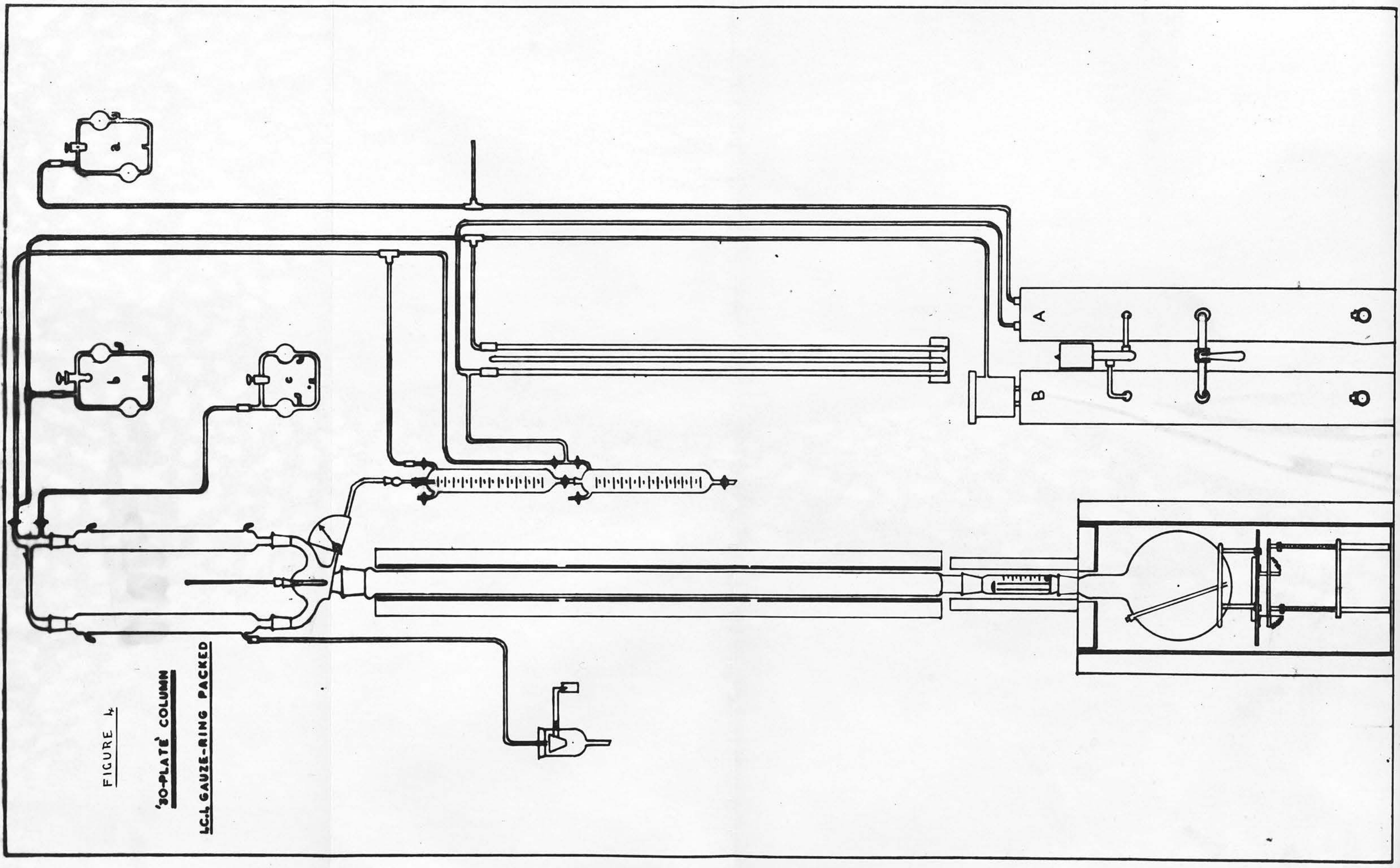
FIGURE 4

'30-PLATE' COLUMN

I.C.I. GAUZE-RING PACKED

A

B

in the laboratories of the Anglo-Iranian Oil Co. Ltd.
and on Institute of Petroleum Specification 25/44,
was supplied as a complete unit by Messrs. Griffin
and Tatlock Ltd., but had been extensively modified
by Messrs. Benzie and Milne (24).

The following is a brief description of the
still and a sketch is shown in Figure 4.

The still-pot is a 5 litre heavy-walled
flask with a B.34 socket on the neck and a B.19
radial neck for a thermocouple.   It is supported on
an asbestos-wound ring which is supported above a
heavy Sindanyo shelf which carries a 1 Kw. heater,
lying directly below, but not touching the flask.
This heater is controlled through a Variac transformer.
The Sindanyo shelf is in turn supported by three
springs and brackets to a tripod whose height is
adjustable by a chain and screw mechanism.   The flask,
heater, etc. are enclosed in a double-walled lagging
box which is lined with asbestos and packed with
glass-wool.

To the neck of the boiler flask is connected
a reflux-meter of the type designed by Messrs. Anglo-
Iranian Oil Co. Ltd., with B.34 cone and socket, and
operated by an external magnet.

The column itself is a heavy-walled glass
tube having an internal diameter of 36 mm. and a
packed/

packed length of 4 feet. It is surrounded by a
lagging shield which consists of a brass tube, wound
with three sections of resistance wire which serve as
heaters and are supplied independently through three
Variac transformers. A layer of "Versil" glass-wool
is wound over these heater windings and the whole is
bound with tape and painted with aluminium paint.
The shield is supplied with three thermocouples for
measurement of the temperature gradient in the column.

The still-head is of the simple weir type
with twin internal spiral condensers, and take-off is
through a grooved stop-cock to two 250 mls. graduated
receivers. These receivers have connections to the
vacuum system, as shown in Figure 4, which make it
possible to empty and re-evacuate the lower receiver
without affecting the pressure in the rest of the
system.

The column is packed with 1/4" x 1/4" I.C.I.
Staybrite rings of 60-mesh square weave gauze. The
static hold-up has been estimated from figures provided
by Messrs. I.C.I. Ltd. (133) for 2:2:4-trimethylpentane
and is approximately 30gms. No figures are available
from which the dynamic hold-up can be calculated, but
this is believed to be correspondingly low.

The efficiency of this column, after pre-
flooding and running to equilibrium for four hours,
was estimated by Benzie and Milne (24) using Benzene /
carbon tetrachloride/

carbon tetrachloride as the test mixture (134) and their results are shown below.

Boil-up Rate (mls/hour)	Theoretical Plates
5,200	20.0
3,600	22.0
2,000	26.2
1,500	33.5
765	48.8

During the present investigation this column was run at a boil-up rate of 1,500mls/hr., and at a reflux ratio of about 30:1.

Vacuum System :- The vacuum system for this column was completely automatic, and variation from the set value was negligible over a period of 24 hours, provided that there was no great change in room temperature. The sensitivity of control of the system varied somewhat according to the working pressure, and at 100 mm. Hg. was less than 0.5 mm., which was sufficiently accurate for the distillations carried out in the column.

The system of control was substantially that described by Coulson and Warner (135), and the following is a description of its operation.

The cylindrical steel buffer vessel (A) has a capacity of about 5 litres, and is connected to a mercury manostat (a) which controls a "Speedivac" pump through a "Sunvic" Hot-Wire Vacuum Switch. The pressure in this primary buffer vessel is reduced to/

to about 20 mm. Hg. below the working pressure, and
the manostat (a) is closed.   Further reduction of
pressure breaks the mercury contact in the manostat,
thus breaking the control circuit of the Hot-Wire
Vacuum Switch and shutting off the pump.   The slight
time delay which is associated with this type of relay
protects the pump from too frequent stopping and
starting and allows the pressure in the primary buffer
vessel to vary within certain limits.

The pressure in the secondary buffer (B)
and the rest of the system is then reduced to the
required value, and the mercury-sealed manostat (b)
is closed.   Thus, when air leaks into the system,
the mercury contact in the manostat (b) is made,
causing a momentary opening of the solenoid valve
which connects the primary and secondary buffer
vessels, and bringing the pressure back to the set
value.

The solenoid valve (British Thermostat Co.
Ltd.) operates on 230 volts A.C. and, to avoid
fouling of the mercury in the manostat (b), is
controlled through an electronic valve relay, of the
type described by Coulson and Warner (135), which
operates a miniature telephone-type relay, which in
its turn operates a heavy battery relay controlling
the supply of current to the solenoid valve.

Since this column was left on total reflux
unattended/

unattended overnight, it was considered advisable to
arrange for automatic cutting off of the power supply
in the event of a failure in the vacuum system or
condenser water supply.   This was arranged by
connecting an insensitive manostat (c) (sensitivity -
about 2 mm. Hg.) to a "trip-box".   Thus, if the tap
on the manostat were closed when working at the
required pressure, a mercury contact would be made
if the pressure in the system varied by more than
about 2 mm. Hg. and this, working the relay system
of the "trip-box", would cut off all power to the
panel.   The water control, which was attached to the
condenser outlet and consisted of a counter-balanced
perforated bucket through which the water flowed,
worked in the same way, a mercury contact being made
when the water supply failed.

All ground-glass joints in this system were
secured with Audco Lubricant No.657.   No lubricant
was found for the stop-cocks which would resist the
powerful solvent effects of the pyridine or quinoline
bases.   Apiezon Grease M was used throughout the
present investigation, but the bases soon dissolved
this away, and the stop-cocks were then apt to leak.
The most effective method found for preventing these
leakages was to pack the outside of the cocks with
some such lubricant as Audco Lubricant No.356.

100-Plate/

FIGURE 5.

'100-PLATE' COLUMN
I.C.I. GAUZE-RING PACKED.

CONDENSER

TIPPING BUCKET STILL HEAD
WITH SOLENOID

RECEIVERS

HEATER WINDING

FIBREGLASS LAGGING

MAGNETIC VALVE

REFLUX METER

ISOMANTLES

DIFFERENTIAL
THERMOCOUPLES
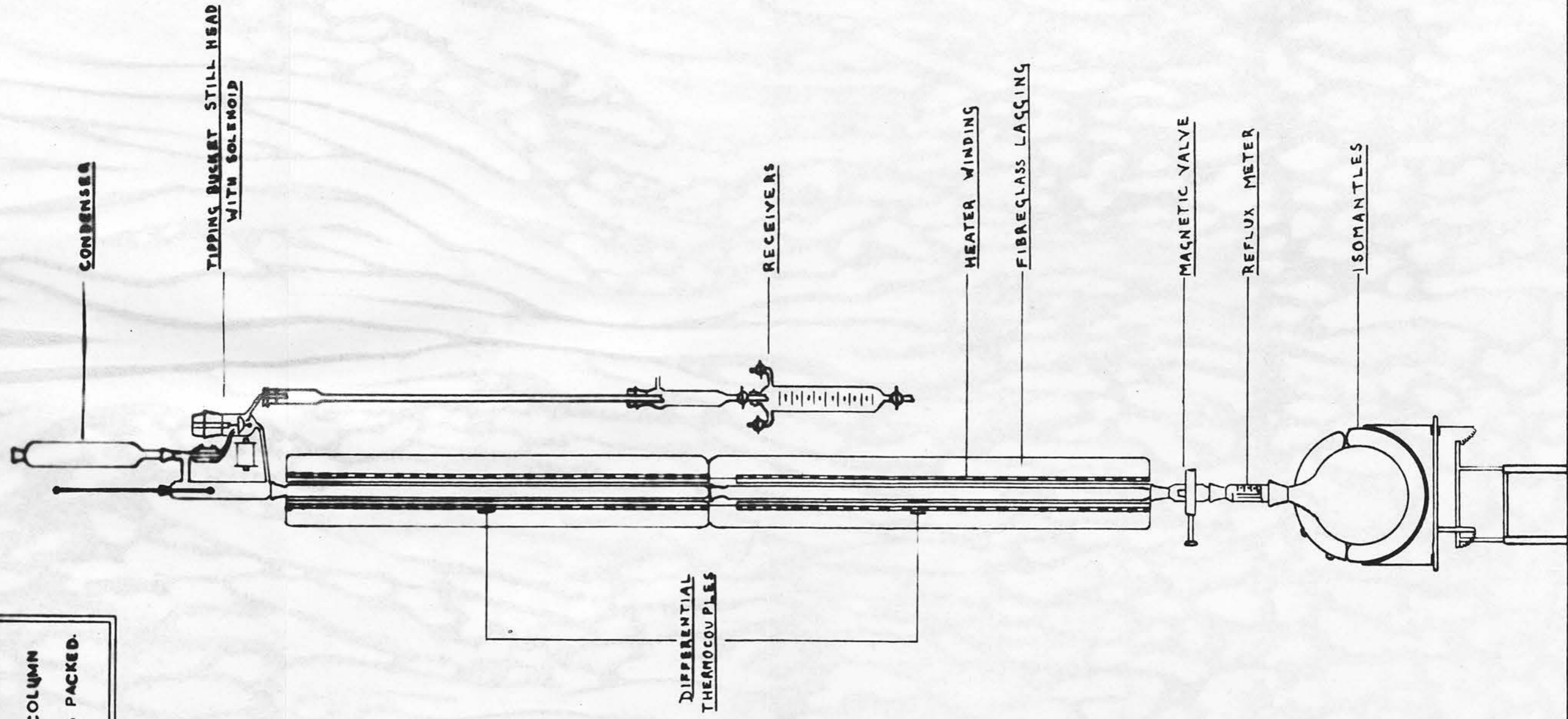
100-Plate, I.C.I. Gauze Ring Packed, Column.

This column, which was almost entirely constructed by Messrs. Benzie and Milne (24) and was modified during the present investigation, was very similar in general details to the 30-plate column.

The following is a description of the still and a sketch is shown in Figure 5.

The still consists of a 2 litre heavy-walled flask with a B.24 socket on the neck. It is supported in an asbestos heating mantle ("Isomantle") which completely surrounds the flask. The lower half of the Isomantle is contained in an aluminium frame which is fixed to a heavy Sindanyo shelf. This shelf is supported by three springs and brackets to a tripod whose height is adjustable by a chain and screw mechanism.

The isomantle has been adopted as a means of heating the still-pot of this column, in preference to the radiator type of heater, as it lessens the risk of serious bumping. It also lessens the risk of a fire resulting from a broken flask. The heat input to the Isomantle is controlled through a Variac Transformer.

To the neck of the flask is fitted a ball and socket reflux-meter with B.24 cone and socket. Between this meter and the column itself is fitted a magnetic/

a magnetic valve of the type designed by Messrs. I.C.I.
Ltd. (147), which consists of a short length of glass
tubing with a B.24 joint at either end, in which is
situated a simple "butterfly" type valve containing
a short bar magnet and operated by an external system
of moveable magnets.   The purpose of this valve is
to limit the return of reflux liquid when flooding
the column prior to carrying out a distillation.
Thus, when the valve is closed, the reflux liquid
builds up from the bottom of the column until the
entire packing is submerged;   then on gradually
opening the valve, the reflux liquid drains back
into the flask at a controlled rate while a steady
reflux is maintained in the column-head.

The column itself consists of two sections
of 20 mm. precision bore Pyrex tubing fitted with
B.24 cone and socket joints.   Each section is packed
for a length of 82.5 cms. with 1/16" x 1/16" I.C.I.
Staybrite rings of 100-mesh square weave gauze.
This gives a total packed length of 165 cms.   The
packing is supported at the bottom of each section
with a spiral of nichrome wire which rests on a
slight constriction of the column wall, and a few
glass rings are placed immediately above these spirals
so that the small gauze rings do not fall through.
The, packing is held in position at the top of each
section with a circle of Staybrite gauze fitting
tightly just below the joint.

Each/

Each column section is provided with an electrically wound compensating lagging, consisting of a length of 1.25" bore "Fibreglass" steam pipe lagging 0.75" in thickness, covered with three thicknesses of asbestos paper, on which is wound 100 turns of "Brightray" nichrome tape with a resistance of 11 ohms per yard, making a total resistance of about 250 ohms. The turns of the winding are spaced more closely towards the top and bottom ends of the upper and lower sections respectively to compensate for end losses. The windings are held in position by a further layer of asbestos paper, hardened with a coating of sodium silicate solution, and by a close-fitting outer layer of 1.5" Fibreglass lagging of 6" external diameter.

At the centre of each lagging section is situated a differential thermocouple consisting of two copper leads joined by a short constantan lead. One junction of each thermocouple is attached to a small sheet copper collecting plate on the inner wall of the lagging, adjacent to the wall of the column, while the other junction, the E.M.F. of which opposes that of the first, is attached to a similar collecting plate in close thermal contact with, but electrically insulated from, the winding. Using a sensitive galvonometer with these thermocouples, any lateral heat flow is immediately indicated by a deflection, the direction of which indicates whether heat is

flowing/

flowing to or from the column.   Thus close adiabatic
conditions may be easily maintained.

The lagging heaters are independently
controlled through two Variac transformers, and the
heat input is adjusted so that there is a slight but
insignificant loss of heat from the column.

The still-head is of the tipping-bucket
type as designed in the laboratories of Messrs. Anglo-
Iranian Oil Co. Ltd. (136).   It is a total reflux,
variable take-off head.   The reflux liquid, after
returning from the main condenser, passes through a
small auxiliary condenser to a small glass bucket,
the overflow of which is returned to the column.
The take-off is effected by an external solenoid
which, when energised, attracts a small counterweight
which is attached to the bucket and ejects a measured
volume of liquid into the receivers.   The rate of
take-off is determined by the setting of a timer
which controls the supply of current to the solenoid.

The vapour up-riser on this head is provided
with a silvered vacuum jacket which is fitted with
a Fibreglass lagging supplied with a heater winding
and differential thermocouple to prevent excessive
condensation of vapour when dealing with high-boiling
fractions.   The column-head temperature is read by
means of a wide scale mercury thermometer for which
a pocket is provided in the head.   The main condenser
is/

is of the double-surface spiral type and is fitted
with a vacuum jacket.

This still-head proved very satisfactory in
this present investigation, the absence of stop-cocks
providing a decided advantage for vacuum operation.
I t possessed the disadvantage, however, that, when
materials were distilling over which were solid at
at room temperature, the solid was apt to clog the
liquid return lines.   This difficulty was alleviated
by providing these lines with heater windings so that,
when any solid began to appear, the auxiliary condenser
water could be drained and the heaters turned on.

The receiver assembly is very similar to
that of the 30-plate column and is shown in Figure 3.

To eliminate the difficulties due to
variation in the mains voltage supply which were
experienced with the 30-plate column, the power supply
to this column,was fed through a constant voltage
transformer (Advance Components Ltd.).   This trans-
former has proved very useful, maintaining, for the
most part, a constant output of 230 volts $\pm$ about 1%
but, at times, "load shedding" has been so severe
that the transformer has not been able to cope with
the variations.   It has, therefore, been found
neccessary to keep a close watch on the column
whenever "load shedding" was liable to occur.

Throughout/

Throughout the present work this column has been operated at reduced pressure in order to avoid the danger of thermal decomposition of the bases, due to prolonged heating, as the time of distillation for a normal batch of 1 Kg. was about ten days and all the bases distilled boiled over 180°C/760mm. Hg.

The vacuum system of this column was very similar to, that of the 30-plate column but followed more closely the system described by Coulson and Warner (135). It was thought neccessary to describe here only the differences between this system and that of the 30-plate column as follows.

The low pressure buffer vessel (A, Fig.3), manostat (a) and the pump serve both systems, and if the two stills are to be operated simultaneously at different pressures, the pressure in A is maintained at about 20 mm. below the lower working pressure.

The place of the buffer vessel B is taken by a large bolt-head flask, enclosed for safety in a metal casing. The solenoid valve is replaced by a flap valve of the type described by Coulson & Warner. This valve is supported inside the 10 litre buffer flask by a rubber bung through which passes the connection between the buffer vessel A and the valve and and vacuum connections to still-head receiver system. To protect the valve from the possibility of damage due/

due to accidental flooding, a 2 litre catch-pot (bolt-head flask) is placed in the line between the 10 litre flask and the still.   This gives a total effective buffering volume of approximately 12 litres, which is maintained at the still operating pressure and thus reduces the effect of leakages.

The manostat b is replaced by a sulphuric acid manostat of the type described by Hershberg and Huntress (137) which is more sensitive than the simple mercury type.   This manostat can be rotated by a a pivot and screw mechanism for ease in making minor adjustments.   It is connected to the 10 litre flask via a small safety trap and, to eliminate the effect of ambient temperature, is enclosed in a thermostati-cally controlled box (Sunvic thermostat, type T.S.3) whose temperature is maintained at a few degrees above room temperature by means of a heater consisting of a 25 Watt lamp.

The electrical relay system between the sulphuric acid manostat and the flap valve consists of an electronic valve relay (135) which operates a 40 volt local battery circuit energising the coil on the flap valve.

The sensitivity of this system is of the order of 0.1 - 0.2 mm. Hg. at 100mm. Hg. operating pressure, and the useful working range of the still extends to about 20 mm. Hg., below which the pressure drop/

drop due to the column packing cancels out the
advantage of lower working pressures.

As this column was run unattended overnight
it was neccessary to instal safety cut-outs on the
vacuum system and condenser water supply similar to
those on the 30-plate column.

Automatic Receiver Changing.

Particulars about the construction of
various types of automatic receiver changers have
been published from time to time.   The installation
of such a device on the 100-plate column, if practi-
cable, would have resulted in reducing greatly the
time required for a distillation, as the still could
then have been run continuously.   It was considered
impracticable, however, as it would have neccessitated
the use of an automatic temperature recorder, and no
such instrument was available.   There would also
have been difficulties due to clogging of the lines
with the solids distilling over and to probable
leakages in the vacuum system.

During the latter part of this investigation
a "Tektor Proximity Switch" (Fielden Electronics Ltd.)
was installed on the 100-plate column, and by means
of this device it was sometimes possible to leave the
still taking off overnight with the Proximity Switch
stopping the take-off at any required temperature.

The/

The operation of this device was as follows:-
A thin strip of metal was secured to the column-head
thermometer at the point where the cut was to be
terminated. The metal strip was then connected to
the cable of the Proximity Switch and the latter
connected to the power supply of the solenoid on the
still-head, turned on and set. Distillation was
then allowed to continue, and when, owing to rise in
the column-head temperature, the mercury thread in
the thermometer rose up to the metal strip, it caused
the capacity of a condenser, of which the metal strip
formed one plate, to alter, and this, operating
through a series of relays incorporated in the
Proximity Switch, shut off the power to the solenoid,
thereby putting the still on to total reflux.

Efficiency of the 100-Plate Column.

The following data for the column were
calculated from figures supplied by Messrs. I.C.I. Ltd.(133).

Static Hold-up. - This was calculated from
data given for the hold-up of 100gms. of 1/16" 100-
mesh Staybrite gauze rings using 2:2:4-trimethyl-
pentane and draining for 10 minutes. It was found
to be 21.2gms.

Dynamic Hold-up. - The dynamic hold-up
varies with the boil-up rate and using the figures
given for 2:2:4-trimethylpentane an approximation
was obtained of 84gms. at 1000mls./hr.

Theoretical/

Theoretical Plates. - Benzie & Milne (24) obtained the following results for the efficiency of this column by calculation from figures supplied by Messrs. I.C.I. Ltd.

Boil Up Rate. (Gms./hr)	Theoretical Plates
800	136
1000	112
1200	95
1400	83

The efficiency of this column was too high to permit of its being estimated by the common test mixture of benzene - carbon tetrachloride.   It can be measured, however, using the system of n-heptane - methylcyclohexane (138), and this was carried out as follows :-

The still-pot was charged with a mixture of n-heptane and methylcyclohexane whose composition was calculated so that, when the still was running, the molar composition of the overheads would be the opposite of that of the contents of the still-pot. This was calculated using the figures of Leckey and Ewell (124), and on the assumptions that the still had an efficiency of approximately 100 theoretical plates, that the total hold-up was 100gms., and that the molar composition of the hold-up was 1:1.

A sampling tube which dipped well below the surface of the liquid was inserted in the still-pot/

pot.   The column was then flooded and the still run to equilibrium at the required boil up rate.   When equilibrium had been attained samples were taken simultaneously from the overhead by means of the tipping-bucket, and from the still-pot by applying vacuum to the sampling tube.

.   The refractive indices of these samples were determined and hence the mole fractions of the two components were found from the tables (124). The plate efficiency was then calculated from the tables provided.

The plate efficiency of this column was determined at three different boil up rates, and the results are shown below.

B.U.R.	Mole fractions of n-heptane		Theoretical
	Still-head	Boiler	Plates
1500	0.72	0.07	50
1200	0.81	0.015	80
1000	0.95	0.015	101

It can be seen that the values obtained were lower than those obtained by calculation, but these practical results confirm that at the boil up rate of 900-1000mls./hr. used throughout the present investigation, a fractionating efficiency equivalent to at least 100 theoretical plates will have been obtained.

EXPERIMENTAL.

A-Distillations.

Initial Fractionation of the Naphthalene Oil Bases.

180 Litres of the crude Naphthalene Oil
Bases were distilled in the 20-gallon still of Messrs.
Midland Tar Distillers Ltd. in three batches of 54
litres, 54 litres and 72 litres as follows :-

The measured volume of bases was charged
to the still, and a suitable number of the still-pot
heaters turned on.   When the bases were refluxing
steadily, and an even temperature gradient had been
obtained in the fractionating column, the take-off
line was opened and the take-off rate adjusted to
about 2 litres per hour.   Distillation was then
continued until all the "hydrate" boiling below
110°C. had distilled.   The still was allowed to
cool, the "hydrate" treated with solid caustic soda
and the liberated dry bases returned to the still.

The heaters were then turned on again, and
when equilibrium had been attained in the column,
the take-off line was re-opened and the take-off rate
adjusted to about 2 litres per hour.   Frequent
readings of temperature and volume were taken, and
the/

the distillate was divided up into five degree
fractions.   When the column-head temperature reached
220°C., the still was closed down and the residue
run off, while still warm, and weighed.   Similar
cuts from the three distillations were bulked together.

Throughout these three A-distillations,
which were all carried out in a precisely similar
manner, an attempt was made to maintain a steady
reflux rate but this may not always have been achieved
as the only method of measuring the reflux rate was
by a sight-glass on the liquid return line from the
condenser.

This still was run for sixteen hours per day,
and during the remaining eight hours, when it had to
be left unattended, one or two heaters were turned
off so that the bases were refluxing about half way
up the column.   This avoided loss of time in re-starting.

The results of these distillations are
shown in Table I (overleaf).

Graph 1 shows the weights, densities and
refractive indices plotted against the mid-points of
the cuts, and indicates that a fair degree of
fractionation was obtained in these distillations.

Graph 1.

NAPHTHALENE OIL BASES. (A-Distillations)
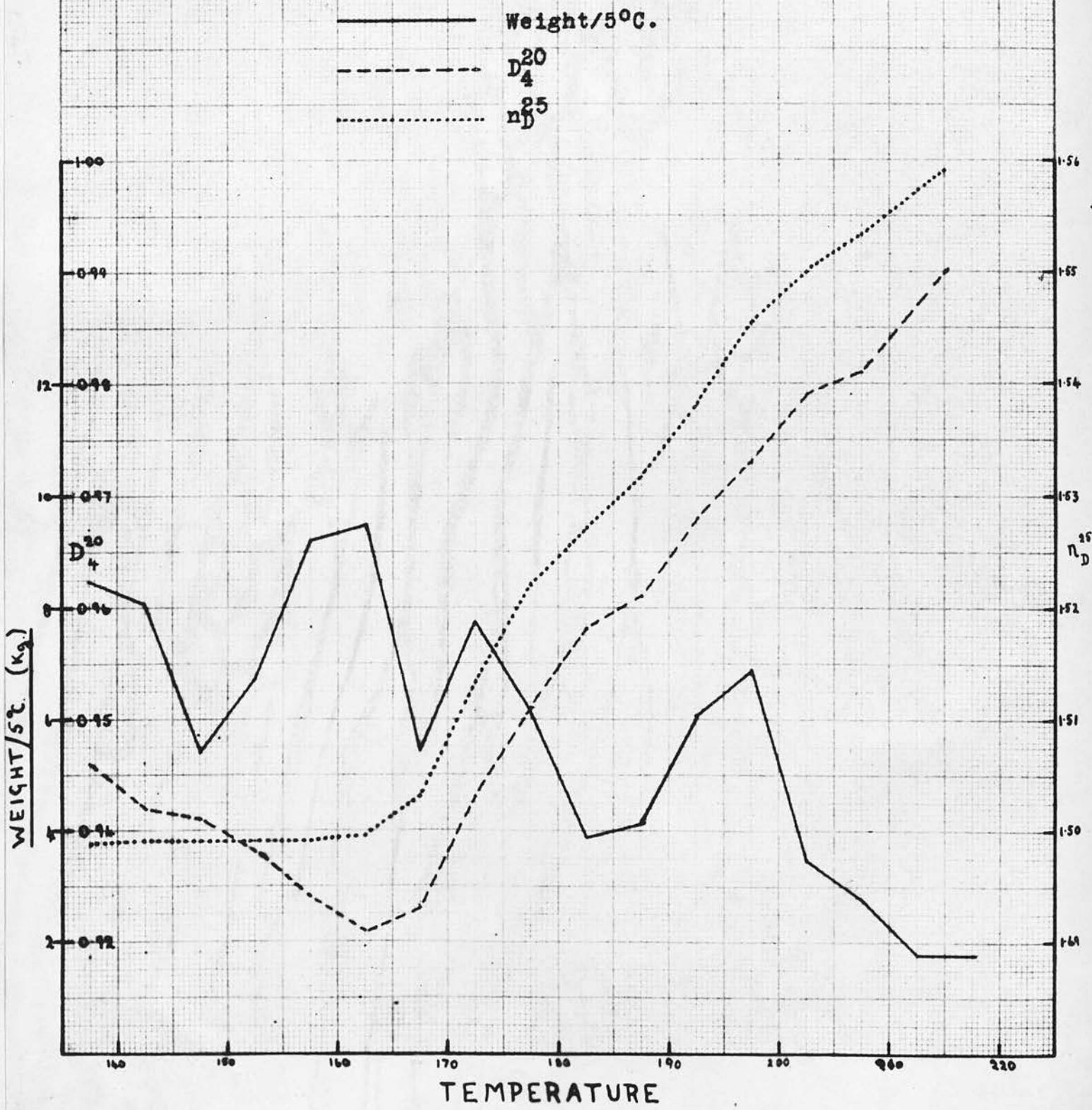
Table I.   (Naphthalene Oil Bases,   A-Distillations)

Distn Range of Fraction	Volumes			Total Volume	D_4^{20}	n_D^{25}	Total Weight	Weight % of the Charge
	Charge A 54L.	Charge B 54L.	Charge C 72L.					
Water	4.75L.	3.75L.	5.90L.	14.40L.	1.000		14.40Kg	7.82
0 - 110°	4.70	4.28	6.20	15.18	0.999	1.4295	15.16	8.23
110 - 135	2.35	1.98	2.25	6.58	0.967	1.4932	6.36	3.45
135 - 140	3.15	2.85	2.95	8.95	0.946	1.4987	8.46	4.60
140 - 145	0.80	2.87	4.88	8.55	0.942	1.4990	8.05	4.37
145 - 150	1.41	1.16	3.17	5.74	0.941	1.4990	5.40	2.93
150 - 155	2.68	1.59	2.90	7.17	0.938	1.4990	6.72	3.65
155 - 160	3.97	3.85	2.00	9.82	0.934	1.4990	9.17	4.98
160 - 165	2.65	2.22	5.30	10.17	0.931	1.4995	9.47	5.14
165 - 170	1.56	2.20	2.07	5.83	0.933	1.5030	5.44	2.96
170 - 175	2.32	3.22	2.65	8.19	0.943	1.5133	7.73	4.20
175 - 180	2.02	1.45	3.00	6.47	0.951	1.5220	6.15	3.34
180 - 185	1.05	1.44	1.55	4.04	0.958	1.5270	3.87	2.10
185 - 190	2.15	1.14	1.00	4.29	0.961	1.5317	4.12	2.24
190 - 195	1.80	1.87	2.60	6.27	0.968	1.5382	6.07	3.30
195 - 200	1.92	1.90	3.20	7.02	0.973	1.5455	6.84	3.72
200 - 205	1.10	1.00	1.45	3.55	0.979	1.5500	3.48	1.89
205 - 210	0.67	0.70	1.40	2.84	0.981	1.5532	2.78	1.51
210 - 220	0.85	1.20	1.55	3.60	0.990	1.5590	3.56	1.93
Residue	30.5 lb	31.5 lb	40.5 lb				47.80	25.96

B-Distillations.

Initial Fractionation of the Benzol Absorbing Oil Bases.

162 Litres of the crude Benzol Absorbing Oil Bases were distilled in the 20-gallon still in three batches of 54 litres, as follows :-

The measured volume of bases was charged to the still and the still run to equilibrium. When equilibrium had been attained the take-off line was opened and the take-off rate adjusted to about 2 litres per hour. Distillation was then continued, taking frequent readings of temperature and volume, and dividing the distillate up into suitable cuts: The first cut was taken up to 150°C., the second from 150 -170°C., and from this point to 240°C. 5°C. cuts were taken. When the column-head temperature reached 240°C. the still was shut down, allowed to drain and the residue run to storage while still hot.

When all three batches had been distilled to 240°C., the three residues were re-charged to the still and distilled as follows, at reduced pressure to reduce the risk of thermal decomposition.

All the stop-cocks being in their approp-riate positions, the vacuum pump motor was turned on and the system evacuated to 10" Hg. The air-bleed valve was set at a position to maintain the pressure

at/

at this level and the heaters turned on.   When the
bases were refluxing steadily and an even temperature
gradient had been obtained in the fractionating
column, the take-off line was opened and the take-off
rate adjusted to 2 litres per hour.   Distillation
was then continued at the same pressure and taking
5°C. cuts up to 220°C./10" Hg.   At this point the
still was shut down and an attempt made to drain off
the residue while it was still hot.   The residue had
set hard, however, and had to be extracted with
acetone.   This extraction still left quite an amount
of solid matter in the still-pot which could not be
extracted.

The results of these distillations can be
seen in Table 2.(overleaf).   Graph 1a shows the
weights, densities and refractive indices of the cuts
plotted against the mid-points of the cuts.

It will be noted that the losses in these
distillations are very high.   This is partly due to
the fact that coking took place and the weights
found for the residues were low as these did not
include the solid material which could not be
discharged from the still.   A contributary factor
was that the still had to be discharged, cleaned and
re-charged at one point in the distillations as
Messrs. Midland Tar Distillers Ltd. required the use
of their still for another purpose.

Graph 1b.

BENZOL ABSORBING OIL BASES. (B-Distillations.)

Table 2. (Benzol Absorbing Oil Bases, B-Distillations)

Distn Range of Fraction	Volumes Charge 1 54L.	Volumes Charge 2 54L.	Volumes Charge 3 54L.	Total Volume	D_4^{20}	n_D^{25}	Total Weight	Weight % of the Charge
97 - 150°	5.38L.	6.36L.	4.72L.	16.46L.	0.997	1.4208	16.40Kg	9.39
150 - 170	2.90	1.33	2.98	7.21	0.942	1.4989	6.80	3.89
170 - 175	0.75	0.68	0.50	1.93	0.940	1.5042	1.81	1.04
175 - 180	0.68	0.98	0.35	2.01	0.940	1.5064	1.89	1.08
180 - 185	0.80	1.33	1.78	3.91	0.944	1.5107	3.69	2.11
185 - 190	0.52	0.40	1.20	2.12	0.947	1.5138	2.01	1.15
190 - 195	0.70	0.60	0.57	1.87	0.952	1.5167	1.78	1.02
195 - 200	1.20	1.70	1.55	4.45	0.957	1.5214	4.26	2.44
200 - 205	1.35	1.10	1.05	3.50	0.963	1.5260	3.37	1.93
205 - 210	1.70	2.18	1.78	5.66	0.970	1.5308	5.49	3.14
210 - 215	0.65	0.80	0.68	2.13	0.987	1.5366	2.10	1.20
215 - 220	0.30	0.35	0.77	1.42	0.995	1.5442	1.41	0.81
220 - 225	0.72	0.45	1.36	2.53	1.025	1.5601	2.59	1.48
225 - 230	3.70	1.40	1.50	6.60	1.044	1.5785	6.89	3.94
230 - 235	7.40	5.22	5.31	17.93	1.065	1.5962	19.10	10.93
235 - 240	6.45	2.50	4.27	13.22	1.077	1.6064	14.24	8.15
Residue	18.74	23.15	25.07				66.96	38.30
-190°/10"Hg				8.13	1.081	1.5842	8.80	5.04
190-195 "				2.58	1.077	1.6082	2.78	1.59
195-200 "				3.83	1.068	1.6065	4.09	2.34
200-205 "				2.64	1.063	1.6035	2.81	1.61
205-210 "				3.89	1.060	1.6025	4.12	2.36
210-215 "				3.22	1.058	1.6025	3.40	1.95
215-220 "				6.70	1.057	1.6025	7.08	4.05
Residue							22.25	12.73

C-Distillations.

Second Fractionation of the Naphthalene Oil Bases.

These distillations were carried out in the 30-plate column at a boil up rate of 1500mls./hr. and a reflux ratio of approximately 30:1.

First of all the size of batch to be used had to be decided as there were two possible alternatives :-

1) To take a fixed proportion of the five degree cuts from the A-distillations (e.g. 1/3). This would enable a weight balance to be drawn up simply and without resort to approximations. It would be very inconvenient for working, however, as, taking 1/3 as the proportion, the batch size would vary between approximately 1 and 3 Kg. There would be the additional disadvantage that much time would be consumed in the distillation of the more common cuts (such as the β-picoline fraction), which are of little interest in this investigation, whereas insufficient of the smaller cuts would be obtained, unless the proportion were set at a high level.

2) To take a uniform sample of each of the five degree cuts (e.g. 2 litres). This would complicate the calculation of a weight balance, as each batch could only be distilled down to a residue of about 200cc., and an approximation would have to be/

be made as to the composition of this residue.   It
would be very convenient to work, however, as a batch
of 2 litres could be completed in exactly one week
(approximately 50 hrs. working), and workable quantities
of the smaller, though important, cuts would be obtained.
It was therefore decided to adopt this latter alter-
native.

Approximately 2 litre samples of each of the
A fractions 1 - 11 inclusive, A.1 having been dried
previously with solid NaOH, were distilled at atmos-
pheric pressure in the 30-plate column, as follows :-

The charge was weighed into the still-pot
along with some tile chips.   The heaters were adjusted
to give a boil up rate of 1500mls./hr., as shown by
the reflux meter, and an even temperature gradient in
the fractionating column, as shown by the thermocouple
readings.   When this had been attained the column
packing was flooded by suddenly applying vacuum to the
column.   The flooding was then allowed to subside
gradually, while maintaining a steady reflux in the
column, by slowly releasing the vacuum.   The still
was allowed to run to equilibrium for three hours.

When equilibrium had been attained, the
take-off line was opened and the take-off rate was
adjusted to 50mls./hr.   Distillation was then allowed
to proceed at this rate, frequent readings being
taken of column-head temperature, volume of distillate,
thermocouple/

thermocouple readings (indicating the still-pot and
column temperatures), Variac settings and boil up rate.
The column-head temperatures were corrected to 760mm. Hg.
by the Crafts Equation :-

$$\Delta T = c(273 + t)(760 - p)$$

where ΔT is the correction factor to be added.
   c. is 0.00012
   t^oC. is the observed temperature.
and p mm. is the observed pressure.

Cuts were taken to coincide with the distil-
lation flats and those with the same distillation
range from different batches were bulked together.
The distillations were continued throughout the day,
and during the night the still was left on total
reflux.   Each of the distillations was continued down
to a residue of approximately 200gms., the distillation
being stopped, when possible, on a climb in the
distillation graph.   After draining the column, the
residue was weighed and the next batch was weighed
in on top of this residue.

As it had been observed during the distil-
lation of the higher boiling fractions, that there
had been a tendency for the column-head temperature
to fluctuate, and as it was thought that there was
a possibility of thermal decomposition of the bases
due to the prolonged heating at the high temperatures
attained, it was decided to carry out the remainder
of the C-distillations at the reduced pressure of
100 mm. Hg.

The/

The procedure for these reduced pressure distillations was precisely similar to the atmospheric pressure distillations, except that the vacuum was set before heating was commenced and flooding was accomplished by momentarily reducing the pressure.

During the first part of the first distillations under diminished pressure, as there was considerable overlap of the five degree cuts from the A-distillations, it was neccessary to convert the temperatures to 760 mm. Hg., so that the cuts could be bulked with cuts of the same distillation range from the lower boiling batches. This was achieved by the application of Dühring's Rule, using the figures given by Riley & Bailey (140). The distillation flats acted as a check to this conversion.

In the final batches distillation was only carried as far as 145°C./100mm., as it was considered that there would be some bases boiling around this temperature remaining in the residues from the A-distillations, and no quantitative estimate of their amount was possible.

Finally a quantity of the water azeotrope (C.1) was treated with caustic soda to liberate the bases which were then dried over solid caustic soda and subjected to a distillation at atmospheric pressure in the 30-plate column down to the smallest possible/

Graph 2

DISTILLATIONS 1C, 2C, 3C & 4C.

(Carried out in the 30-plate
column at atmospheric pressure.)

-64-
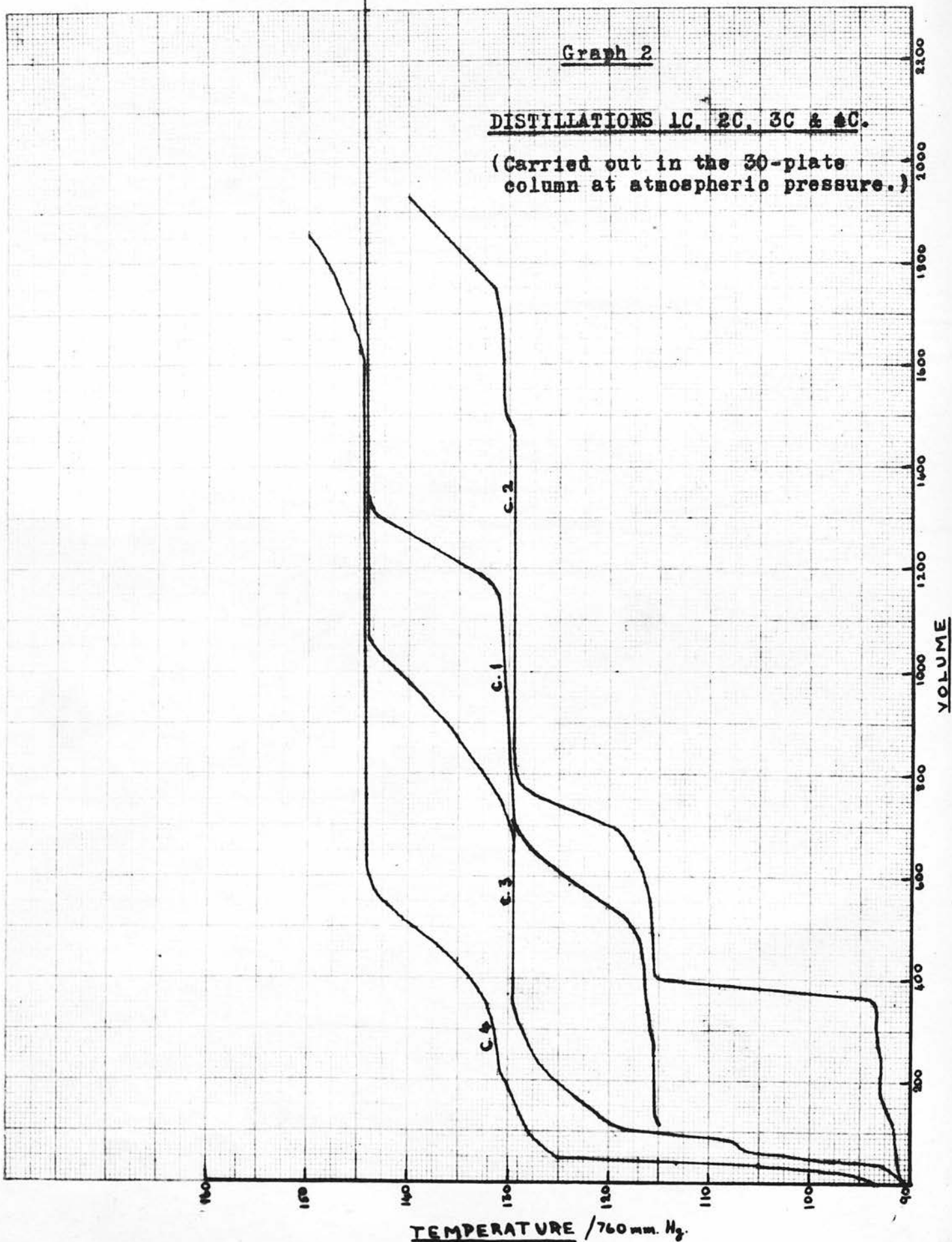
possible residue.   This residue was then assumed to
consist entirely of the cut C.7, as the distillation
was still on this flat when closed down.

The following are the weight balances
obtained for the individual batches, the cuts being
as follows :-

C.1.   0-115° 2. 115-117° 3. 117-129° 4. 129-130°
C.5. 130-132° 6. 132-140° 7. 140-145° 8. 145-157°
C.9. 157-160° 10. 160-162° 11. 162-169° 12. 169-173° ⎫760mm. Hg.
C.13 173-175° 14. 175-179° 15. 179-181° 16. 181-183°
C.18 183-186°.

18. 1225-124° 19. 124-126° 20. 126-131° 21. 131-135° ⎫100mm. Hg.
22.   135-137° 23.137-1385° 24.1385-140° 25. 140-145°

Distillations :-

1.C.   Charge 1620gms.

Fractions 1436gms.   Residue 182gms.   Loss 2gms.

Fract. No.	1 . 2 . 3 . 4 . 5 . 6 . 7 .
Weight	115.342.184.220.233. 92.250 gms.

2.C.   Charge 2338gms.

Fractions. 1723gms.   Residue 590gms.   Loss 25gms.

Fract. No.	1 . 2 . 3 . 4 . 5 . 6 .
Weight	411.213.201.591.242. 65 gms.

3.C.   Charge 1985gms.   Previous Residue 570gms.

Fractions. 2406gms.   Residue 98gms.   Loss 51gms.

Fract. No.	1 . 2 . 3 . 4 . 5 . 6 . 7 .
Weight	59. 9 .254.357. 73.180.1474 gms.

4.C./

Graph 4

DISTILLATIONS 8C, 9C, 10C & 11C.

(Carried out in the 30-plate
column at atmospheric pressure.)

VOLUME

TEMPERATURE /760 mm. Hg.
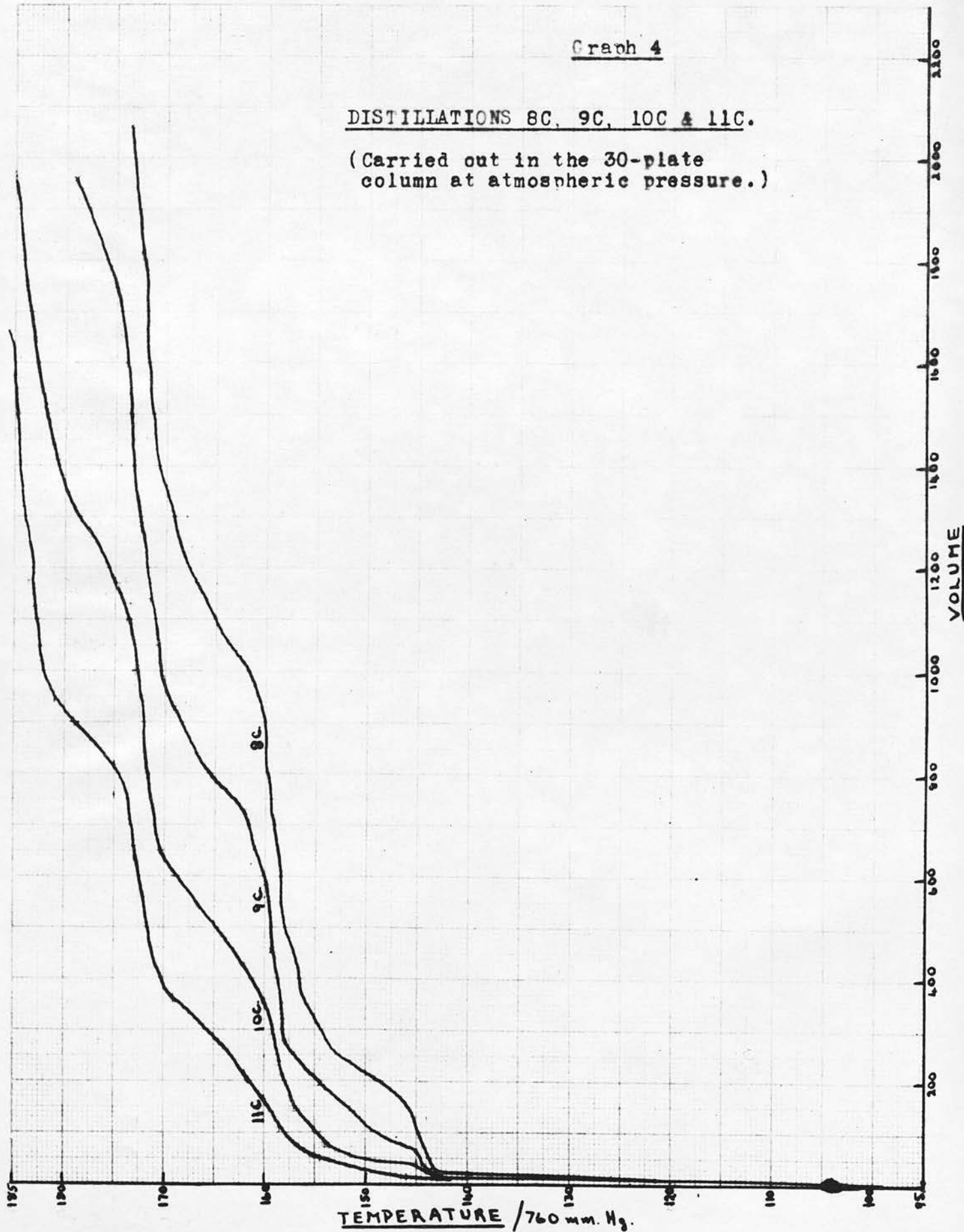
Graph 3

DISTILLATIONS 5C, 6C, & 7C.

(Carried out in the 30-plate
column at atmospheric pressure.)

VOLUME

TEMPERATURE /760 mm. Hg.
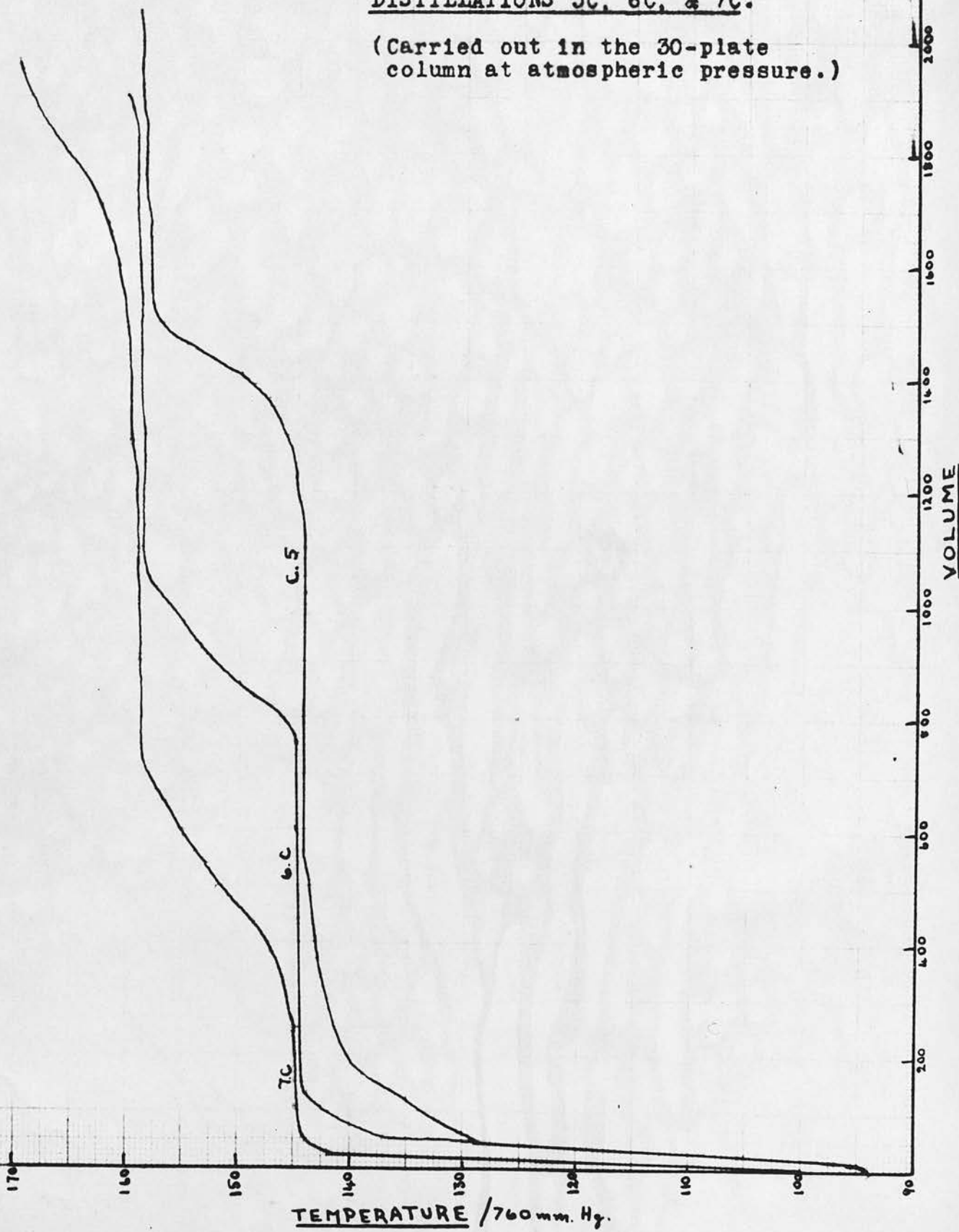
4.C.   Charge 2007gms.   Previous Residue 98gms.

Fractions 1788gms.   Residue 280gms.   Loss 37gms.

Fract. No.	1	2	3	4	5	6	7	8 ※
Weight	33.	6 .	126.	13.	182.	132.	1054.	202. gms.

5.C.   Charge 2125gms.   Previous Residue 280gms.

Fractions 1920gms.   Residue 200gms.   Loss 5gms.

Fract. No.	1	2	3	4	5	6	7	8	9
Weight	30.	5 .	16.	10.	20.	95.	953.	295.	496. gms.

6.C.   Charge 2088gms.   Previous Residue 200gms.

Fractions 1787gms.   Residue 317gms.   Loss -22gms.

Fract. No.	1	2	3	4	5	6	7	8	9
Weight	30.	2 .	12.	1 .	3 .	20.	641.	245.	831. gms.

7.C.   Charge 1876gms.   Previous Residue 317gms.

Fractions 1812gms.   Residue 382gms.   Loss -1gm.

Fract. No.	1	3	6	7	8	9	10.	11.	12 ※
Weight	10.	8 .	5 .	200.	391.	581.	354.	210.	53. gms.

8.C.   Charge 1821gms.   Previous Residue 382gms.

Fractions 1934gms.   Residue 245gms.   Loss 24gms.

Fract. No.	1	3	6	7	8	9	10.	11.	12.	13 ※
Weight	12.	9 .	5 .	74.	305.	410.	115.	230.	572.	202. gms.

9.C.   Charge 1830gms.   Previous Residue 245gms.

Fractions 1777gms.   Residue 272gms.   Loss 26gms.

Fract. No	1.	3.	6.	7	8	9	10.	11.	12.	13.	14.
Weight	7.	5.	2.	43.	172.	305.	122.	185.	407.	344.	185. gms.

10.C./

Graph 5

DISTILLATIONS 12C, 13C, 14C &15C.

(Carried out in the 30-plate column
at a pressure of 100mm. Hg.)
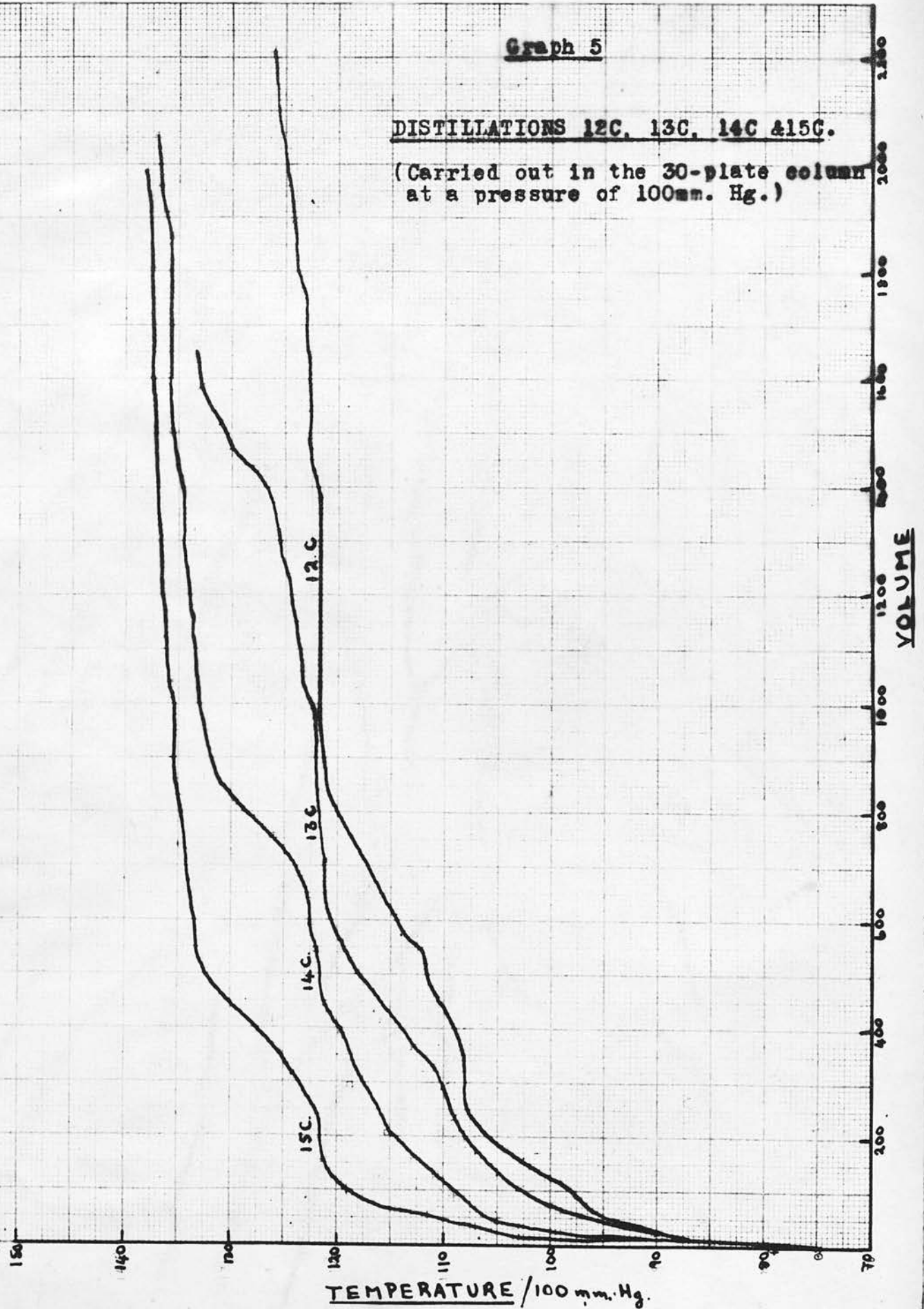
10.C.   Charge 1842gms.   Previous Residue 272gms.

Fractions 1806gms.   Residue 299gms.   Loss 9gms.

Fr. No	1.	3.	6.	7.	8.	9	.10.	11.	12.	13.	14.	15.	16.	17.	
Weight	10.	8.	5.	15.	97.	188.	63.	159.	368.	142.	132.	125.	190.	304.	gms.

11.C.   Charge 1827gms.   Previous Residue 299gms.

Fractions 1570gms.   Residue 540gms.   Loss 16gms.

Fr. No	6	. 7	. 8	. 9	. 10.	11.	12.	13.	14.	15.	16.	17.	
Weight	6	. 5	. 57.	81.	48.	138.	270.	143.	74.	36.	175.	537.	gms.

12.C.   Charge 1840gms.   Previous Residue 540gms.

Fractions 2088gms.   Residue 280gms.   Loss 12gms.

Fr. No	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	
Weight	9.	56.	39.	19.	112.	195.	84.	120.	18.	55.	678.	345.	358.	gms.

13.C.   Charge 1849gms.   Previous Residue 280gms.

Fractions 1573gms.   Residue 552gms.   Loss 4gms.

Fr. No	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	
Weight	5.	7.	37.	13.	11.	106.	134.	30.	66.	67.	54.	408.	155.	216.	144.	120.	gms.

14.C.   Charge 1870gms.   Previous Residue 552gms.

Fractions 2037gms.   Residue 343gms.   Loss 42gms.

Fr. No	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	
Weight	5.	5.	11.	7.	9.	27.	48.	27.	60.	46.	110.	195.	82.	60.	103.	550.	692.	gms.

15.C.   Charge 1902gms.   Previous Residue 343gms.

Fractions 1887gms.   Residue 340gms.   Loss 18gms.

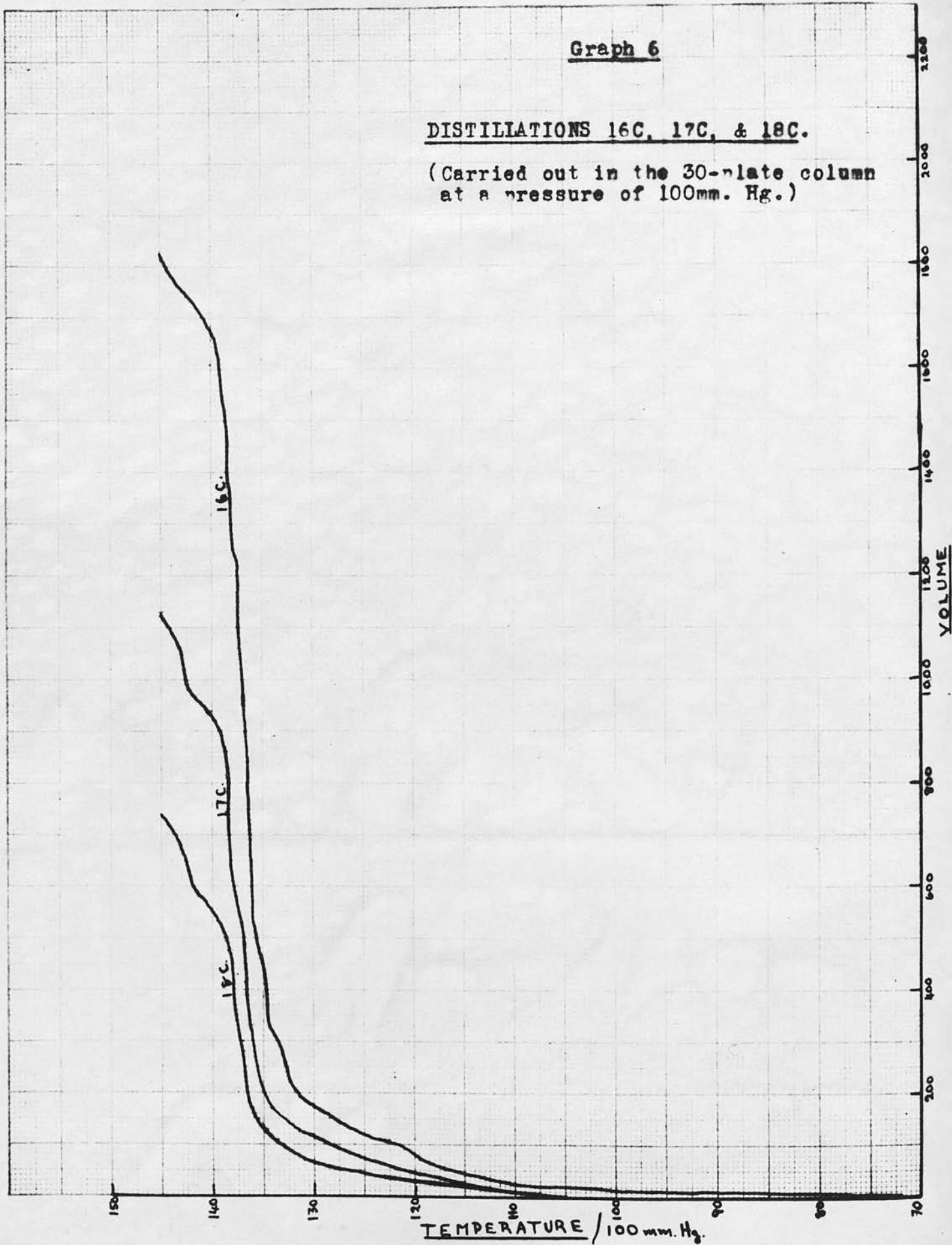| Fr. No	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	
Weight	4.	6.	2.	2.	19.	15.	11.	14.	9.	18.	130.	62.	96.	57.	330.	550.	562.	gms.

16.C./

Graph 6

DISTILLATIONS 16C, 17C, & 18C.

(Carried out in the 30-plate column
at a pressure of 100mm. Hg.)

16.C.   Charge 1830gms.   Previous Residue 340gms.
Fractions 2168gms.   Residue 389gms.   Loss 2gms.

Fr. No	7.	8.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	
Weight	4.	5.	9.	6.	9.	16.	6.	9.	34.	22.	28.	33.	224.	492.	420.	258.	204.	gms.

17.C.   Charge 1870gms.   Previous Residue 389gms.
Fractions 1074gms.   Residue 1175gms.   Loss 10gms.

Fr. No	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	
Weight	7.	6.	5.	11.	6.	6.	11.	11.	16.	28.	75.	292.	296.	118.	186.	gms.

18.C.   Charge 1936gms.
Fractions 705gms.   Residue 1220gms.   Loss 11gms.

Fr. No	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	
Weight	5.	4.	4.	5.	3.	3.	7.	5.	13.	24.	39.	170.	171.	68.	184.	gms.

Graphs of the volume distilled against the
temperature of distillation, for all of these C-
distillations are shown in graphs 2 - 6 inclusive.
(Note. Fractions denoted with an asterisk were incomplete.)

Total Weight Balance For The Naphthalene Oil Bases.

In order to obtain a total "weight /
temperature" balance for any batch, it was neccessary
to make the assumption that the residue from each
distillation was of the same composition as the
residue obtained from the next higher batch on distil-
lation to the same temperature.   Thus, as it was
usual to distil each batch to a temperature of about
5°C. above that of the previous batch, it was assumed
that/

TOTAL WEIGHT BALANCE ON NAPHTHALENE OIL BASES. (Table 3)

Total weight of bases processed.... 184.00Kg.

Water removed in A-distillations.... 14.40Kg.

Loss on A-distillations.............. 3.17Kg.

Residue from the A-distillations.... 47.80Kg.

These temperatures (C.17 onward) are at a pressure of 100mm. Hg.

Distillation Range	Water	C.1 0-115°	C.2 115-117°	C.3 117-129°	C.4 129-130°	C.5 130-132°	C.6 132-140°	C.7 140-145°	C.8 145-157°	C.9 157-160°	C.10 160-162°	C.11 162-169°	C.12 169-173°	C.13 173-175°	C.14 175-179°	C.15 179-181°	C.16 181-183°	C.17 183-186°	C.18 122.5-124°	C.19 124-126°	C.20 126-131°	C.21 131-135°	C.22 135-137°	C.23 137-138.5°	C.24 138.5-140°	C.25 140-145°	Residue	Loss
A.1 0-110°	7.21	0.56	1.68	0.91	1.08	1.15	0.45	2.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.10
A.2 110-135°	-	1.12	0.58	0.55	1.61	0.66	0.34	1.30	0.05	0.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.11
A.3 135-140°	-	0.25	0.04	1.08	1.52	0.31	0.51	4.24	0.15	0.12	0.13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.11
A.4 140-145°	-	0.13	0.02	0.51	0.05	0.73	0.53	4.23	0.89	0.75	0.02	0.01	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.15
A.5 145-150°	-	0.09	0.02	0.05	0.03	0.06	0.28	2.79	0.81	1.16	0.04	0.02	0.03	0.02	-	-	-	0.02	-	-	-	-	-	-	-	-	-	nil
A.6 150-155°	-	0.11	0.01	0.04	-	0.01	0.07	2.28	0.87	2.43	0.32	0.19	0.22	0.10	0.03	0.01	0.01	0.02	-	-	-	-	-	-	-	-	-	nil
A.7 155-160°	-	0.05	-	0.04	-	-	0.02	0.98	1.91	2.84	1.12	0.72	0.80	0.40	0.10	0.02	0.03	0.04	0.01	0.02	-	-	-	-	-	-	-	0.07
A.8 160-165°	-	0.06	-	0.05	-	-	0.03	0.39	1.59	2.13	0.60	1.20	2.00	0.79	0.22	0.04	0.06	0.11	0.03	0.03	0.01	0.02	-	-	-	-	-	0.11
A.9 165-170°	-	0.02	-	0.02	-	-	0.01	0.13	0.51	0.91	0.36	0.55	1.21	0.83	0.34	0.07	0.10	0.17	0.05	0.05	0.01	0.01	0.02	-	-	-	-	0.07
A.10 170-175°	-	0.04	-	0.03	-	-	0.02	0.06	0.41	0.79	0.27	0.67	1.54	0.50	0.55	0.37	0.57	0.95	0.29	0.29	0.04	0.08	0.08	0.04	-	-	-	0.04
A.11 175-180°	-	-	-	-	-	-	0.02	0.02	0.20	0.27	0.16	0.46	0.91	0.48	0.25	0.12	0.59	1.75	0.32	0.33	0.05	0.08	0.08	0.04	-	-	-	0.02
A.12 180-185°	-	-	-	-	-	-	nil	0.02	0.12	0.08	0.04	0.24	0.41	0.18	0.25	0.04	0.12	1.43	0.33	0.34	0.05	0.09	0.09	0.03	0.01	-	-	nil
A.13 185-190°	-	-	-	-	-	-	0.01	0.02	0.08	0.03	0.02	0.24	0.30	0.07	0.15	0.15	0.12	0.91	0.35	0.48	0.21	0.39	0.40	0.14	0.02	0.01	0.03	-0.01
A.14 190-195°	-	-	-	-	-	-	0.02	0.02	0.04	0.02	0.03	0.09	0.16	0.09	0.20	0.15	0.36	0.63	0.27	0.20	0.33	1.31	1.37	0.49	0.06	0.03	0.10	0.10
A.15 195-200°	-	-	-	-	-	-	-	0.01	0.02	0.01	0.01	0.07	0.05	0.04	0.05	0.03	0.06	0.47	0.22	0.35	0.21	1.19	1.98	1.46	0.16	0.10	0.29	0.06
A.16 200-205°	-	-	-	-	-	-	-	0.01	0.01	-	-	0.02	0.01	0.02	0.03	0.01	0.02	0.06	0.04	0.05	0.06	0.41	0.90	0.60	0.33	0.20	0.67	0.03
A.17 205-210°	-	-	-	-	-	-	-	-	-	-	-	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.04	0.11	0.44	0.44	0.17	0.28	1.17	nil
A.18 210-220°	-	-	-	-	-	-	-	-	-	-	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.07	0.31	0.31	0.13	0.34	2.24	0.02
C.1 Azeotrope	1.13	-	0.27	0.15	0.18	0.19	0.07	0.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	nil
TOTAL WT.	8.34	-	2.62	3.43	4.47	3.11	2.38	18.97	7.66	11.58	3.12	4.50	7.69	3.54	2.20	1.03	2.06	6.57	1.94	2.18	1.05	3.76	5.67	3.55	0.88	0.96	4.40	0.98

WEIGHT PERCENT DISTILLED PER DEGREE

Graph 7.

DISTRIBUTION GRAPH FOR THE TOTAL

NAPHTHALENE OIL BASES.

Total weight of dry bases processed 161.26Kg
Total loss on A & C-distillations... 4.15Kg
Total Residue.......................... 52.20Kg

= Pyridine (115.3°)

= 2-Methylpyridine (129.3°)
= Pyrrole (131°)

= 3-Methylpyridine (144.0°)
= 2:6-Dimethylpyridine (144.4°)
= 4-Methylpyridine (145.3°)

= 2:5-Dimethylpyridine (157.0°)
= 2:4-Dimethylpyridine (157.9°)
= 2:3-Dimethylpyridine (160.8°)
= 2-Methyl-6-Ethylpyridine (160-161°)

= 4-Ethylpyridine (165.0°)

= 2:4:6-Trimethylpyridine (170.3°)
= 3:5-Dimethylpyridine (171.6°)
= 2:3:5-Trimethylpyridine (172.8°)

= 3:4-Dimethylpyridine (178.9°)
= 2-Methyl-4-ethylpyridine (179.0°)

= Aniline (184.0°)

= 2:3:5-Trimethylpyridine (186.6°)
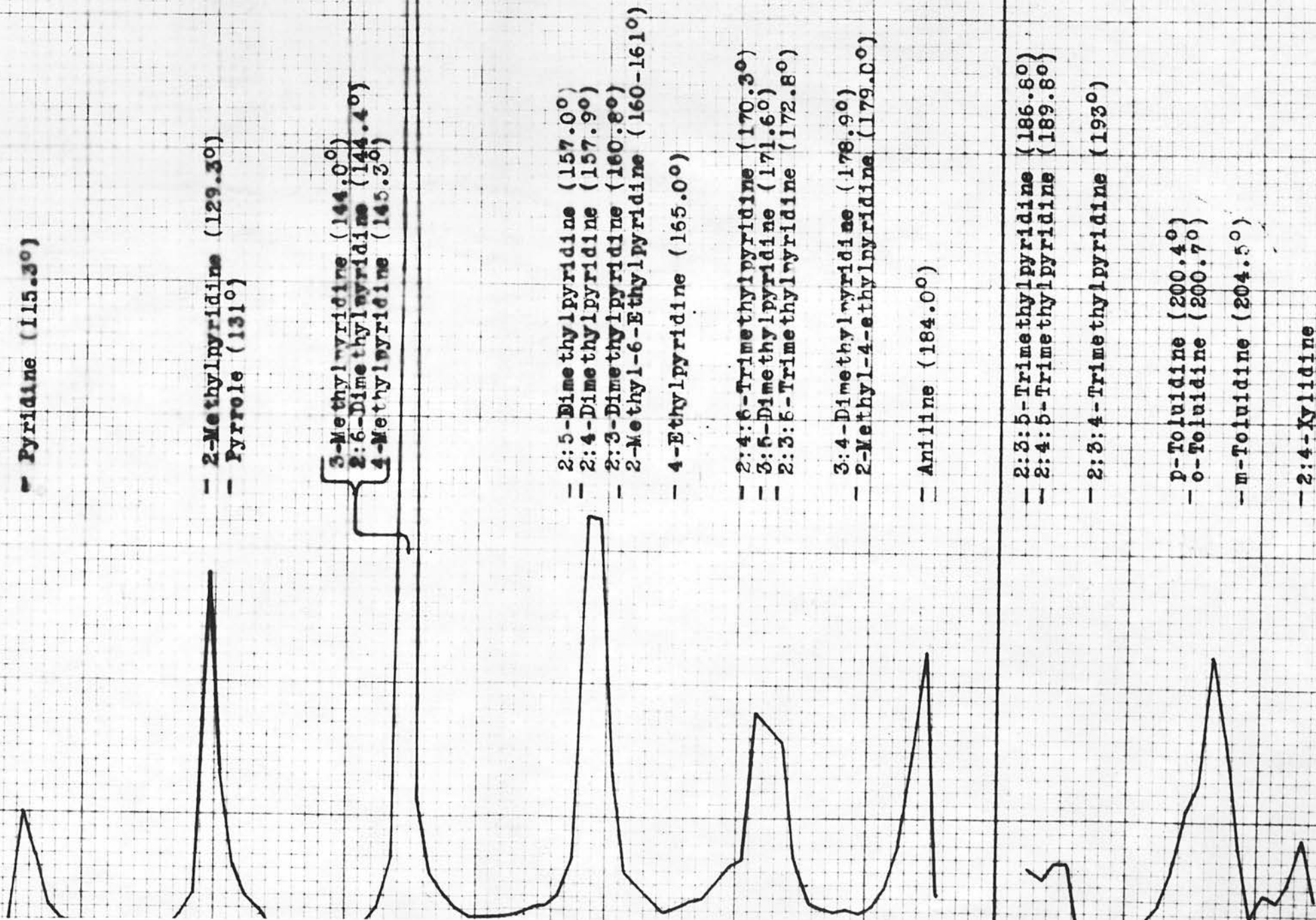= 2:4:5-Trimethylpyridine (189.8°)

= 2:3:4-Trimethylpyridine (193°)

= p-Toluidine (200.4°)
= o-Toluidine (200.7°)

= m-Toluidine (204.5°)

= 2:4-Xylidine

that this distillate was derived from the previous residue and from the batch in process, in quantities proportional to the amount of each present. By continuation of this type of calculation a total weight balance for each of the batches was obtained.

The weight balance for the total crude Naphthalene Oil Bases was then obtained by multiplying the weight of each individual cut by the factor - Weight of the total A-fraction / Weight of batch taken.

The results are shown in Table 3.

A graph (7) was then prepared of the weight distilled per degree centigrade against the temperature of distillation, making use of this table, the distribution inside the various cuts being estimated from the distillation graphs. The boiling points of the bases which had already been isolated from coal tar are indicated on this graph and it can be seen that the distillation "peaks" correspond very well with these..

Examination of the C-Fractions.

The specific gravities and refractive indices of all the C-fractions were determined and are shown in Table 4. From a study of these constants and of Graph 7 it can be seen that a good degree of separation was achieved in these C-distillations.

Table 4/

Graph 8

DENSITIES & REFRACTIVE INDICES OF C-FRACTIONS.
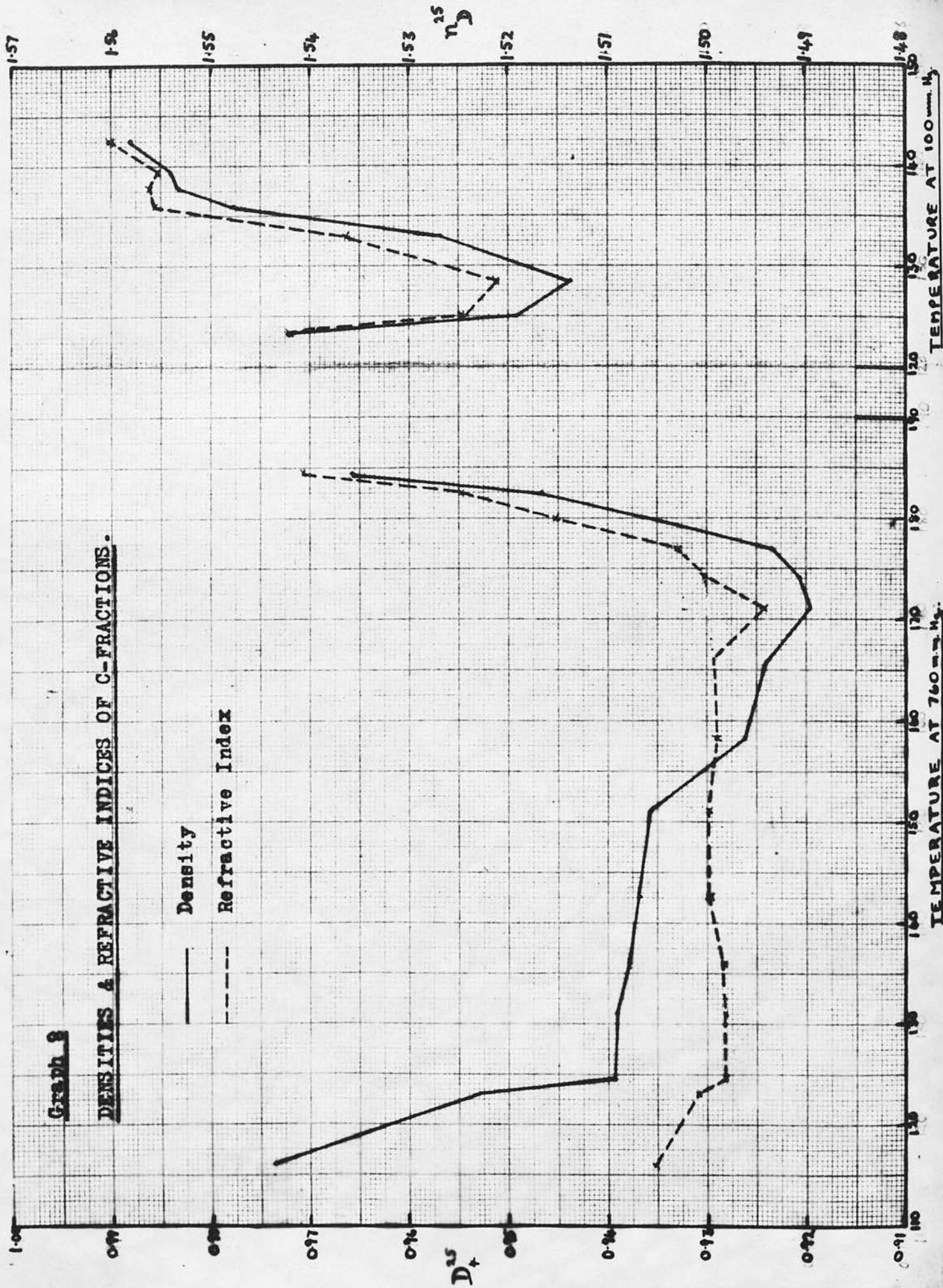
Density ———————
Refractive Index – – – – –

Table 4.

Fract. No.	Distn. Range	D_4^{25}	n_D^{25}
C.2	115-117°/760mm.	0.9757	1.5052
C.3	117-129° "	0.9530	1.5008
C.4	129-130° "	0.9397	1.4982
C.5	130-132° "	0.9396	1.4982
C.6	132-140° "	0.9378	1.4984
C.7	140-145° "	0.9368	1.4998
C.8	145-157° "	0.9357	1.4999
C.9	157-160° "	0.9263	1.4984
C.10	160-162° "	0.9265	1.4990
C.11	162-169° "	0.9243	1.4993
C.12	169-173° "	0.9196	1.4991
C.13	173-175° "	0.9206	1.5003
C.14	175-179° "	0.9235	1.5030
C.15	179-181° "	0.9365	1.5154
C.16	181-183° "	0.9466	1.5249
C.17	183-186° "	0.9658	1.5406
C.18	122.5-124°/100mm.	0.9724	1.5440
C.19	124-126° "	0.9492	1.5247
C.20	126-131° "	0.9439	1.5311
C.21	131-135° "	0.9569	1.5364
C.22	135-137° "	0.9778	1.5555
C.23	137-138.5° "	0.9832	1.5561
C.24	138.5-140° "	0.9840	1.5554
C.25	140-145° "	0.9880	1.5600

Graph/

Graph 8 shows the densities and refractive indices plotted against the mid-points of the cuts.

In order to obtain a quantitative estimate of the amounts of pyridine, 2-, 3- & 4-methylpyridines and 2:6-dimethylpyridine present in the total crude Naphthalene Oil Bases, the lower fractions were examined as follows :-

C.2. This fraction was assumed to consist entirely of pyridine as the boiling point, density and refractive index corresponded well with the values given for pure pyridine. The purity, as estimated by titration with standard sulphuric acid using screened methyl orange as indicator, was found to be 99%.

C.3. This fraction was assumed to consist entirely of a mixture of pyridine and 2-methylpyridine. A small sample of the fraction was freed from non-basic material by acidifying with HCl, steam-distilling the non-basic material, making alkaline with NaOH and distilling off the purified bases in steam. After drying the purified bases by refluxing over solid KOH, the percentages of the two components were estimated by the method of Hamer, Pomfret & Stubbings (141).

Results   Pyridine.........45%

2-Methylpyridine.55%

C.4./

C.4.   Owing to the very close similarity
of the boiling point, density and refractive index of
this fraction with those given for 2-methylpyridine,
it was assumed that this cut consisted entirely of
2-methylpyridine.   The purity as estimated by acid
titration was found to be 100%.

C.5.   The refractive index and density of
this fraction were almost identical with those of C.4.
The fraction did, however, contain pyrrole, as was
shown by the "match test", but the quantity of this
compound present must have been very small as, on
picration, an almost quantitative yield of 2-methyl-
pyridine picrate was obtained.   It was therefore
assumed that the fraction contained at least 95% of
2-methylpyridine.

C.7.   This fraction was assumed to consist
of a mixture of 3- and 4-methylpyridines and 2:6-
dimethylpyridine.   A sample of the fraction was freed
from non-basic material, which was present only as
traces, and dried by refluxing over solid KOH.   The
percentages of all three constituents in the sample
were then found by the method of S.J. Angyal (142)

Results.   3-Methylpyridine......32.9%

4-Methylpyridine......16.9%

2:6-Dimethylpyridine..50.2%

C.6.   This fraction was intermediate
between the flats C.4-5 and C.7 and was assumed to
consist/

consist of a mixture of the two. As no quantitative
method of estimation was available, the approximation
was made that it consisted of a 50:50 mixture of
2-methylpyridine and the fraction C.7.

From the above estimations and Table 3, the
percentages of these five components present in the
total crude Naphthalene Oil Bases were calculated.
These may be of some industrial importance.

    Results.   Pyridine.................2.26%

                     2-Methylpyridine........5.73%

                     3-Methylpyridine........3.60%

                     4-Methylpyridine........1.85%

                     2:6-Dimethylpyridine...5.50%

Note.   The percentages given for the last three
components will be slightly low as they were also
present in the fraction C.8 but could not be esti-
mated therein.

Unfortunately there are no simple methods
by which a quantitative estimate of the individual
pyridine homologues in the higher fractions may be
obtained, and insufficient time was available to
attempt to isolate all the components.

It may be noted from a study of Graph 8
that there is a sharp rise in density and refractive
index as the fractions C.17 and 18 are reached, which
is explained by the presence of aniline. A further
rise/

rise takes place as fractions C.24 and 25 are reached, and this is explained by the presence of toluidines and xylidines, and also of Naphthalene, of which a large amount was found to be present in fraction C.25. The presence of primary amines in fractions C.14 - 25 was shown qualitatively by means of diazotisation.

None of the Naphthalene Oil Base fractions was further examined, with the exception of C.21 which was subjected to a further fractionation in the 100-plate column in the hope of isolating tetramethyl-pyridines.   This is described later (Distillation 1.E).

D-Distillations./

D-Distillations.

Second Fractionation of the Benzol Absorbing Oil Bases.

These distillations were carried out in the 30-plate column, in a manner precisely similar to that used for the C-distillations, using a 2 litre batch size (where possible) of each B-fraction, a boil up rate of 1500 mls./hr. and a take-off rate of 50 mls/hr.

The B-fractions 1-4 inclusive were fractio-nated at atmospheric pressure, column-head temperatures being converted to 760 mm. Hg. as in the C-distillations.

The other fractions (B.5 - 23) were distilled at 100 mm. Hg., the column-head temperatures of the overlapping cuts being converted to 760 mm. Hg. as in the C-distillations.

In the distillation of the last three frac-tions, when the column-head temperatures reached 180°C./100mm. Hg., the pressure was further reduced to 50 mm. Hg. (to reduce the risk of thermal decom-position), the column re-flooded and allowed to regain equilibrium under total reflux and then distillation was continued at 50 mm. Hg. The final distillation was continued to 178°C./50mm.

In the latter half of these D-distillations it was found that the column-head temperature fell when the still was left on total reflux for any length

of/

of time. The temperature very soon regained its
original value, however, once distillation was re-
commenced.

In distillations 19D - 23D inclusive a great
amount of difficulty was experienced due to "load
shedding" and, in spite of constant supervision, it
was found that the boil up rate varied considerably,
as did the heating conditions in the column. For
this reason the degree of fractionation achieved in
these latter distillations was not constant, and the
reliability of the results obtained may be slightly
impaired thereby.

A further difficulty experienced in the
higher of the D-distillations was that of bumping.
This was successfully overcome, however, by packing
the boiler flask with glass wool to a level higher
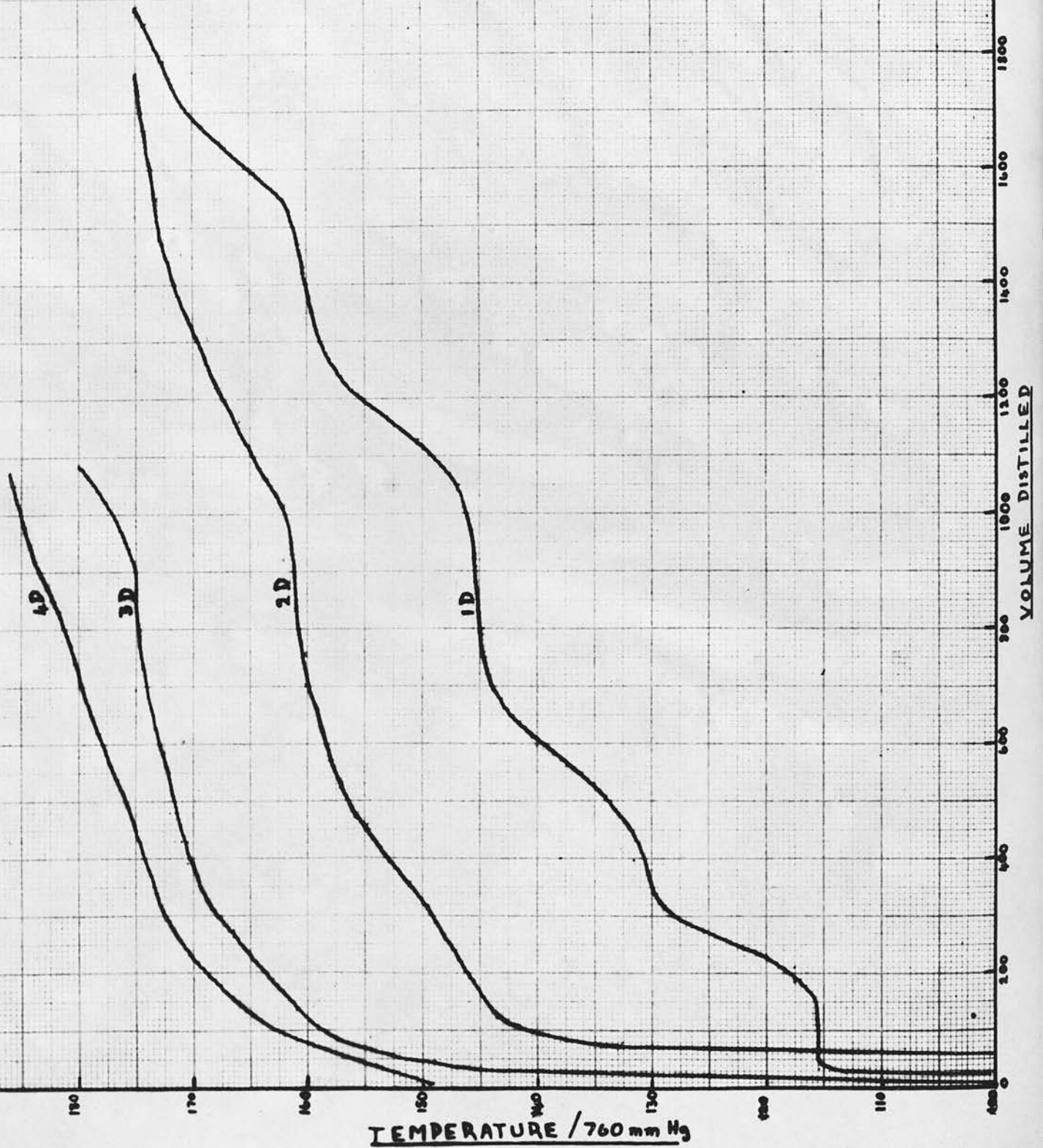than that of the liquid.

The cuts taken during the D-distillations
were as follows :-

D.1. 0-115°	D.2. 115-117°	D.3. 117-129°
D.4. 129-132°	D.5. 132-143.5°	D.6.143.5-145.5°
D.7.145.5-157°	D.8. 157-160°	D.9. 160-162°
D.10. 162-169°	D.11. 169-172°	D.12. 172-175°
D.13. 175-179°	D.14. 179-181°	D.15. 181-183°
D.16. 183-186°		

⎫
⎬760 mm. Hg.
⎭

D.17./

Graph 9

DISTILLATIONS 1D, 2D, 3D &4D.

(Carried out in the 30-plate
column at atmospheric pressure.)

D.17. 122-124°   18.   124-126°   19.   126-131°
D.20. 131-135°   21.   135-137°   22.   137-138.5°
D.23.138.5-140°   24.   140-144°   25.   144-148°
D.26. 148-152°   27.   152-155°   28.   155-158.5°
D.29.158.5-161.5° 30.161.5-163°   31.   163-164°   ⎫
D.32. 164-165°   33.   165-166°   34.   166-167.5°   ⎬ 100mm. Hg.
D.35.167.5-168.5° 36.168.5-170°   37.   170-172°   ⎪
D.38. 172-173°   39.   173-174°   40   174-176°
D.41. 176-178°   42.   178-180°   ⎭

D.43. 158-161°   44.   161-163°   45.   163-165°   ⎫
D.46. 165-168°   47.   168-170°   48.   170-174°   ⎬ 50mm. Hg.
D.49. 174-176°   50.   176-178°.   ⎭

The results of the D-distillations were
as follows :-

1.D.   Charge 1967gms.

Fractions 1751gms.   Residue 240gms.   Loss -24gms.

Fr. No	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	
Weight	48.	106.	222.	78.	205.	260.	234.	162.	132.	114.	82.	108.	gms

2.D.   Charge 1803gms.   Previous Residue 240gms.

Fractions 1618gms.   Residue 416gms.   Loss 11gms.

Fr. No	Water.	4.	5.	6.	7.	8.	9.	10.	11.	12.	
Weight	66	. 5.	56.	55.	324.	152.	198.	312.	148.	302.	gms.

3.D.   Charge 1100gms.   Previous Residue 416gms.
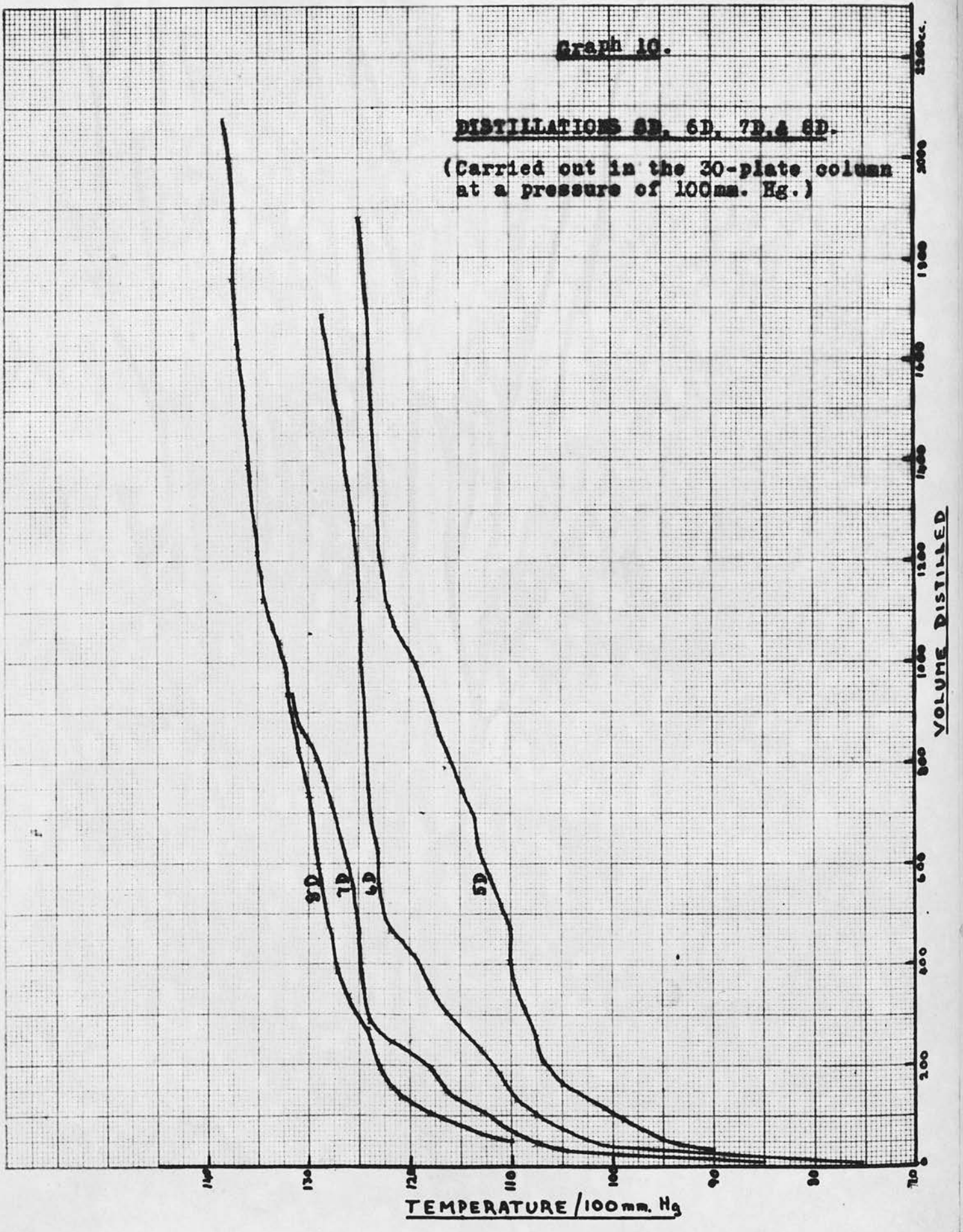
Fractions 989gms.   Residue 525gms.   Loss 2gms.

| Fr. No	Water.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.*	
Weight	20	. 9.	6.	43.	34.	32.	164.	132.	192.	304.	53.	gms.

4.D./

Graph 10.

DISTILLATIONS 5D, 6D, 7D,& 8D.

(Carried out in the 30-plate column at a pressure of 100mm. Hg.)

4.D.   Charge 1104gms.   Previous Residue 525gms.

Fractions 991gms.   Residue 617gms.   Loss 21gms.

Fr. No	Water.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
Weight	26	.19.	28.	18.	104.	72.	158.	187.	112.	97.	170. gms.

5.D.   Charge 1834gms.   Previous Residue 617gms.

Fractions 1832gms.   Residue 616gms.   Loss 3gms.

Fr. No	Water.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18. ✳
Weight	24	.42.	20.	24.	124.	142.	214.	148.	132.	106.	58.	432.	366. gms.

6.D.   Charge 1450gms.   Previous Residue 616gms.

Fractions 1571gms.   Residue 502gms.   Loss -7gms.

Fr. No	Water.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17 .	18.	19. ✳
Weight	14	. 7.	4.	6.	4.	9.	53.	70.	42.	72.	43.	62.	44.	267.	559.	315. gms.

7.D.   Charge 1110gms.   Previous Residue 502gms.

Fractions 866gms.   Residue 736gms.   Loss 10gms.

Fr. No	Water.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20. ✳
Weight	10	. 2.	5.	2.	5.	18.	36.	16.	40.	39.	2.	42.	38.	282.	273.	56. gms.

8.D.   Charge 1728gms.   Previous Residue 736gms.

Fractions 1928gms.   Residue 540gms.   Loss -4gms.

Fr. No	Water.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.
Weight	16	. 3.	2.	5.	10.	10.	14.	20.	12.	20.	30	102.	58.	460.	366.	380.	420.

9.D.   Charge 1735gms.   Previous Residue 540gms.

Fractions 1954gms.   Residue 290gms.   Loss 31gms.

Fr. No	Water.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
Weight	8	. 2.	2.	9.	9.	9.	12.	9.	10.	12.	41.	58.	158.	176.

Fr. No	21.	22.	23.	24.	25.
Weight	222.	338.	256.	517.	106. gms.

10.D./

Graph 11

DISTILIATIONS 9D, 10D, 11D & 12D.

(Carried out in the 30-plate column
at a pressure of 100mm. Hg.)

VOLUME DISTILLED

TEMPERATURE / 100 mm Hg
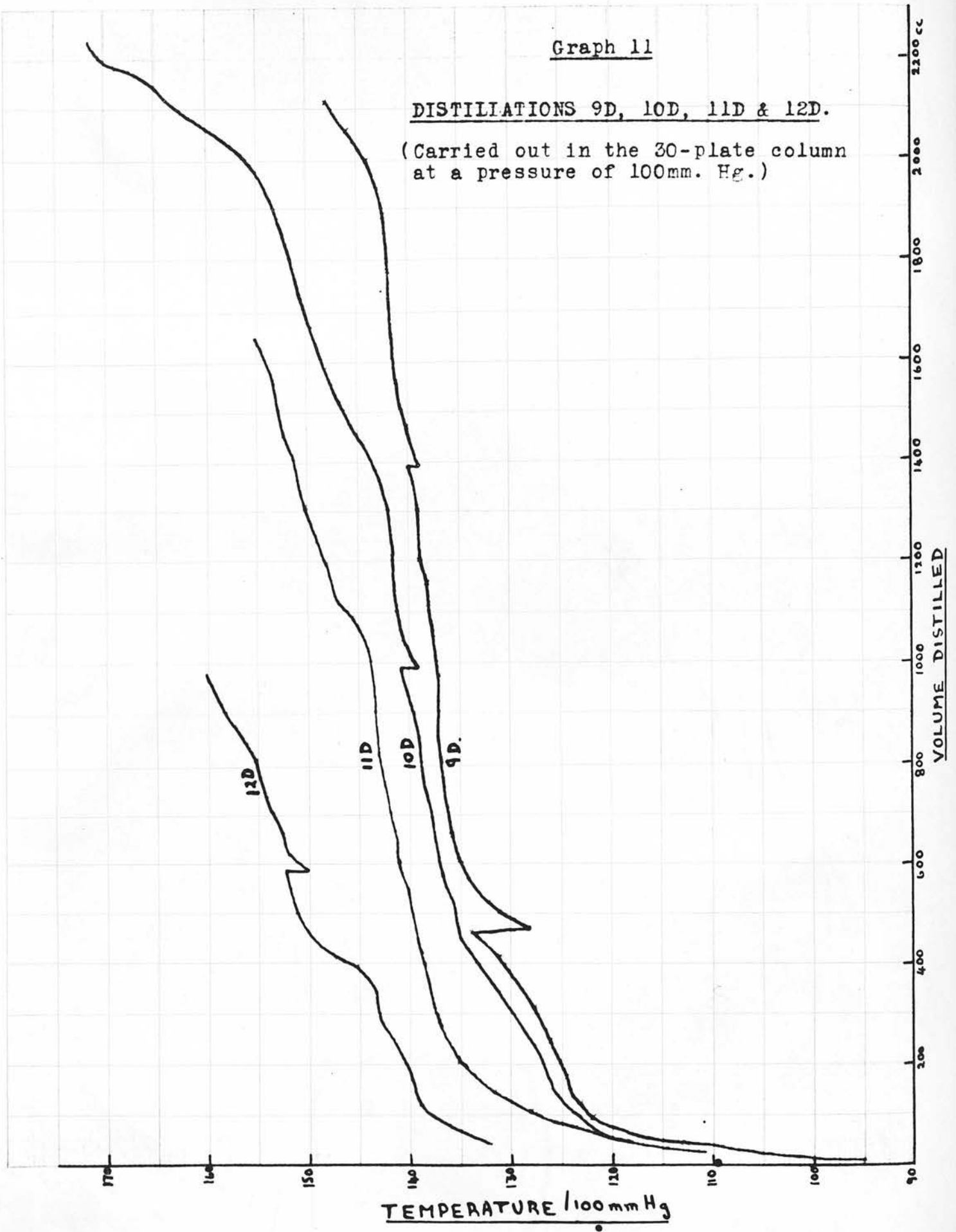
10.D.   Charge 1830gms.   Previous Residue 290gms.

Fractions 2120gms.   Residue nil.   Loss nil.

Fract. No	water.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.
Weight.		12..	7.	5.	5.	10.	7.	9.	12.	26.	46.	173.	108.	160.	128.	168.

Fract. No	24.	25.	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.	37.
Weight	470.	166.	236.	136.	60.	47.	23.	22.	18.	14.	14.	12.	10.	16. gms.

Note.   Batches 11 - 24.D. were fractionated prior to

the fractionation of batches 1 - 10.D.   In order to

obtain a complete weight balance for these lower

batches it was therefore neceessary to distil batch

10.D. until no residue was left.   This was achieved

by mixing the batch with some very high boiling bases

and distilling the mixture until all of batch 10.D.

had distilled over.

11.D.   Charge 1860gms.

Fractions 1583gms.   Residue 283gms.   Loss -6gms.

Fr. No	water.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.
Weight	36	.13.	9.	7.	11.	6.	7.	34.	68.	80.	134.	110.	467.	161.	250.	190.

12.D.   Charge 1015gms.   Previous Residue 283gms.

Fractions 952gms.   Residue 348gms.   Loss nil.

Fr. No	water.	20.	21.	22.	23.	24.	25.	26.	27.	28.
Weight	40	.26.	21.	24.	40.	210.	44.	200.	180.	167. gms.

13.D.   Charge 1978gms.   Previous Residue 348gms.

Fractions 1756gms.   Residue 570gms.   Loss nil.

Fr. No	water.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.	29.	30.	31.
Weight	48	. 4.	7.	13.	19.	15.	36.	120.	146.	184.	300.	157.	128.	321.	258.

14.D./

Graph 13.

DISTILLATIONS 17D, 18D, 19D & 20D.

(Carried out in the 30-plate column at a pressure of 100mm Hg.)

VOLUME DISTILLED

TEMPERATURE / 100mm Hg
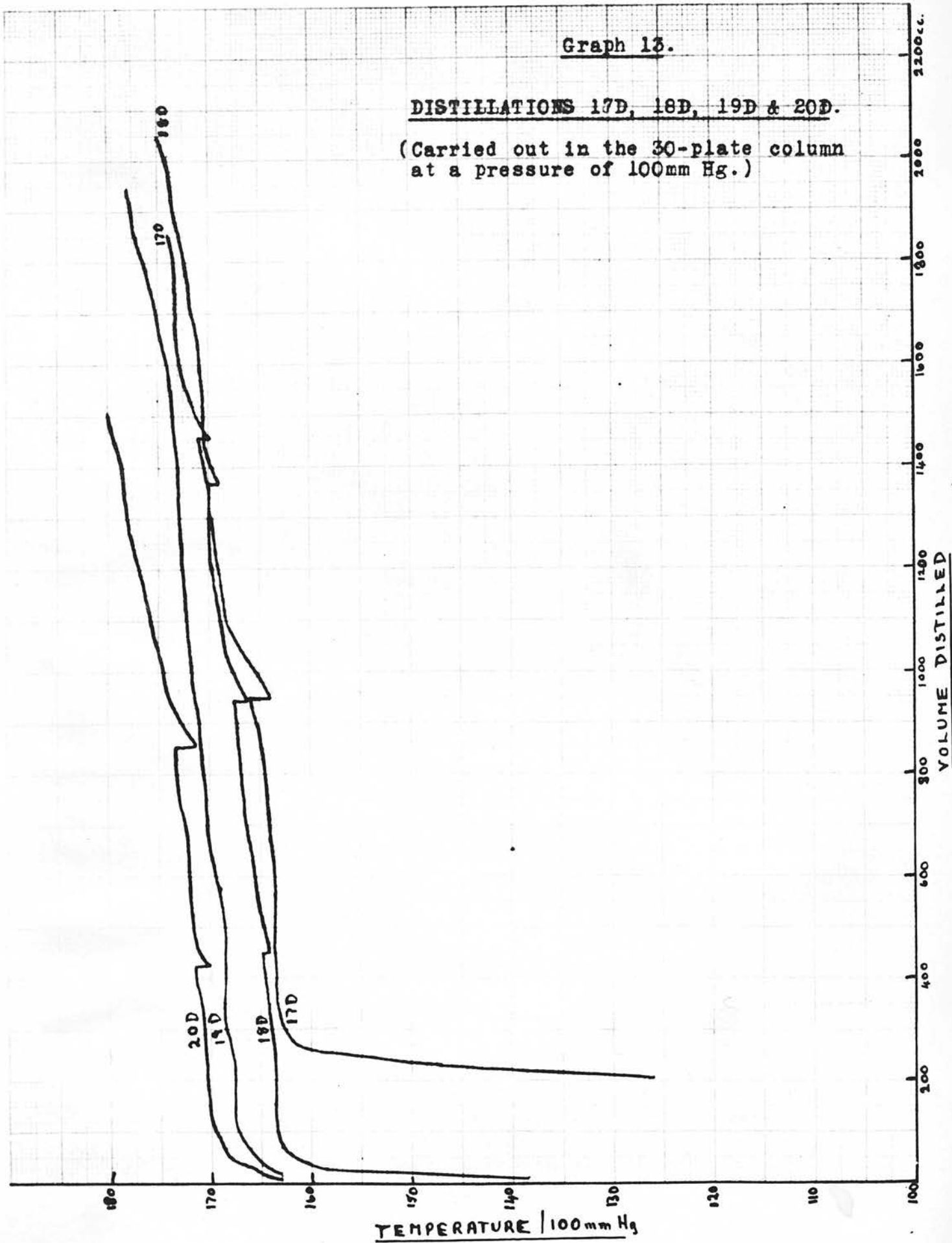
Graph 12.

DISTILLATIONS 13D, 14D, 15D & 16D.

(Carried out in the 30-plate column
at a pressure of 100mm. Hg.)

VOLUME DISTILLED

TEMPERATURE/100mm Hg
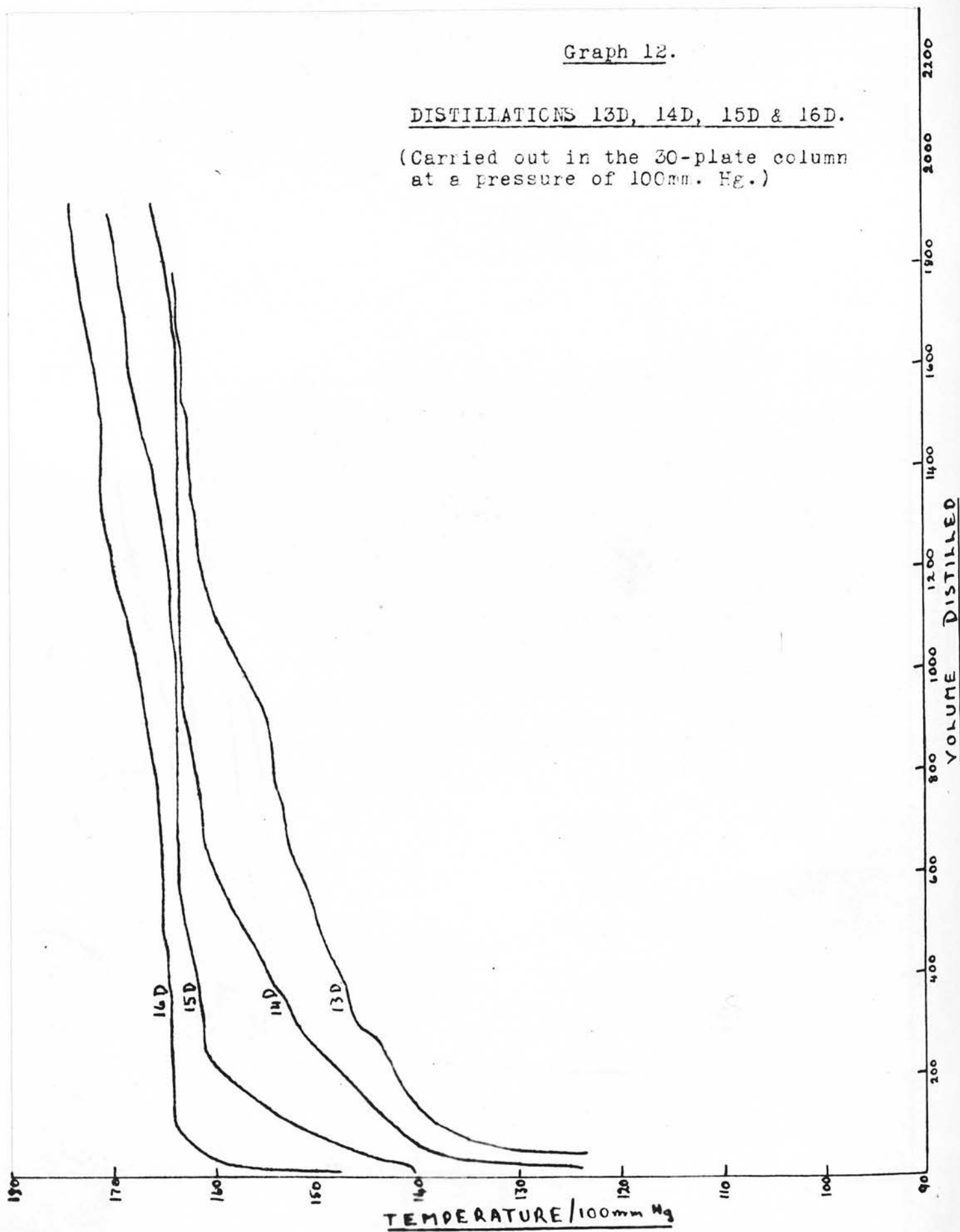
14.D.   Charge 1854gms.   Previous Residue 570gms

Fractions 1988gms.   Residue 426gms.   Loss 10gms.

Fr. No	water.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.	29.	30.	31.	32.	33
Weight		16	.	2.	6.	6.	8.	6.	10.	64.	85.	84.	112.	126.	215.	187.	790.	169.	94

15.D.   Charge 1955gms.   Previous Residue 426gms.

Fractions. 1868gms.   Residue 496gms.   Loss 17gms.

Fr. No	water.	24.	25.	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.	
Weight		22	.	17.	25.	31.	30.	48.	130.	202.	545.	182.	104.	157.	147.	228.	gms.

16.D.   Charge 2025gms.   Previous Residue 496gms.

Fractions 2020gms.   Residue 486gms.   Loss 15gms.

Fr. No	water.	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.	37.	38.	39.
Weight		12	.	6.	6.	5.	14.	25.	34.	404.	355.	278.	20.	170.	380.	144.	167.	gms.

17.D.   Charge 2095gms.   Previous Residue 433gms.

Fractions 1930gms.   Residue 594gms.   Loss 4gms.

Fr. No	water.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.	29.	30.	31.
Weight		206	.	4.	4.	3.	2.	2.	5.	7.	8.	7.	7.	13.	50.	416.

Fr. No	32.	33.	34.	35.	36.	37.	38.	39.
Weight	224.	100.	48.	44.	258.	196.	102.	224.	gms.

18.D.   Charge 2138gms.   Previous Residue 594gms.

Fractions 2143gms.   Residue 588gms.   Loss 1gm.

Fr. No	water.	23.	24.	25.	26.	27.	28.	29.	30.	31.	32.	33.	34.
Weight		10	.	2.	3.	3.	4.	4.	6.	13.	24.	246.	246.	126.	362.

Fr. No	35.	36.	37.	38.	39.	40.※
Weight	76.	350.	392.	88.	144.	44.	gms.

19.D./

Graph 14.

DISTILLATIONS 21D, 22D & 23D.

(Carried out in the 30-plate column
at pressures of 100 & 50mm Hg.)
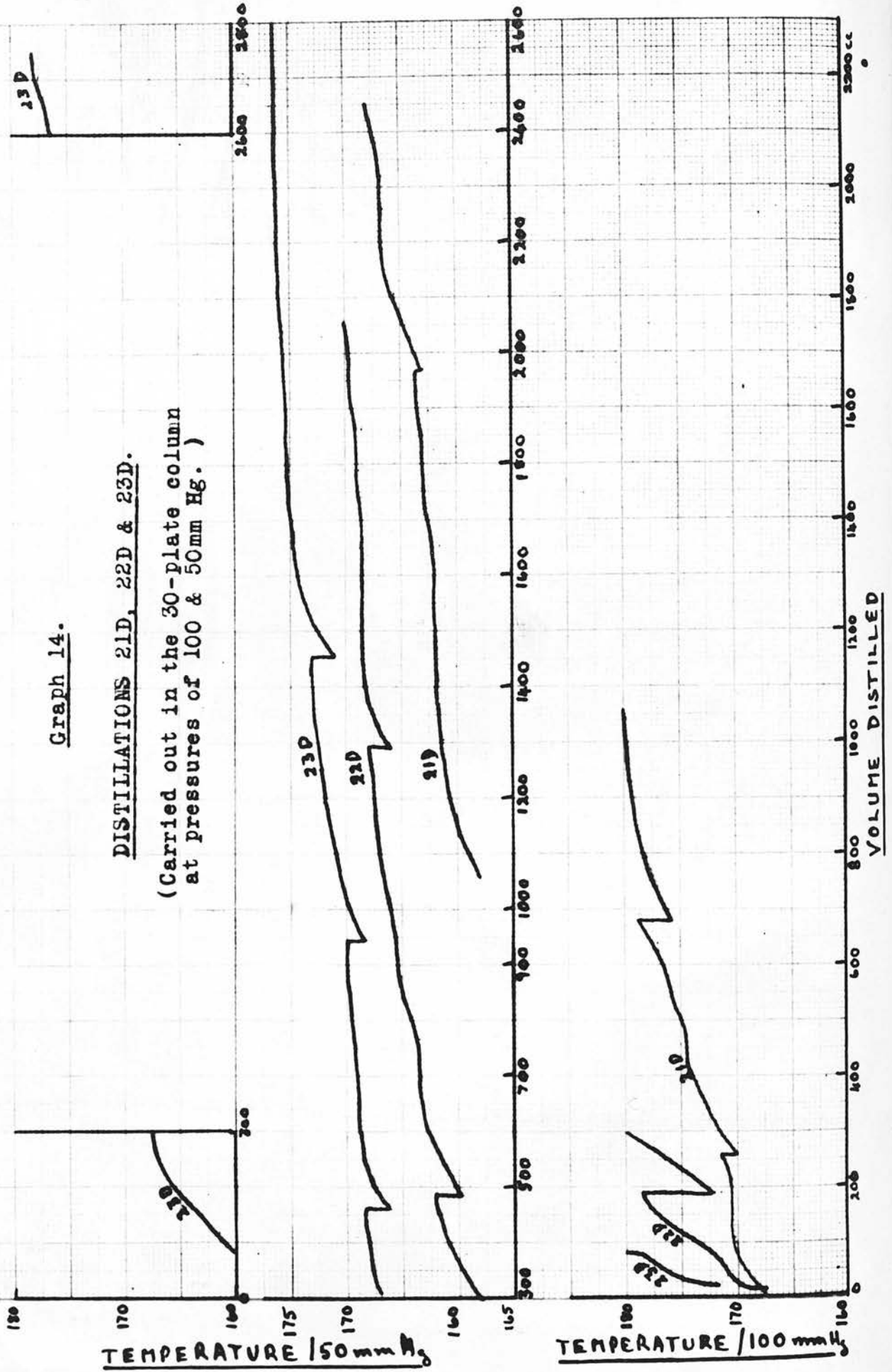
19.D.   Charge 2132gms.   Previous Residue 588gms.

Fractions 2042gms.   Residue 680gms.   Loss -2gms.

Fr. No	water.	31.	32.	33.	34.	35.	36.	37.	38.	39.	40.	41.	
Weight	12	. 8.	12.	30.	88.	186.	360.	430.	332.	218.	200.	166.	gms.

20.D.   Charge 2150gms.   Previous Residue 680gms.

Fractions 1553gms.   Residue 1270gms.   Loss 7gms.

Fr. No	water.	31.	32.	33.	34.	35.	36.	37.	38.	39.	40.	41.	
Weight	4	. 6.	10.	12.	8.	32.	64.	442.	260.	160.	168.	182.	gms.

21.D.   Charge 2150gms.   Previous Residue 1270gms.

Fractions 2552gms.   Residue 878gms.   Loss -10gms.

Fr. No	water.	35.	36.	37.	38.	39.	40.	41.	42.	43.	44.	45.	46.	
Weight	6	.30.	46.	242.	50.	40.	170.	202.	316.	194.	514.	348.	394.	gms.

22.D.   Charge 2168gms.   Previous Residue 878gms.

Fractions 2112gms.   Residue 922gms.   Loss 12gms.

Fr. No	water.	35.	36.	37.	38.	39.	40.	41.	42.	43.	44.	45.	46.	47.	
Weight	10	. 8.	10.	42.	36.	34.	52.	54.	54.	124.	178.	238.	574.	698.	gms.

23.D.   Charge 2264gms.   Previous Residue 922gms.

Fractions 3168gms.   Residue 410gms.   Loss 18gms.

Fr. No	water.	37.	38.	39.	40.	41.	42.	43.	44.	45.	46.	47.	48.	49.	50.	
Weight	10	.10.	4.	4.	14.	22.	22.	33.	35.	46.	286.	464.	612.	652.	544.	gms.

Note.   Fractions denoted with an asterisk were incomplete.

       Graphs of volume distilled against temperature of distillation for all of these D-distillations are shown in Graphs 9 - 14 inclusive.

Total/

TABLE 5.

TOTAL WEIGHT BALANCE ON BENZOL ABSORBING OIL BASES. (Table 5)

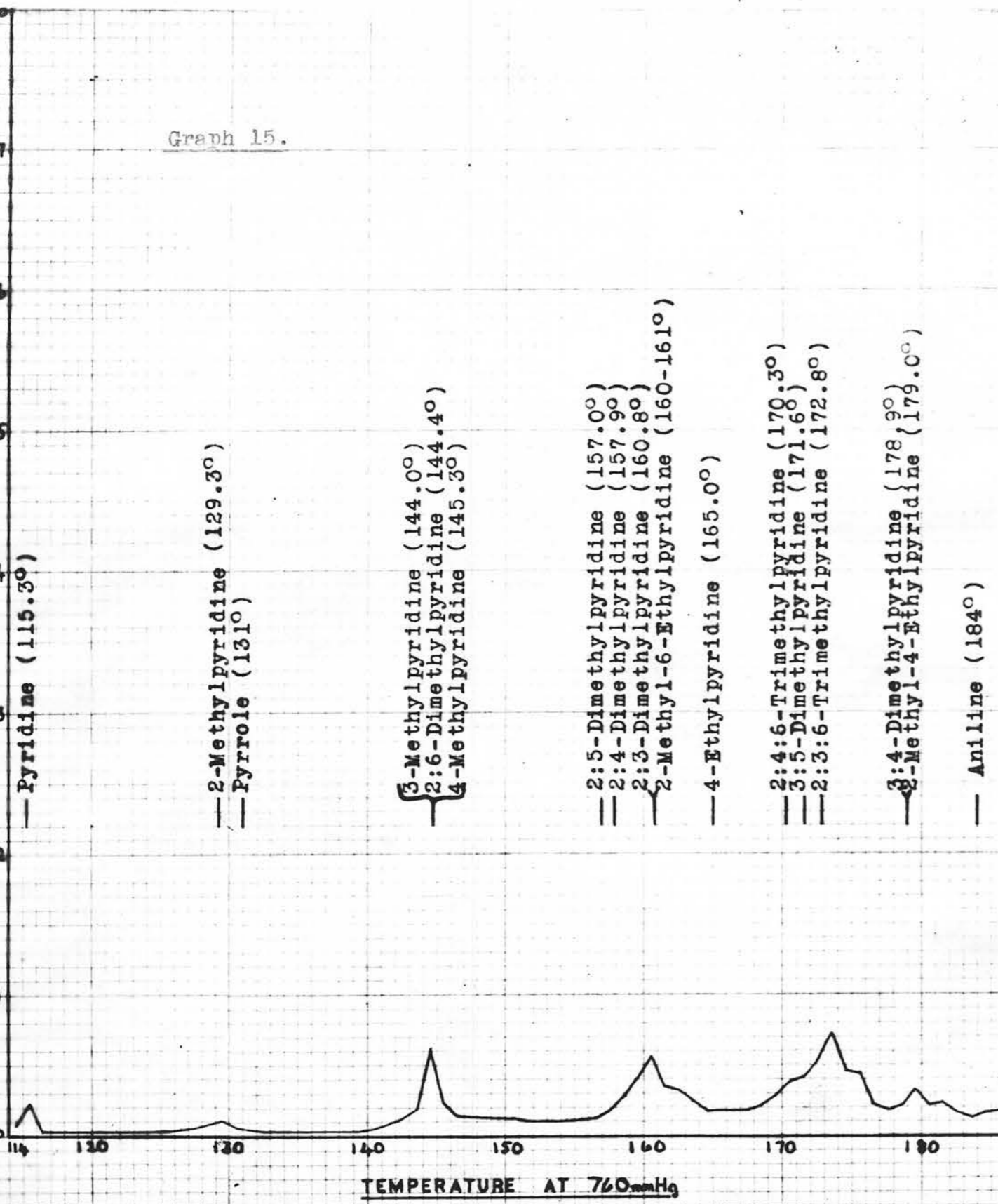Total weight of bases processed...........174.7Kg.

Loss on B-distillations...................25.5Kg.

Residue from the B-distillations..........22.3Kg.

Fraction Number	Water	D.1	D.2	D.3	D.4	D.5	D.6	D.7	D.8	D.9	D.10	D.11	D.12	D.13	D.14	D.15	D.16	D.17	D.18	D.19	D.20	D.21	D.22	D.23	D.24	D.25	D.26	D.27
B.1	8.02	0.20	0.45	0.95	0.33	0.87	1.11	1.00	0.69	0.56	0.48	0.35	0.46	0.35	0.11	0.06	0.11	0.12	0.14	0.06	0.02	0.02	0.02	-	0.01	-	-	-
B.2	0.25	-	-	-	0.02	0.21	0.21	1.22	0.57	0.75	1.18	0.56	1.14	0.23	0.07	0.04	0.07	0.08	0.09	0.04	0.01	0.01	0.01	0.01	-	-	-	-
B.3	0.03	-	-	-	-	0.02	0.01	0.07	0.06	0.05	0.27	0.22	0.32	0.26	0.08	0.05	0.08	0.09	0.11	0.04	0.01	0.01	0.01	-	0.01	-	-	-
B.4	0.04	-	-	-	-	-	-	0.03	0.05	0.03	0.18	0.12	0.27	0.32	0.13	0.07	0.13	0.15	0.18	0.07	0.02	0.02	0.02	0.01	0.01	-	-	-
B.5	0.05	-	-	-	-	-	-	0.08	0.04	0.05	0.25	0.29	0.43	0.30	0.27	0.21	0.11	0.49	0.59	0.22	0.07	0.06	0.07	0.02	0.04	0.01	0.01	0.01
B.6	0.02	-	-	-	-	0.01	0.01	0.01	0.01	0.01	0.07	0.10	0.06	0.10	0.06	0.09	0.06	0.37	0.56	0.21	0.07	0.06	0.07	0.02	0.04	0.01	0.01	0.01
B.7	0.02	-	-	-	-	-	-	0.01	-	0.01	0.03	0.06	0.03	0.06	0.06	-	0.07	0.06	0.45	0.38	0.13	0.11	0.13	0.03	0.07	0.02	0.02	0.01
B.8	0.04	-	-	-	-	-	-	0.01	0.01	0.01	0.02	0.02	0.03	0.05	0.03	0.05	0.07	0.25	0.14	1.13	0.57	0.51	0.57	0.16	0.32	0.o7	0.07	0.04
B.9	0.02	-	-	-	-	-	-	-	-	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.08	0.11	0.31	0.34	0.43	0.66	0.26	0.54	0.11	0.12	0.07
B.10	0.04	-	-	-	-	-	-	-	-	-	0.02	0.02	0.02	0.03	0.02	0.03	0.04	0.08	0.14	0.52	0.32	0.48	0.38	0.50	1.41	0.50	0.36	0.21
B.11	0.04	-	-	-	-	-	-	-	-	-	-	-	-	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.08	0.09	0.15	0.12	0.53	0.18	0.28	0.21
B.12	0.06	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	0.03	0.03	0.06	0.29	0.06	0.28	0.25
B.13	0.06	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01	0.01	0.02	0.02	0.02	0.05	0.16	0.19	0.24	0.39
B.14	0.06	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01	0.02	0.02	0.03	0.03	0.06	0.24	0.32	0.31	0.42
B.15	0.21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.17	0.24	0.30	0.29
B.16	0.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	0.04
B.17	0.87	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02	0.02	0.01	0.01	0.01	0.02	0.03	0.03	0.03
B.18	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01	0.01
B.19	0.02	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B.20	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B.21	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B.22	0.02	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B.23	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	10.01	0.20	0.45	0.95	0.35	1.11	1.34	2.43	1.43	1.48	2.52	1.76	2.78	1.73	0.86	0.63	0.77	1.78	2.54	3.07	1.72	1.89	2.18	1.31	3.84	1.74	2.08	1.9

D.26	D.27	D.28	D.29	D.30	D.31	D.32	D.33	D.34	D.35	D.36	D.37	D.38	D.39	D.40	D.41	D.42	D.43	D.44	D.45	D.46	D.47	D.48	D.49	D.50	Residue	Loss
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.10
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.03
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01
0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04
0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02
0.02	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.03
0.07	0.04	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01
0.12	0.07	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.36	0.21	0.09	0.07	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.06
0.28	0.21	0.07	0.04	0.06	0.09	0.02	0.01	0.01	0.01	0.01	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-
0.28	0.25	0.07	0.03	0.06	0.09	0.02	0.01	0.01	-	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.02
0.24	0.39	0.20	0.17	0.29	0.46	0.07	0.04	0.03	0.03	0.04	0.03	0.01	0.01	0.01	0.01	-	-	-	-	-	-	-	-	-	-	-
0.31	0.42	0.47	0.80	0.69	2.04	0.32	0.18	0.12	0.12	0.19	0.13	0.04	0.06	0.04	0.03	-	-	0.01	-	0.01	-	-	-	-	-	-
0.30	0.29	0.47	1.27	1.97	5.32	1.78	1.02	0.89	0.84	1.30	0.91	0.33	0.39	0.27	0.19	0.02	0.01	0.03	0.01	0.01	0.02	0.01	-	-	-	0.03
0.04	0.04	0.04	0.10	0.18	0.24	2.84	2.50	1.95	0.14	1.19	1.54	0.56	0.67	0.45	0.31	0.11	0.06	0.15	0.10	0.11	0.10	0.03	0.04	0.03	0.02	0.19
0.03	0.03	0.03	0.05	0.21	1.75	0.94	0.42	0.20	0.19	1.08	0.82	0.43	0.94	0.15	0.10	0.18	0.08	0.21	0.14	0.17	0.16	0.06	0.07	0.06	0.04	0.20
0.01	0.01	0.01	0.02	0.03	0.32	0.32	0.16	0.47	0.10	0.46	0.51	0.11	0.19	0.01	0.01	0.06	0.03	0.08	0.05	0.06	0.06	0.02	0.02	0.02	0.02	0.02
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-	0.01	-	-	-	-	0.01
-	-	-	-	-	0.02	0.02	0.06	0.17	0.36	0.69	0.83	0.64	0.42	0.20	0.13	0.08	0.04	0.10	0.07	0.08	0.08	0.03	0.03	0.02	0.01	-0.01
-	-	-	-	-	0.01	0.01	0.02	0.01	0.04	0.08	0.58	0.34	0.21	0.22	0.24	0.14	0.07	0.20	0.13	0.15	0.15	0.05	0.06	0.05	0.04	-
-	-	-	-	-	-	-	-	0.06	0.09	0.46	0.10	0.08	0.33	0.39		0.61	0.17	0.44	0.31	0.34	0.33	0.12	0.13	0.11	0.08	-0.04
-	-	-	-	-	-	-	-	0.01	0.02	0.07	0.06	0.05	0.08	0.08		0.08	0.19	0.28	0.37	0.90	0.50	0.18	0.20	0.16	0.12	0.03
-	-	-	-	-	-	-	-	-	-	0-03	0.01	0.01	0.04	0.07		0.07	0.10	0.11	0.14	0.89	1.45	1.11	1.19	1.00	0.75	0.08
2.08	1.99	1.51	2.58	3.54	10.39	6.39	4.46	3.90	1.94	5.18	5.97	2.64	3.03	1.80	1.56	1.35	0.75	1.62	1.32	2.72	2.86	1.61	1.74	1.45	1.08	0.53 Kg.

Graph 15.

DISTRIBUTION GRAPH FOR THE TOTAL

BENZOL ABSORBING OIL BASES.

Total weight of dry bases processed 164.7Kg.
Total Loss on B & D-distillations.. 26.0Kg
Total Residue...................... 23.3Kg
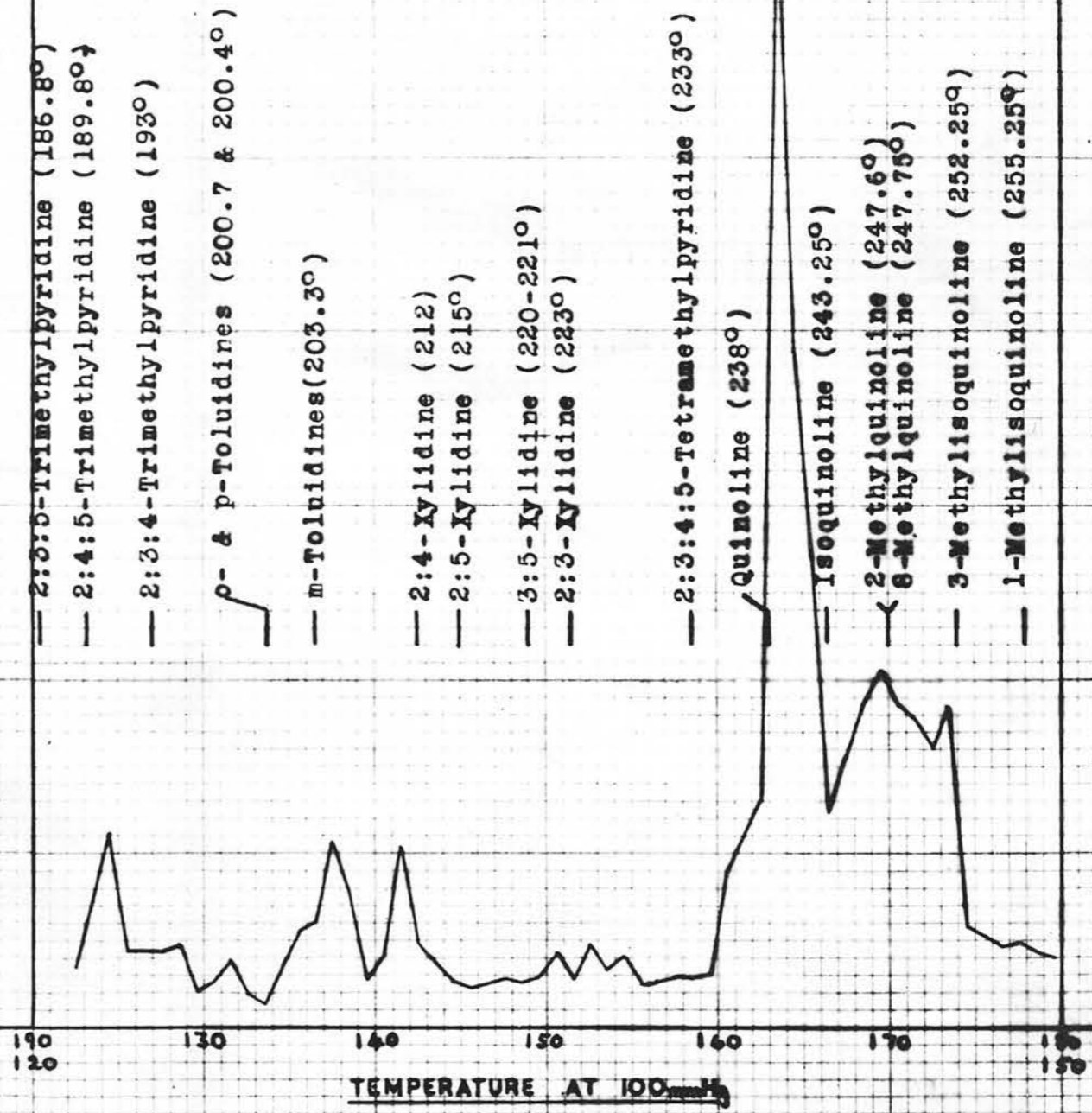
Graph 15.

WEIGHT PERCENT DISTILLED PER DEGREE

See Graph 21.

Pyridine (115.3°)

2-Methylpyridine (129.3°)
Pyrrole (131°)

3-Methylpyridine (144.0°)
2:6-Dimethylpyridine (144.4°)
4-Methylpyridine (145.3°)

2:5-Dimethylpyridine (157.0°)
2:4-Dimethylpyridine (157.9°)
2:3-Dimethylpyridine (160.8°)
2-Methyl-6-Ethylpyridine (160-161°)

4-Ethylpyridine (165.0°)

2:4:6-Trimethylpyridine (170.3°)
3:5-Dimethylpyridine (171.6°)
2:3:6-Trimethylpyridine (172.8°)

3:4-Dimethylpyridine (178.9°)
2-Methyl-4-Ethylpyridine (179.0°)

Aniline (184°)

2:3:5-Trimethylpyridine (186.8°)
2:4:5-Trimethylpyridine (189.8°)

2:3:4-Trimethylpyridine (193°)

o- & p-Toluidines (200.7 & 200.4°)

m-Toluidines(203.3°)

2:4-Xylidine (212)
2:5-Xylidine (215°)

3:5-Xylidine (220-221°)
2:3-Xylidine (223°)

2:3:4:5-Tetramethylpyridine (233°)

Quinoline (238°)

Isoquinoline (243.25°)

2-Methylquinoline (247.6°)
8-Methylquinoline (247.75°)

3-Methylisoquinoline (252.25°)

1-Methylisoquinoline (255.25°)

TEMPERATURE AT 760mmHg

TEMPERATURE AT 100mmHg

TEMPERATURE AT 50mm

Total Weight Balance for the Benzol Absorbing Oil Bases.

"Weight distilled / temperature of distil-
lation balances" were calculated for each of these
batches using the same assumptions and procedure as
are described in the section on the C-distillations.
The weight balance for the total crude Benzol Absorbing
Oil bases was then obtained by multiplying the weight
of each individual cut by the factor - Weight of the
total B-fraction / weight of batch taken.

The results are shown in Table 5.

A graph (15) was then prepared of the weight
distilled per degree centigrade against the temperature
of distillation, making use of this table, the
distribution inside the various cuts being estimated
from the distillation graphs.   The boiling points
of the bases which have already been isolated from
coal tar are indicated on this graph, and it can be
seen that the distillation "peaks" correspond very
well with these.

Examination of the D-Fractions.

The specific gravities and refractive
indices of all the D-Fractions were determined and
are shown in Table 6.   From a study of these constants
and of Graph 15 it can be seen that a good degree of
separation was achieved in these D-distillations.

Table 6/

Graph 16.

DENSITIES & REFRACTIVE INDICES OF D-FRACTIONS.
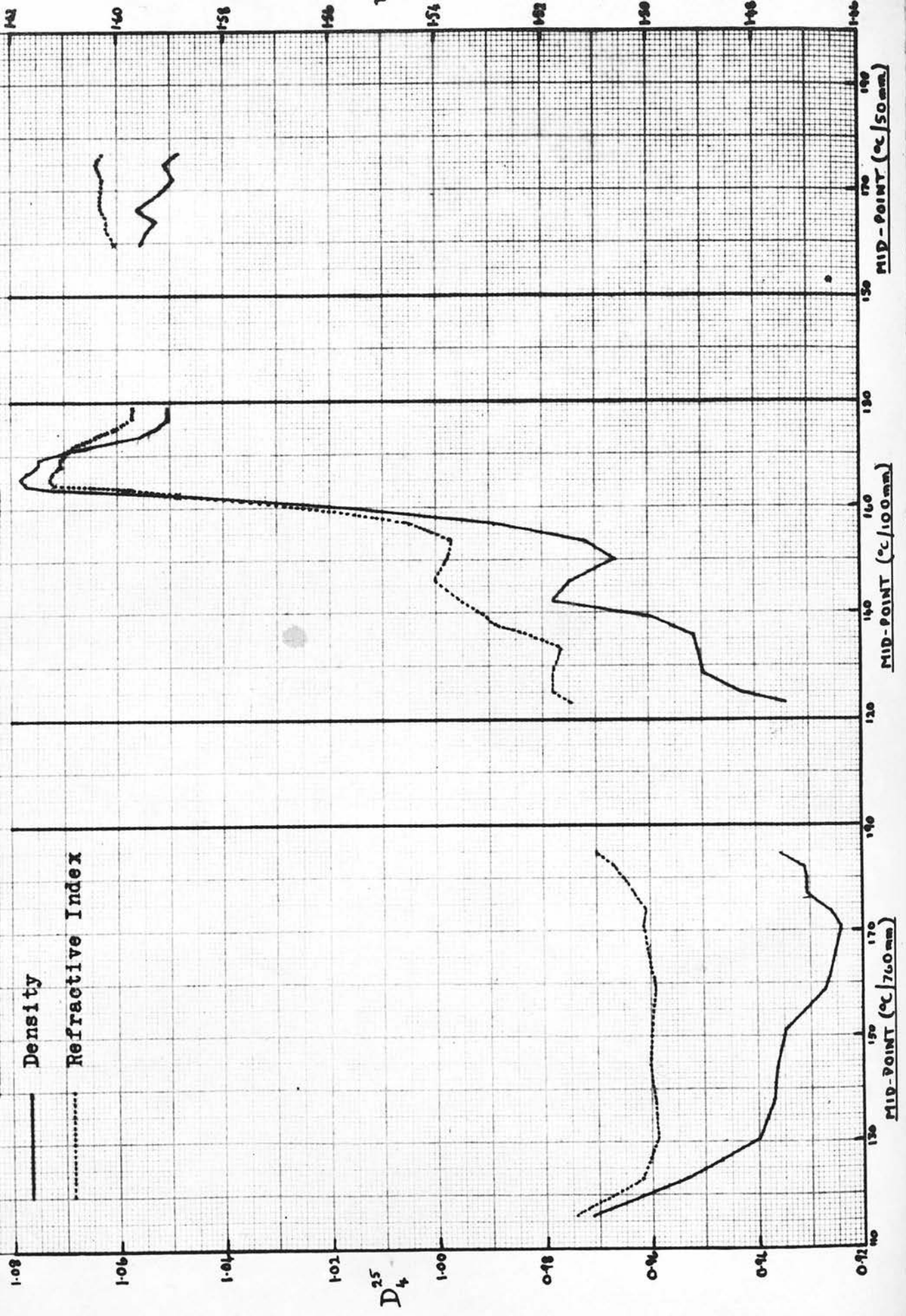
Table 6.

Fract. No.	Distn. Range	D_4^{25}	n_D^{25}
D.1	0-115°/760mm.		1.4551
D.2	115-117° "	0.9712	1.5041
D.3	117-129° "	0.9534	1.5020
D.4	129-132° "	0.9397	1.4989
D.5	132-143.5° "	0.9371	1.4992
D.6	143.5-145.5° "	0.9364	1.5000
D.7	145.5-157° "	0.9346	1.4998
D.8	157-160° "	0.9276	1.4990
D.9	160-162° "	0.9263	1.4992
D.10	162-169° "	0.9252	1.5002
D.11	169-172° "	0.9243	1.5011
D.12	172-175° "	0.9265	1.5008
D.13	175-179° "	0.9304	1.5030
D.14	179-181° "	0.9306	1.5050
D.15	181-183° "	0.9310	1.5064
D.16	183-186° "	0.9352	1.5100
D.17	122-124°/100mm.	0.9341	1.5145
D.18	124-126° "	0.9427	1.5180
D.19	126-131° "	0.9494	1.5180
D.20	131-135° "	0.9502	1.5165
D.21	135-137° "	0.9516	1.5232
D.22	137-138.5° "	0.9550	1.5288
D.23	138.5-140° "	0.9596	1.5302
D.24	140-144° "	0.9774	1.5350
D.25	144-148° "	0.9745	1.5400
D.26	148-152° "	0.9659	1.5380

Table 6. (Continued)

Fract. No.	Distn. Range	D_4^{25}	n_D^{25}
D.27	152-155°/100mm.	0.9716	1.5370
D.28	155-158.5° "	0.9890	1.5450
D.29	158.5-161.5° "	1.0200	1.5650
D.30	161.5-163° "	1.0490	1.5883
D.31	163-164° "	1.0718	1.6075
D.32	164-165° "	1.0773	1.6120
D.33	165-166° "	1.0781	1.6125
D.34	166-167.5° "	1.0771	1.6120
D.35	167.5-168.5° "	1.0750	1.6105
D.36	168.5-170° "	1.0748	1.6105
D.37	170-172° "	1.0680	1.6090
D.38	172-173° "	1.0606	1.6062
D.39	173-174° "	1.0559	1.6040
D.40	174-176° "	1.0526	1.6003
D.41	176-178° "	1.0502	1.5970
D.42	178-180° "	1.0505	1.5970
D.43	158-161°/50mm.	1.0557	1.6005
D.44	161-163°/50mm.	1.0541	1.6020
D.45	163-165° "	1.0526	1.6020
D.46	165-168° "	1.0562	1.6030
D.47	168-170° "	1.0523	1.6030
D.48	170-174° "	1.0491	1.6028
D.49	174-176° "	1.0511	1.6038
D.50	176-178° "	1.0481	1.6028

Graph/

Graph 16 shows the densities and refractive indices of the fractions plotted against the mid-points of their distillation ranges.   The "peaks" which appear on this graph at about 128° & 145°C./100mm. are explained by the presence of primary aromatic amines which were detected by qualitative tests, and the higher densities and refractive indices obtained for the fractions boiling over 160°C./100mm. are due to the quinoline and isoquinoline homologues which form the main bulk of these fractions.

The further examination of the D-fractions was confined to certain chosen ranges from which it was hoped that previously unidentified coal tar bases might be isolated.   A description of this work is given in the next section. (Distillations 2.E. - 9.E.)

E-Distillations/

E-Distillations.

The isolation of pure bases from the C- or D-fractions without further fractional distillation would have been, in most cases, an arduous task, and for this reason it was decided to subject certain chosen ranges to further fractional distillation in the "100-plate" column.   The fractions chosen were those from which it was considered most likely that previously unidentified bases might be isolated.

The chosen fractions were first freed from traces of non-basic material which had been present in the crude bases and were still present at this stage.   This was accomplished by acidifying with concentrated hydrochloric acid, removing the non-basic material by either steam distillation or extraction with ether and regenerating the bases by neutralisation with caustic soda.   In batches 1.E - 4.E the non-basic material was removed by steam distillation and the purified bases were recovered from the neutralised solution by this means also.   In batches 5.E - 8.E steam distillation was unsuitable owing to the high boiling ranges of the fractions, so the non-basic material was removed by extraction with ether and the purified bases were recovered from the neutralised solution by extraction with ether and removal of the ether from the resulting extract by distillation, after/

after drying over caustic soda.   The purified bases

were dried by refluxing over solid caustic soda prior

to distillation in the "100-plate column".

The E-distillations were carried out in the

"100-plate" column under diminished pressure at a

boil-up rate of 1000mls./hour and a take-off rate of

10mls./hour, the procedure being as follows :-

The charge was weighed into the boiler

flask, which had previously been packed with glass wool

to prevent bumping during the distillation.   The

vacuum was set to the required value.   The boil-up

rate was then adjusted to 1000mls./hour and the column

flooded by closing the magnetic valve. (Note: When

traces of water were found to be still present, these

were removed prior to flooding.)   After slowly de-

flooding the column, the vacuum and boil-up rate were

checked and the column heaters brought to the correct

temperature as indicated by zero readings on the

differential thermocouple galvonometer.   The column

was then run to equilibrium for 10 - 12 hours and the

take-off started at the correct rate.   Distillation

was then continued, taking short range cuts to

correspond with distillation "flats", and maintaining

the correct boil-up rate and adiabatic conditions

throughout the column.

The still was run continuously throughout

each batch, being left on total reflux overnight.

After/

After the installation of the Tektor Proximity Switch,
however, it was sometimes possible to leave the still
taking off overnight when on a distillation "flat".

Distillation 1.E.

Naphthalene Oil Bases. C.21 (131-135°C./100mm.)

This range was refractionated in the hope
of isolating 2:3:5:6- and 2:3:4:6-tetramethylpyridines,
which boil at 131° and 135°C./100mm. respectively (24)
and have not hitherto been reported as coal tar
constituents.

3.76 Kg. of this cut was obtainable from
184 Kg. of the crude bases (i.e. 2.04%).

A portion of the fraction was first freed
from non-basic material.   A yield of 2.10% non-basic
material was obtained.

A sample of the purified bases was then
fractionated in the "100-plate" column at a pressure
of 100 mm. Hg.   The weight balance for the distil-
lation is shown below and the distillation graph is
shown in Graph 17.

Charge..........916gms. D_4^{25} 0.9569 n_D^{25} 1.5364

Fractions.......766gms.

Residue.........140gms.

Loss............ 10gms.

Fract. No./

Graph 17

DISTILLATION 1.E

(Carried out in the 100-plate column
at a pressure of 100mm. Hg.)
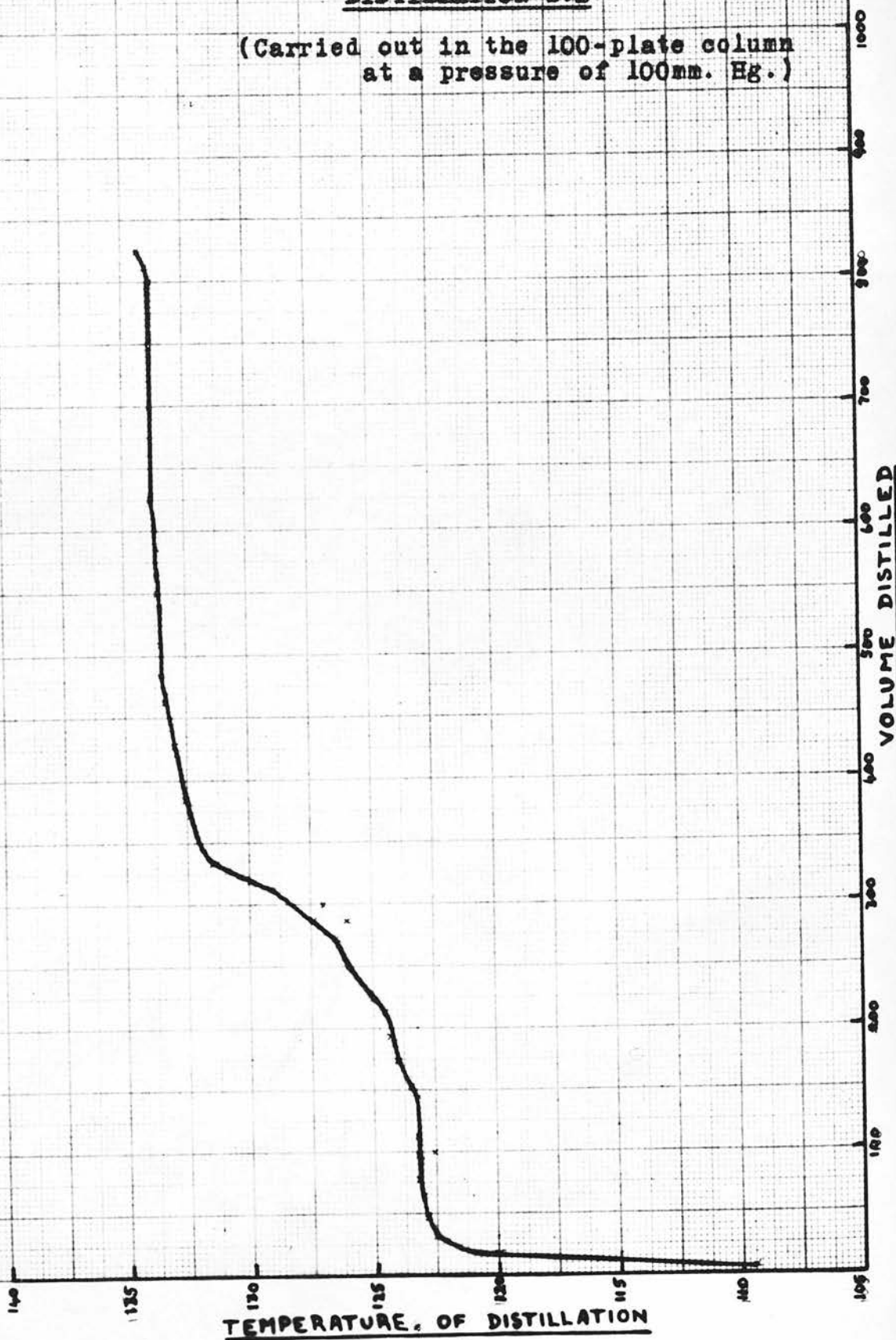
Fract. No.	Distn. Range	Weight	n_D^{25}
Water		6gms.	
1E/1	109-122.5°/100mm.	23gms.	1.5055
1E/2	122.5-123.5°/100mm.	108gms.	1.5040
1E/3	123.5-125° /100mm.	69gms.	1.5090
1E/4	125-130° /100mm.	80gms.	1.5090
1E/5	130-131.5°/100mm.	13gms.	1.5168
1E/6	131.5-133° /100mm.	69gms.	1.5280
1E/7	133-133.5°/100mm.	92gms.	1.5402
1E/8	133.5-133.8°/100mm.	101gms.	1.5518
1E/9	133.8-133.8°/100mm.	148gms.	1.5590
1E/10	133.8-133.9°/100mm.	32gms.	Solid
1E/11	133.9-134.4°/100mm.	25gms.	Solid

From the table and graph it can be seen that the only distillation "flats" obtained were at about 123°C./100mm. and 134°C./100mm., and that no "flat" was obtained corresponding to the boiling point of 2:3:5:6-tetramethylpyridine.

Converting the distillation temperature of the 123°C. "flat" to 760mm. a value of 190°C. was obtained which is in good agreement with the boiling point given for 2:4:5-trimethylpyridine (9), a compound which has been isolated from coal tar previously. That this "flat" does consist mainly of 2:4:5-trimethylpyridine has been proved, and the isolation of this compound is fully described in the next section.

Converting/

Converting the distillation temperature of the 134°C. "flat" to 760mm. a value of 201°C. was obtained which is close to the values given for the o- and p-toluidines (200.7 and 200.4°C. respectively) which have been isolated from coal tar previously (17). As the fractions distilling in this region were found to consist almost entirely of primary bases it was assumed that these fractions consisted essentially of o- and p-toluidines.   The solid distilling at the top of the range, on recrystallisation from ether, gave a melting point of 45°C. which is identical with that given for p-toluidine, and a mixed melting point of the solid with an authentic sample of p-toluidine showed no lowering.

As this investigation was not concerned with primary bases this range was not examined further.

Distillation 2.E.

Benzol Absorbing Oil Bases. D.19. (126-131°C./100mm.)

This range was refractionated in the hope of isolating 2:3:5:6-tetramethylpyridine.

3.07 Kg. of this cut was obtainable from 175 Kg. of the crude wet bases (i.e. 1.76%).

A portion of the fraction was first freed from non-basic material.   A yield of 0.78% non-basic material was obtained.

A/

Graph 18

DISTILLATIONS 2E & 3E.

(Carried out in the 100-plate column
at a pressure of 100mm. Hg.)
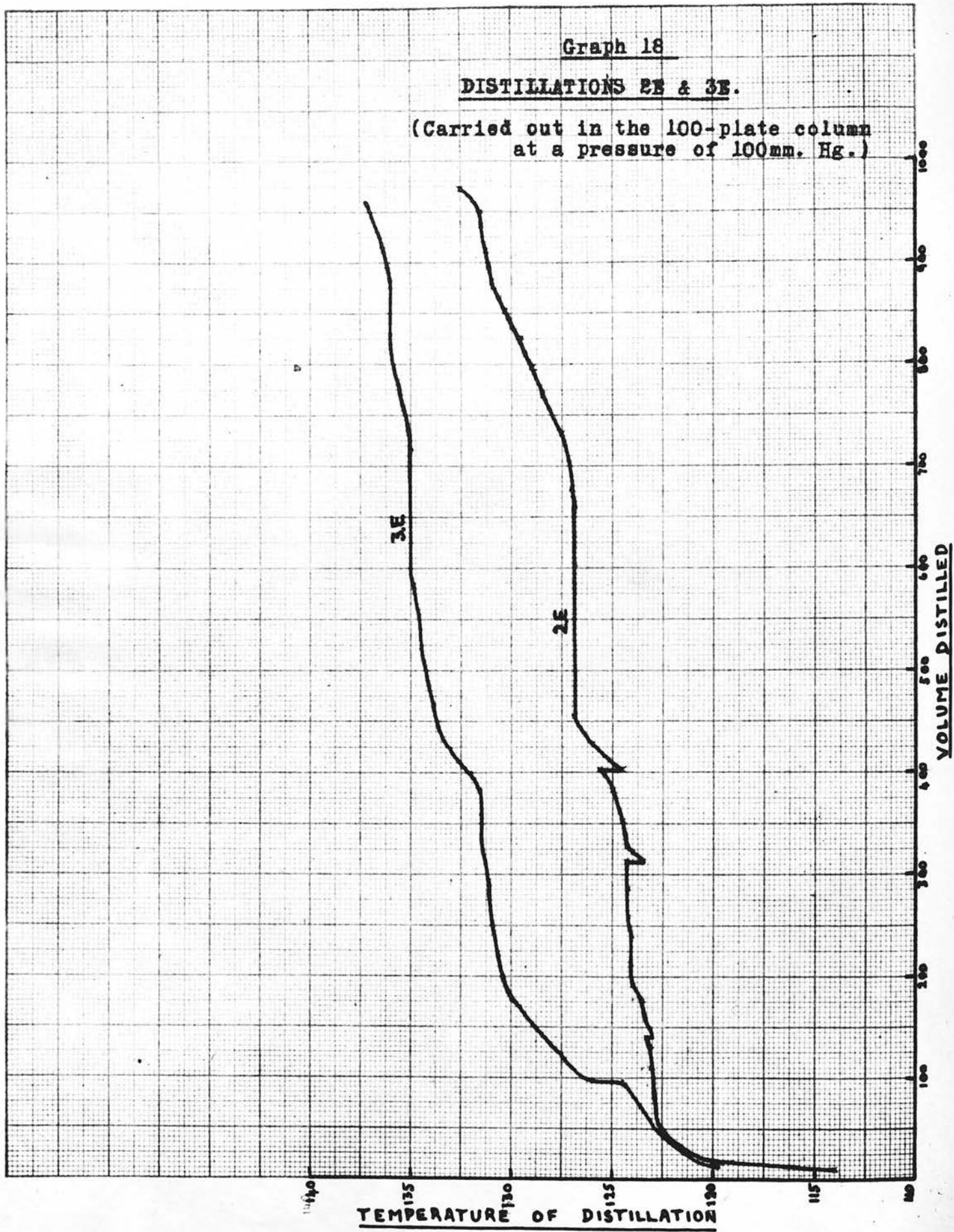
VOLUME DISTILLED

TEMPERATURE OF DISTILLATION

A sample of the purified bases was then
fractionated in the "100-plate" column at a pressure of
100 mm. Hg.   The weight balance for this distillation
is shown below and the distillation graph is shown
in Graph 18.

Charge.......1000gms. D_4^{25} 0.9494 n_D^{25} 1.5180

Fractions.... 863gms.

Residue...... 100gms.

Loss......... 37gms.

Fract. No.	Distn. Range	Weight	n_D^{25}
Water		10gms.	
2E/1	114-122.5°/100mm.	32gms.	1.5030
2E/2	122.5-123° /100mm.	55gms.	1.5050
2E/3	123-124° /100mm.	79gms.	1.5090
2E/4	124-124.5°/100mm.	137gms.	1.5255
2E/5	124.5-126.9°/100mm.	91gms.	1.5242
2E/6	126.9-127° /100mm.	193gms.	1.5190
2E/X	124.8-126.9°/100mm.	13gms.	rejected
2E/7	127-128.5°/100mm.	79gms.	1.5175
2E/8	128.5-130° /100mm.	56gms.	1.5130
2E/9	130-131° /100mm.	42gms.	1.5185
2E/10	131-131.3°/100mm.	44gms.	solid
2E/11	131.3-131.4°/100mm.	20gms.	solid
2E/12	131.4-132.5°/100mm.	22gms.	solid

From the above table and the distillation
graph it can be seen that the "flats" occurred as
follows/

follows :-

     1) At about 123°C./100mm.   This "flat" was assumed to be of the same composition as the first "flat" in distillation 1.E.

     2) At 124 - 124.5°C./100mm.   The examination of this fraction is described in the next section.

     3) At 126°C./100mm.   Converting to 760mm., a distillation temperature of 193°C. was obtained which corresponds well with the value of 192-193°C. given for 2:3:4-trimethylpyridine (8), a compound which has been reported as a coal tar constituent previously.   The isolation of this compound is described in the next section.

     4) At 131 - 131.5°C./100mm.   The isolation of 2:3:5:6-tetramethylpyridine from this range is described in the next section.

Distillation 3.E.
Benzol Absorbing Oil Bases D.20 & 21.   (131-137°C./100mm.)

     This range was refractionated in the hope of isolating 2:3:4:6-tetramethylpyridine.

     3.64 Kg. of this range was obtainable from 175 Kg. of the crude wet bases. (i.e. 2.06%)

     The fractions D.20 & D.21 were mixed in quantities proportional to their total yields.   A portion of the mixture was freed from non-basic material and fractionated in the "100-plate" column under/

under a pressure of 100mm. Hg.   The yield of non-
basic material amounted to 0.80%.   The weight balance
is shown below and the distillation graph is shown
in Graph 18.

Charge...........1000gms.

Fractions........ 886gms.

Residue......... 98gms.

Loss............ 16gms.

Fract. No.	Distn. Range	Weight	n_D^{25}
Water		6gms.	
3E/1	115-122.5°/100mm.	32gms.	1.5065
3E/2	122.5-124° /100mm.	33gms.	1.5145
3E/3	124-127° /100mm.	24gms.	1.5147
3E/4	127-128.5°/100mm.	31gms.	1.5147
3E/5	128.5-130° /100mm.	28gms.	1.5148
3E/6	130-130.8°/100mm.	31gms.	1.5208
3E/6a	130.8-131° /100mm.	34gms.	1.5225
3E/7	131-131.5°/100mm.	104gms.	solid
3E/8	131.5-132° /100mm.	36gms.	solid
3E/9	132-133.5°/100mm.	43gms.	1.5095
3E/10	133.5-134.5°/100mm.	69gms.	1.5095
3E/11	134.5-135° /100mm.	62gms.	1.5160
3E/12	135-135.2°/100mm.	128gms.	1.5202
3E/13	135.2-136° /100mm.	82gms.	1.5232
3E/14	136-137.2°/100mm.	143gms.	1.5250

From/

From the distillation graph it can be seen
that the "flats" occurred as follows :-

1) At 131 - 131.5°C./100mm.   The examina-
tion of this range is described in the next section.

2) At 135°C./100mm.   The isolation of
2:3:4:6-tetramethylpyridine from this range is
described in the next section.

3) At 136°C./100mm.   The fraction 3E/14 was
found to consist almost entirely of primary bases.
Converting the distillation temperature to 760mm.,
a value of 204.5°C. was obtained which is fairly close
to the literature value for the boiling point of
m-toluidine (203.3°C), a compound which has been
previously identified in coal tar.   This range,
therefore, was not examined further.

Distillation 4.E.

Benzol Absorbing Oil Bases D.27 & 28.   (152-158.5°C./100mm.)

Pentamethylpyridine has neither been
isolated from any natural source nor has it been
prepared, but, calculating its boiling point by means
of an empirical formula derived by Eguchi (9), a
value of 227.3°C./760mm. was obtained (i.e. approxi-
mately 155.5°C./100mm.).   This compound would, in
all probability, be solid at room temperature and,
therefore, would be easily isolated from narrow
boiling range fractions.

This/

Graph 19

DISTILLATION 4E

(Carried out in the 100-plate column
at a pressure of 100mm. Hg.)

VOLUME DISTILLED

TEMPERATURE OF DISTILLATION
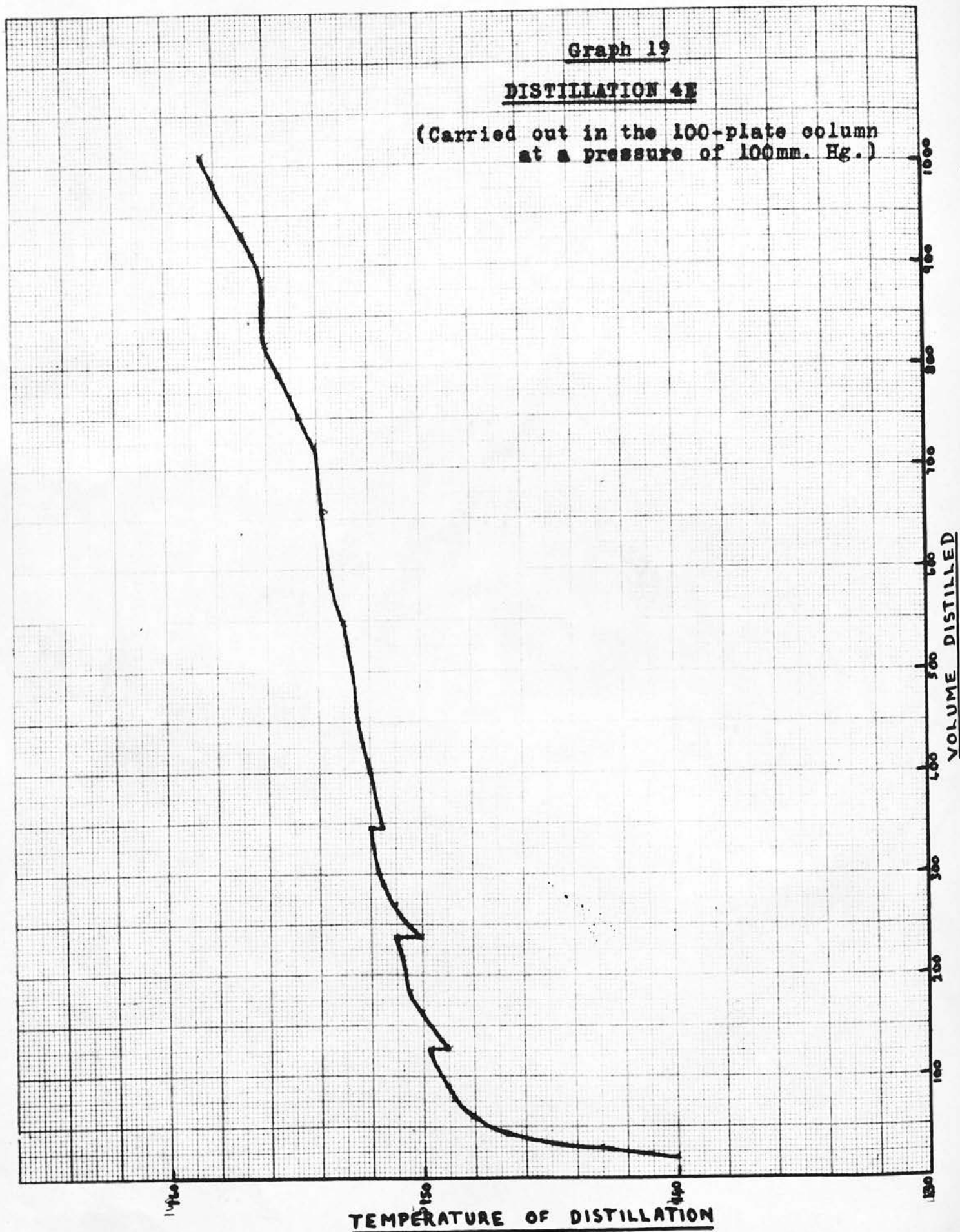
This range (152-158.5°/100mm.), therefore, was refractionated in the hope of isolating penta-methylpyridine, in spite of the fact that these D-fractions had been found to consist essentially of primary bases.

3.50 Kg. of this range was obtainable from 175 Kg. of the crude wet bases. (i.e. 2.0%)

The fractions D.27 & D.28 were mixed in quantities proportional to their total yields.   A portion of the mixture was freed from non-basic material and fractionated in the "100-plate" column under a pressure of 100mm. Hg.   The yield of non-basic material amounted to 3.15%.   The weight balance is shown below and the distillation graph in Graph 19.

Charge 1090gms.   Fractions 980gms.   Residue 110gms.

Fract. No.	Distn. Range .	Weight	n_D^{25}
Water		20gms.	
4E/1	140-148° /100mm.	36gms.	1.5177
4E/2	148-150° /100mm.	88gms.	1.5240
4E/3	150-151.5°/100mm.	136gms.	1.5335
4E/4	151.5-152° /100mm.	106gms.	1.5363
4E/5	152-152.5°/100mm.	60gms.	1.5380
4E/6	152.5-153° /100mm.	84gms.	1.5370
4E/7	153-154° /100mm.	138gms.	1.5355
4E/8	154-155° /100mm.	75gms.	1.5355
4E/9	155.156° /100mm.	53gms	1.5360
4E/10	156-156.5°/100mm.	84gms.	1.5380
4E/11	156.5-158.5°/100mm.	100gms.	1.5390

No/

No solid material could be frozen out from any of these fractions even on cooling to as low a temperature as -70°C., and, as it was found that all the fractions consisted essentially of primary amines, they were not examined further.

Batches D.44 - D.50 inclusive were refractionated, as this range had not been exhaustively examined in the past and as considerable doubts were entertained as to the reliance which could be placed on the weight balance obtained for this range in the D-distillations.

All these batches were refractionated in the "100-plate" column under a pressure of 50mm. Hg.

Distillation 5.E.

Benzol Absorbing Oil Bases D.44 & 45. (161-165°C./50mm.)

The fractions D.44 and D.45 were mixed in quantities proportional to their yields, and a portion of the mixture was freed from non-basic material which amounted to 5.12%. The weight balance for the distillation of this purified material is shown below and the distillation graph is shown in Graph 20.

Charge..........1164gms.

Fractions.......1072gms.

Residue........ 70gms.

Loss........... 22gms.

Fract. No./

Graph 20.

DISTILLATIONS 5E, 6E, 7E & 8E.

(Carried out in the 100-plate column
at a pressure of 50mm Hg.)

VOLUME OF DISTILLATE

TEMPERATURE OF DISTILLATION
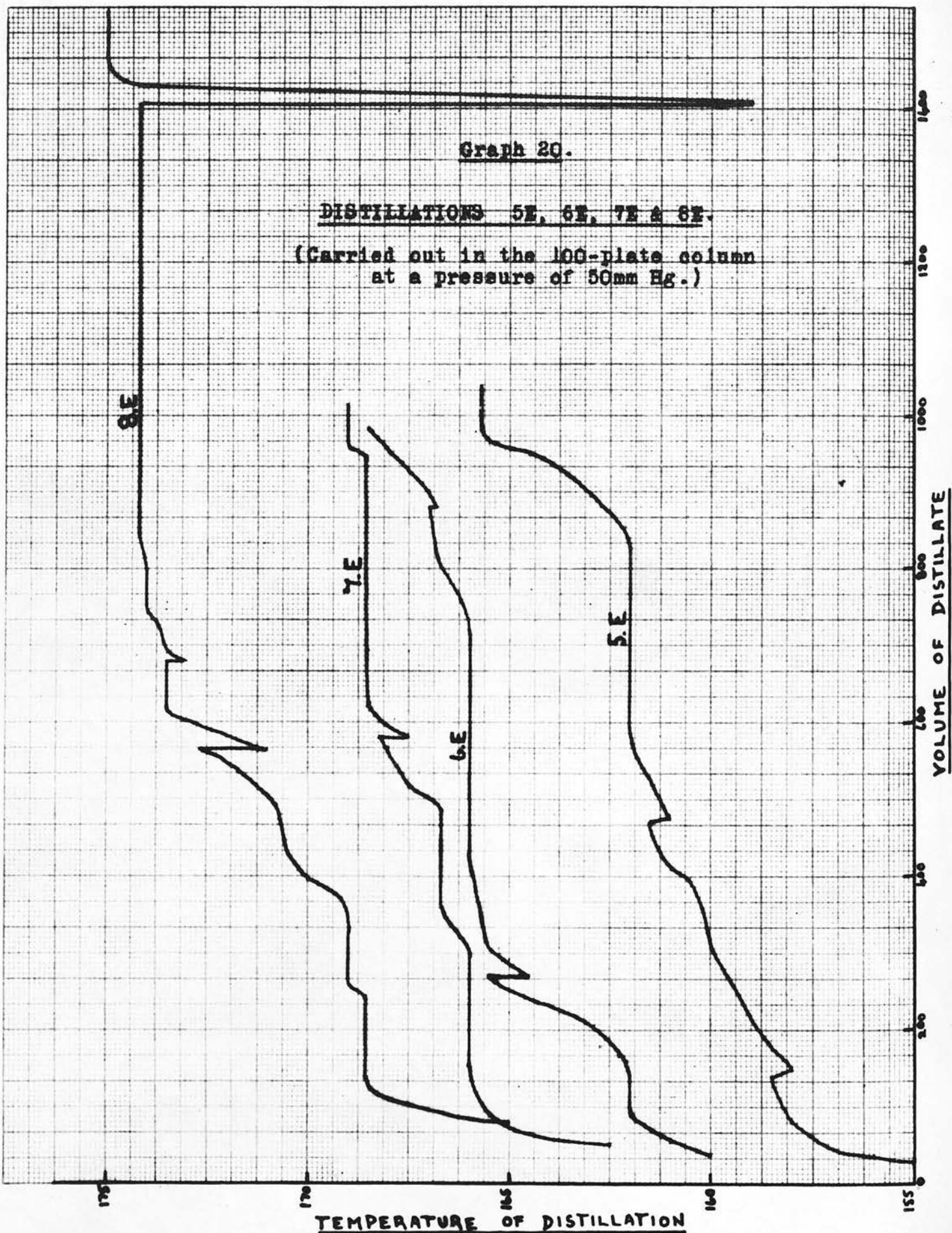
Fract. No.	Distn. Range	Weight	n_D^{25}
Water		16gms.	
5E/1	154.8-157° /50mm.	8gms.	Solid
5E/2	157-158° /50mm.	21gms.	1.5995
5E/3	158-159° /50mm.	36gms.	1.6042
5E/4	159-160° /50mm.	127gms.	1.6070
5E/5	160-161° /50mm.	122gms.	1.6080
5E/6	161-162° /50mm.	190gms.	1.6062
5E/7	162-162° /50mm.	128gms.	1.6020
5E/8	162-162.3°/50mm.	158gms.	1.6020
5E/9	162.3-165.8°/50mm.	112gms.	1.5980
5E/10	165.8-165.8°/50mm.	58gms.	1.5975

Distillation 6.E.

Benzol Absorbing Oil Bases D.46.   (165-168°/50mm.)

The yield of non-basic material from this fraction amounted to 3.85%.   The purified material was charged on top of the residue from the previous distillation.   The weight balance for the distillation is shown below and the distillation graph is shown in Graph 20.

        Charge..........1066gms + 70gms of previous residue

        Fractions.......1012gms.

        Residue......... 132gms.

        Loss............ -8gms.

Fract. No./

Fract. No.	Distn. Range	Weight	n_D^{25}
Water		26gms.	
6E/0		5gms.	
6E/1	160-162° /50mm.	64gms.	1.5995
6E/2	162-162.3°/50mm.	78gms.	1.5985
6E/3	162.3-165.5°/50mm.	130gms.	1.5945
6E/4	165.5-166° /50mm.	265gms.	1.6060
6E/5	166-166.2°/50mm.	206gms.	1.6110
6E/6	166.2-166.8°/50mm.	62gms.	1.6120
6E/7	166.8-167° /50mm.	90gms.	1.6136
6E/8	167-168.5°/50mm.	86gms.	1.6085

Distillation 7.E.

Benzol Absorbing Oil Bases D.47.   (168-170°C./50mm.)

The yield of non-basic material from this fraction amounted to 5.45%.   The purified material was charged on top of the residue from the previous distillations.   The weight balance for the distillation is shown below and the distillation graph is shown in Graph 20.

Charge.........1066gms. + 132gms. of previous residue.

Fractions.....1036gms.

Residue....... 172gms.

Loss.......... -10gms.

Fract. No./

Fract. No.	Distn. Range	Weight	n_D^{25}
Water		42gms.	
7E/0		10gms.	
7E/1	162.5-166° /50mm.	54gms.	1.6018
7E/2	166-166.2°/50mm.	170gms.	1.6093
7E/3	166.2-166.7°/50mm.	96gms.	1.6110
7E/4	166.7-167° /50mm.	156gms.	1.6120
7E/5	167-168.5°/50mm.	108gms.	1.6060
7E/6	168.5-169° /50mm.	352gms.	1.6030
7E/7	169-169° /50mm.	48gms.	1.6010

Distillation 8.E.

Benzol Absorbing Oil Bases D.48-50. (170-178°C./50mm)

Fractions D.48, D.49 and D.50 were mixed in quantities proportional to their total yields. The non-basic material removed from this fraction amounted to 5.60%. The purified material was charged on top of the residue from the previous distillations. The weight balance for the distillation is shown below and the distillation graph is shown in Graph 20.

Charge........1470gms. + 172gms. of previous residue.

Fractions.....1542gms.

Residue....... 110gms.

Loss.......... -10gms.

Fract. No./

DISTRIBUTION GRAPH FOR THE HIGHER BENZOL ABSORBING OIL BASES. (Graph 21.)

(Obtained from the distillations 5E - 8E, the weights being those obtainable from 174Kg. of the total crude wet bases.)

5:8-Dimethylquinoline (>270°) ?

6-Methylisoquinoline (265.8°)
5- or 7-Methylisoquinoline (264.9°)
4-Methylquinoline (264.2°)
3-Methylquinoline (262.7°)
1:3-Dimethylisoquinoline (262.4°)

3-Methylquinoline (259.55°)
6-Methylquinoline (258.6°)
7-Methylquinoline (257.6°)

2:8-Dimethylquinoline (255.25°)

TEMPERATURE OF DISTILLATION (PRESSURE - 50 mm Hg)

TOTAL WEIGHT PER ½°C (GMS.)
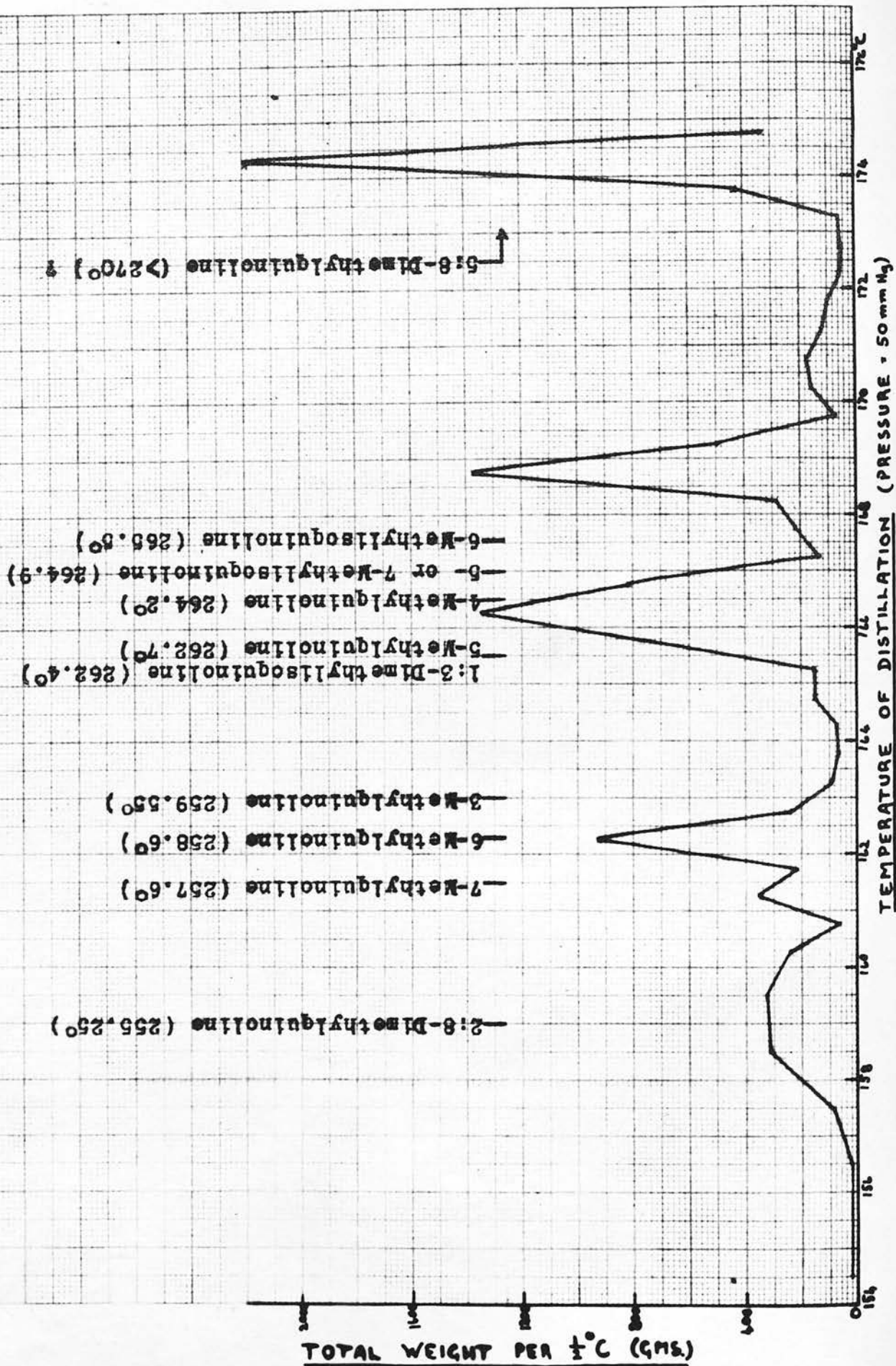
Fract. No.	Distn. Range	Weight	n_D^{25}
Water		76 gms.	
8E/0		4 gms.	
8E/1	165-168.5°/50mm.	58 gms.	1.6005
8E/2	168.5-169° /50mm.	136 gms.	1.6005
8E/3	169-169.2°/50mm.	110 gms.	Solid
8E/4	169.2-170° /50mm.	24 gms.	Solid
8E/5	170-170.5°/50mm.	32 gms.	Solid
8E/6	170.5-170.7°/50mm.	36 gms.	Solid
8E/7	170.7-170.8°/50mm.	36 gms.	Solid
8E/8	170.8-173.5°/50mm.	122 gms.	1.6030
8E/9	173.5-174° /50mm.	134 gms.	1.6030
8E/10	174-174.2°/50mm.	252 gms.	1.6047
8E/11	174.2-174.2°/50mm.	250 gms.	1.6053
8E/12	174.2-174.2°/50mm.	162 gms.	1.6065
8E/13	159-174° /50mm.	18 gms.	1.6195
8E/14	174-175° /50mm.	102 gms.	1.6105

A graph (21) was prepared of the weight distilled per $\frac{1}{2}$°C. against the temperature for the range covered by these four batches, using the same assumptions and procedure as were used in the construction of distribution graphs for the C- and D-distillations. The boiling points of bases which had already been reported as coal tar constituents are indicated on this graph

From/

From this graph it can be seen that the
most profitable ranges for close examination were
those occurring between 168° and 175°C./50mm. Hg.,
and a description of the examination of these fractions
is included in the next section.   A description of
the isolation of 3-methylisoquinoline from the fore-
runnings of distillation 5.E. is also included.

EXAMINATION OF THE E-FRACTIONS.

All the E-fractions examined in this work
have consisted essentially of tertiary bases of the
pyridine, quinoline or isoquinoline type.   The
isolation of the pure components from these fractions
has been effected by methods described earlier in
this thesis.

The pure compounds isolated have generally
been identified by the following means :-

1)   Comparison of their physical constants
(melting point, boiling point, density and refractive
index) with values given in the literature.

2)   Preparation of three or more derivatives
for each compound isolated and comparison of their
melting points with values given in the literature.
This method was particularly useful in the case of
methylated quinolines as Manske (86) had published
the melting points of the picrates, styphnates and
trinitro-m-cresolates of all the possible mono- and
dimethylquinolines, which he had prepared by
unambiguous routes, and had shown that the identity
of any mono- or dimethylquinoline could be established
conclusively by the determination of the melting
points of its picrate, styphnate and trinitro-m-
cresolate.   Where possible, additional confirmation
was obtained by carrying out mixed melting points
with authentic samples.

3)

3)   The infra-red absorption spectrograms
for all the compounds isolated have been prepared
through the courtesy of Dr. E.A. Coulson of the
Department of Scientific and Industrial Research and [*]
compared with reference spectra where available.
([*] and of Mr. L.J. Bellamy of the Ministry of Supply.)

Fraction 1E/2.   (122.5-123.5°C./100mm.)

Isolation of 2:4:5-Trimethylpyridine.

This fraction consisted entirely of tertiary
bases and showed an equivalent weight of 121 on
titration with standard hydrochloric acid using
screened methyl orange as indicator.   This value is
in perfect agreement with the equivalent weight of
trimethylpyridines ($C_8H_{11}N = 121$), and the main
constituent of the fraction has been shown to be
2:4:5-trimethylpyridine, a compound which has been
reported as a coal tar constituent previously.(60, 61)

75 Gms. of the fraction was treated with
the theoretical amount of picric acid (based on the
equivalent weight found) as a saturated solution in
boiling 95% ethyl alcohol.   This treatment was
carried out in three stages, one third of the total
amount of picric acid being added at each stage and
the precipitated picrates filtered and washed, after
thorough cooling.   In this manner the following
three batches of picrate were obtained.

1E/2a/

1E/2a. Colour - Dark yellow. Crystalline form- homogeneous.
        m.p. - 160-161°C.   Yield - 49.8gms.

1E/2b. Colour - Similar to a. Crystalline form - as 1E/2a.
        m.p. - 159-160°C.   Yield - 55.2gms.

1E/2c. Colour - Paler than above. Cryst. form - non-homogeneou
        m.p. - 140-152°C.   Yield - 38.5gms.

Fractions 1E/2a and 1E/2b were bulked together
and recrystallised from 95% alcohol giving a product
which melted at 160-161°C. Repeated recrystallisations
from alcohol did not alter this melting point nor did
a recrystallisation from acetone. This latter crystal-
lisation showed that a pure product had been obtained.

The resulting yield of pure picrate was then
treated with caustic soda to liberate the free base
which was steam distilled out, dried over solid caustic
soda and redistilled.

The physical characteristics of this pure
base were determined, and the picrolonate and meth-
iodide were prepared by the normal methods and
recrystallised to constant melting points.

Below are listed the physical characteristics
of the base and the melting points of its derivatives,
along with the literature values of these constants
for 2:4:5-trimethylpyridine and also mixed melting
points of the derivatives with the derivatives
prepared from an authentic sample of 2:4:5-trimethyl-
pyridine/

pyridine.

B.p.	189.5°C/755mm.	Literature value	189.8°/760mm.	(9)
D_4^{25}	0.9327	"	"	0.9330 (9)
n_D^{25}	1.5055	"	"	1.5054 (9)
Picrate m.160-161°C		"	"	161°C. (9)

Mixed melting point 160-161°C.

Picrolonate m.218°C. Literature value 218°C. (24)

The mixed melting point showed no lowering.

Methiodide m.244°C. Literature value 244°C. (24)

The mixed melting point showed no lowering.

The agreement of the above figures together with the evidence of mixed melting points was sufficient to prove that this compound was 2:4:5-trimethylpyridine. Additional confirmation was provided by the infra-red absorption spectrogram (Appendix II) which was found to be identical with the spectrogram obtained by Benzie and Milne for 2:4:5-trimethylpyridine.

A microscopic examination of the crystalline form of the picrate fraction 1E/2c showed that this consisted of a mixture of which the main constituent was identical in crystalline form with 2:4:5-tri-methylpyridine picrate. This picrate fraction was not examined further.

No quantitative estimate of the amount of 2:4:5-trimethylpyridine present in the crude Naphthalene Oil Bases was possible from these results as it was isolated/

isolated from fraction C.21 whose boiling range
(131-135°C./100mm.) was well above the boiling point
of the pure compound (123°C./100mm.) and, therefore,
much larger proportions of this compound would be
expected to occur in the lower C-fractions which were
not thoroughly examined.

The presence of 2:4:5-trimethylpyridine in
the bases derived from the Benzol Absorbing Oil was
also shown by the isolation of a picrate from fractions
2E/3 and 2E/4 which melted at 160-161°C. and whose
mixed melting point with 2:4:5-trimethylpyridine
picrate showed no lowering.

Fraction 2E/6. (126.9-127°C./100mm.)

Isolation of 2:3:4-Trimethylpyridine.

This fraction consisted entirely of tertiary
bases and showed an equivalent weight of 120.5 on
titration with standard hydrochloric acid using
screened methyl orange aś indicator. This value is
in good agreement with the equivalent weight of tri-
methylpyridines ($C_8H_{11}N = 121$), and the main constituent
of the fraction has been shown to be 2:3:4-trimethyl-
pyridine, a compound which has been reported as a
coal tar constituent previously (61).

60 Gms. of the fraction was treated with
the/

the theoretical amount of picric acid (based on the
equivalent weight found) as a saturated solution in
boiling 95% alcohol.   This treatment was carried out
in three stages, one third of the total amount of
picric acid being added at each stage and the
precipitated picrate filtered and washed after thorough
cooling.   In this manner the following three batches
of picrate were obtained.

2E/6a   Colour - Bright yellow.   Crystalline form - homogemeous.
       m.p.   - 162-164°C.   Yield 53gms.
2E/6b   Colour - As 2E/6a   Crystalline form - as 2E/6a
       m.p.   - 162-163°C.   Yield 58gms.
2E/6c   Colour - Darker than above. Cryst. Form - heterogeneous
       m.p.   - 150-154°C.   Yield 20gms.

       Owing to their great similarity, the fractions
2E/6a and 2E/6b were bulked together.   On repeated
recrystallisation of these combined fractions from
alcohol a product was obtained which melted sharply
at 164°C.   The melting point of this product could not
be raised by further recrystallisation from alcohol
nor by recrystallisation from acetone.   It was
considered, therefore, that a pure product had been
obtained, and the free base was regenerated from this
total yield of pure picrate in the manner described
for 2:4:5-trimethylpyridine, and dried and redistilled.

       The physical characteristics of this pure

base/

base were determined and the picrolonate and methiodide were prepared by the normal methods and recrystallised to constant melting points.

Below are listed the physical characteristics of the base and the melting points of its derivatives together with the literature values of these constants for 2:3:4-trimethylpyridine. Unfortunately no authentic sample of 2:3:4-trimethylpyridine was available for comparison.

B.p. 193°/755mm. Literature value $192-193^\circ$ (8)

D_4^{25} 0.9490 " " D_4^{23} 0.9511 (74)

n_D^{25} 1.5130 " " n_D^{22} 1.5129 (74)

Picrate m.164°C " " 164.5°C. (8)

Picrolonate m.242°C (Ex. alcohol) " 239°C. (74)

Methiodide m.160°C (Ex. absolute alcohol)

The agreement of the above figures was sufficient to prove that this compound was 2:3:4-trimethylpyridine. An infra-red absorption spectrogram was obtained for this compound (Appendix II), but unfortunately no reference spectrum was available for direct comparison.

On repeated recrystallisation of picrate fraction 2E/6c from alcohol a product was finally obtained which melted at 164°C. and whose mixed melting point with 2:3:4-trimethylpyridine picrate showed no lowering. It was considered, therefore, that the fraction/

fraction 2E/6c consisted essentially of 2:3:4-tri-methylpyridine picrate together with small quantities of some impurity, probably 2:4:5-trimethylpyridine picrate.   The fraction was not examined further.

A quantitative estimate of the amount of 2:3:4-trimethylpyridine in the crude Benzol Absorbing Oil Bases was made on the assumption that the whole of fraction 2E/6 consisted of this compound.   The value found was - 0.34% on the total crude wet bases.
                    i.e.0.0068% on the Benzol Absorbing Oil.

The assumption that the whole of fraction 2E/6 consisted of 2:3:4-trimethylpyridine was not strictly correct, but the presence of this compound in the neighbouring fractions 2E/5 and 2E/7 would have more than compensated for the impurities in 2E/6. For this reason and because the neighbouring D-fraction 18 might also have contained a proportion of 2:3:4-trimethylpyridine (the other neighbouring fraction, D.20, contained only negligible quantities, as can be seen from the graph of distillation 3.E), the above estimate will be low, and the actual percentage might have been anything up to two times as great as this estimated value.

It is interesting to note that no indication of the presence of this compound in the Naphthalene Oil Bases was obtained from distillation 1.E.

Fractions/

Fractions 2E/10 - 12.   (131-132.5°C./100mm.)

   and 3E/7 and 8.   (131-132°C./100mm.)

Isolation of 2:3:5:6-Tetramethylpyridine.

The solid which separated out from these
fractions has been proved to be 2:3:5:6-Tetramethyl-
pyridine, a compound which has not hitherto been
reported as a constituent of coal tar. (Note. A
preliminary note has been published on this part of
the investigation.) (139).

The solid which separated out from these
fractions was filtered off and washed with petroleum
ether ("40-60°").   After repeated recrystallisations
of this solid material from petroleum ether, a product
was obtained which consisted of small white glistening
platelets with a pleasant odour and a melting point
of 76°C. which could not be raised by further recryst-
allisations from the same solvent.   From this pure
product, the picrate, picrolonate and methiodide were
prepared and recrystallised to constant melting points.

These melting points are listed below, and
in each case they are identical with the melting
points of the same derivatives prepared from a tertiary
base ($C_9H_{13}N$), of the same melting and boiling points,
isolated from the mixed pyridine bases in shale oil
by Benzie and Milne (24).   Mixed melting points
showed no lowering either in the case of the base
itself/

itself or of its derivatives.

    Picrate (Ex. alcohol)   m. 176°C.

    Picrolonate (Ex. alcohol)   m. 259-260°(decompn.)

    Methiodide (Ex. absolute alcohol)   m. 178°C.

        Benzie and Milne suggested tentatively that
their compound was 2:3:5:6-tetramethylpyridine on the
basis of a comparison of its dissociation constant
with those of other methylated pyridines, and this was
further supported by analogy of the tetramethylpyridines
to the tetramethylbenzenes.

        There are few references in the literature
to the preparation of this compound.   Oparina (60),
however, obtained a solid tertiary base in the reaction
products on passing a mixture of formaldehyde, methyl-
ethyl ketone and ammonia over alumina in a heated
copper tube.   This solid base melted at 73-74°C. and
its picrate melted at 173-174°C.   This work has been
repeated in this college by R.T. Smith, who obtained
a solid product which on purification melted at 76°C.
and the picrate of which melted at 176°C.   The mode
of preparation of this compound strongly indicates
the 2:3:5:6- configuration.   The identity of this
base with that isolated from coal tar was proved by
the fact that the mixed melting points of the pure
bases and of the picrates showed no lowering, and
also by the fact that the infra-red absorption
spectrograms for the two samples were identical (Appendix II).

        OParina/

Oparina (105) has recently repeated his earlier work and obtained a product which melted at 81°C. and the picrate of which melted at 173.5°C. On partial oxidation of this free base with permanganate he obtained 2:6-dimethylpyridine-3:5-dicarboxylic acid which on distillation with lime yielded 2:6-dimethylpyridine.   Oxidation with excess permanganate yielded a crude tetracarboxylic acid which on heating lost carbon dioxide to give an acid melting at 308-309°C.   From the mother liquors of the oxidation the 3:5-dicarboxylic acid and 2:5-dimethylpyridine-3:6-dicarboxylic acid were obtained.

This work proves quite conclusively that the product obtained by Oparina was 2:3:5:6-tetramethylpyridine, and, on the grounds that their reaction conditions were almost identical, it can be assumed that the product obtained by Smith was also 2:3:5:6-tetramethylpyridine, in spite of discrepancies in the melting points, and hence that the base isolated from coal tar was 2:3:5:6-tetramethylpyridine.

In order to obtain an approximate quantitative estimate of the amount of 2:3:5:6-tetramethylpyridine present in the crude tar bases, a portion of the bulked fractions 2E/10-12 and 3E/7 & 8 was subjected to the following treatment.

The/

The sample was cooled with a "dry ice"/ methyl alcohol mixture, the solid filtered off and the liquid removed for re-freezing. The solid was washed with a small quantity of chilled petroleum ether, the ether removed from the washings by distillation and the resulting residue bulked with the above liquid fraction for re-freezing. This whole series of operations was repeated until no more solid could be separated.

Finally a liquid portion was obtained consisting entirely of tertiary bases and amounting to 17.5% of the bulked fractions.

3:4:5-Trimethylpyridine has neither been isolated from any natural source nor has it been prepared, but, calculating its boiling point by means of an empirical formula derived by Eguchi (9), a value of 199.3°C./760mm. was obtained, i.e. approximately the same as that of the solid base. It was therefore considered possible that 3:4:5-trimethylpyridine might be present in the liquid residue, and for this reason the liquid was subjected to a fractional treatment with picric acid as has been described before. In this manner the following three batches of picrate were obtained.

A. m. 172-174°C.   B. m. 174-176°C.   C. m. 160-170°C.

On recrystallisation of the bulked fractions A. and B. from 95% alcohol a product was obtained which melted/

melted at 176°C. and whose mixed melting point with
2:3:5:6-tetramethylpyridine picrate showed no lowering.
On repeated recrystallisation of fraction C. an
identical product was obtained, thus proving that the
liquid consisted essentially of 2:3:5:6-tetramethyl-
pyridine with only traces of impurities.   As no
indication of the presence of 3:4:5-trimethylpyridine
had been found, this range was not examined further.

The investigation described above showed
that the bulked fractions 2E/10-12 and 3E/7 & 8
consisted almost entirely of 2:3:5:6-tetramethylpyridine.
A quantitative estimate of the amount of this compound
present in the total oils was made, using the same
approximations as were used in the estimation of
2:3:4-trimethylpyridine.
The value found was   0.46% on the total crude wet bases.
i.e.0.0092% on the Benzol Absorbing Oil.
Here again it must be remembered that the true value
might have been anything up to two times as great as
this approximation.

It is interesting to note that, as in the
case of 2:3:4-trimethylpyridine, no indication of the
presence of 2:3:5:6-tetramethylpyridine in the bases
derived from the Naphthalene Oils was obtained from
distillation 1.E.   In addition, the presence of the
o- and p-toluidines in the Naphthalene Oil Bases was
shown in distillation 1.E., but no indication of their
presence/

presence in the Benzol Absorbing Oil Bases was obtained
from distillations 2.E. and 3.E.   These facts illus-
trate the profound differences which exist between
base fractions of the same boiling range derived from
different tar oil fractions.   This difference is
probably due to the fact that in the distillation of
the crude tar the bases distil over as some type of
complex with phenols, and the boiling points of these
complexes may not vary in the same order as those of
their base constituents.

    For this reason the absence of a base in any
single tar oil fraction does not prove the absence
of that base in the total tar.

Fraction 3E/12.   (135-135.2°C./100mm.)

Isolation of 2:3:4:6-Tetramethylpyridine.

    This fraction, which consisted for the most
part of tertiary bases together with a small amount
of primary bases, showed an equivalent weight of 133
on titration with standard hydrochloric acid using
screened methyl orange as indicator.   This value is
in good agreement with the equivalent weight of the
tetramethylpyridines ($C_9H_{13}N = 135$), and the main
constituent of the fraction has been shown to be
2:3:4:6-tetramethylpyridine, a compound which has not
hitherto been reported as a constituent of coal tar.

70 Gms. of the fraction was treated with the
theoretical amount of picric acid (based on the
equivalent weight found) as a saturated solution in
boiling 95% ethyl alcohol.   This treatment was carried
out in three stages, one third of the total amount
of picric acid being added at each stage, and the
precipitated picrate filtered and washed after thorough
cooling.   In this manner the following three batches
of picrate were obtained.

3E/12a Colour - As 3E/12b.   Crystalline form - homogeneous.
          m.p. - 110-120°C.   Yield - 70gms.
3E/12b Colour - As 3E/12a.   Crystalline form - homogeneous.
          m.p. - 110-120°C.   Yield - 60gms.
3E/12c Colour - Darker than above. Cryst. form - heterogeneou
          m.p. - 150-170°C (decompn.) Yield - 38gms.

Owing to their great similarity the fractions
3E/12a and 3E/12b were bulked together.   On repeated
recrystallisation of these fractions from alcohol
a product was obtained which melted sharply at 122.5-
123°C.   The melting point of this product could not
be raised by further recrystallisation from alcohol,
nor by recrystallisation from acetone.

It was considered therefore that a pure
product had been obtained, and the free base was
regenerated from the total yield of pure picrate.
The free base was then dried and redistilled.

The/

The physical characteristics of this pure
base were determined, and the picrolonate and the
methiodide were prepared by the normal methods and
recrystallised to constant melting points.

Below are listed the physical characteristics
of the base and the melting points of its derivatives
along with the literature values of these constants
for 2:3:4:6-tetramethylpyridine. The mixed melting
points of the picrate and picrolonate with the same
derivatives obtained from a sample of 2:3:4:6-tetra-
methylpyridine, isolated from the mixed pyridine bases
in shale oil by Benzie and Milne (24), showed no
lowering.

B.p. 203°C/750mm.   Literature value 203.3°/760mm.(9)

D_4^{25} 0.9322   "   "   0.9345 (24)

n_D^{25} 1.5087   "   "   1.5084 (9)

Picrate (Ex. acetone) m.122.5-123°C.
Literature value....... 122.5-123°C.(24)

Picrolonate (Ex. alcohol) m.225.5°C. (decompn.)
Literature value........... 225.5°C. (24)

Methiodide (Ex. absolute alcohol) m.192-193°C.

The agreement of the above figures, together
with the evidence of mixed melting points, was sufficient
to prove that this compound was 2:3:4:6-tetramethyl-
pyridine. Additional confirmation was provided by
the infra-red absorption spectrogram (Appendix II)
which was found to be identical with the spectrogram
obtained for 2:3:4:6-tetramethylpyridine by Benzie
and/

and Milne.

3E/12c
The picrate fraction was shown to contain
a proportion of a primary base by regeneration of the
free bases and diazotisation.   This primary base was
probably m-toluidine which has previously been reported
as a coal tar constituent (17) and which boils at
203.3°C./760mm.   The fraction was not examined further
as it was considered most likely that it consisted of
a mixture of m-toluidine and 2:3:4:6-tetramethylpyridine.

The investigation described above showed
that the fraction 3E/12 consisted essentially of
2:3:4:6-tetramethylpyridine contaminated with a small
proportion of m-toluidine.   An approximate quantitative
estimate of the amount of this tetramethylpyridine
present in the total oils was made using the same
approximations as were used before.

The value found was   0.26% on the total crude wet bases.
                i.e.   0.0052% on the Benzol Absorbing Oil.

Here again it must be remembered that the
true value might have been considerably greater than
this approximation, even more so than in the case of
2:3:5:6-tetramethylpyridine where the solid character
of the base facilitated its isolation from a wider
distillation range.

Fraction/

Fraction 5E/1.   (154.8-157°C./50mm.)

Isolation of 3-Methylisoquinoline.

The solid which separated from this fraction
has been proved to be 3-methylisoquinoline, a compound
which has been reported as a coal tar constituent
previously (78).

The solid which separated from the fraction
on thorough cooling was filtered off and washed with
petroleum ether.   After repeated recrystallisation
of this solid material from petroleum ether a product
was obtained with a melting point of 64.5°C. which
could not be raised by further recrystallisations
from the same solvent.   From this pure product the
picrate, sulphate and methiodide were prepared and
recrystallised to constant melting points.

The melting points of the free base and of
its derivatives are shown below together with the
literature values of these constants for 3-methyliso-
quinoline.

    Free base   m.64.5°C.
    Literature Value 64.7°C.(78)

    Picrate (Ex. alcohol) m.199-200°C.
    Literature value........ 197-198°C.(25)

    Sulphate (Ex. absolute alcohol) m.154.5°C.
    Literature value.................. 154.5-155°C.(78)

    Methiodide (Ex. alcohol) m.221°C.
    Literature value.......... 219°C.(143)

      Unfortunately/

Unfortunately no authentic sample of 3-methylisoquinoline was available for carrying out mixed melting points, but the agreement of the above figures was sufficient to prove that this compound was 3-methylisoquinoline.

An infra-red absorption spectrogram was obtained for this compound (Appendix II) but no reference spectrum was available for comparison.

No quantitative estimate of the amount of 3-methylisoquinoline in the total oil could be obtained from the above investigation, as the fraction was obtained from the fore-runnings of distillation 5.E., and it was to be expected that the greater part of the 3-methylisoquinoline present would occur in the lower D-fractions whose distillation ranges were more close to the boiling point of the pure base.

The fraction 5E/1 was not examined further.

Fractions 7E/6 and 8E/2.   (168.5-169°C./50mm.)

Isolation of 2:7-Dimethylquinoline.

A solid base has been isolated from the fractions 7E/6 and 8E/2, which has been proved to be 2:7-dimethylquinoline, a compound which has not hitherto been isolated from any natural source.

On/

On cooling a portion of the bulked fractions
7E/6 and 8E/2 with a freezing mixture of ice and salt,
a white solid separated out.   This solid base was
filtered off, washed with petroleum ether and recrys-
tallised repeatedly from petroleum ether to constant
melting point.   Finally a product was obtained
consisting of clear needle-shaped crystals which
melted at 61°C.   From this pure base the picrate,
styphnate and trinitro-m-cresolate were prepared and
recrystallised to constant melting points.

These melting points are listed below
together with the literature values of these constants
for 2:7-dimethylquinoline.   A mixed melting point
of the free base with an authentic sample of 2:7-di-
methylquinoline, prepared according to the method
described by Doebner and Miller (144) from m-toluidine,
paraldehyde and concentrated hydrochloric acid, showed
no lowering.   (Note - The product obtained by means
of the Doebner & Miller synthesis from m-toluidine
and paraldehyde was assigned the 2:5- formula by
Decker and Remfry (147), but Manske (86) has since
shown that this is untrue and that the true
configuration is that of 2:7-dimethylquinoline.)

        Free base........m.61°C.
        Literature value.. 61°C.(86)

        Picrate (Ex. acetone) m.196°C.
        Literature value........ 196°C.(86)

        Styphnate (Ex. acetone) m.220°C.
        Literature value.......... 222°C.(86)

    Trinitro-/

Trinitro-m-cresolate (Ex. "cellosolve") m.250°C.
Literature value......................... 250°C.(86)

The agreement of the above figures, together
with the evidence of the mixed melting point, was
sufficient to prove that this compound was 2:7-di-
methylquinoline.

Additional confirmation was obtained from
the infra-red absorption spectrogram (Appendix II),
which was found to be identical with that obtained
for the authentic sample of 2:7-dimethylquinoline
which had been prepared.

In order to obtain an approximate estimate
of the amount of 2:7-dimethylquinoline present in the
tar oil, a portion of the bulked fractions 7E/6 and
8E/2 was subjected to the following treatment.

The sample was cooled with a "dry ice"/
methyl alcohol mixture, the solid filtered off and
the liquid removed for re-freezing.   The solid was
washed with a small quantity of chilled petroleum
ether, the ether removed from the washings by distil-
lation and the resulting residue bulked with the above
liquid fraction for re-freezing.   This whole series
of operations was repeated until no more solid could
be separated.

In this manner a total liquid residue which
amounted to 20% of the bulked fractions was finally
obtained/

obtained, and all the solid obtained, although melting below 61°C., melted at an intermediate temperature when mixed with pure 2:7-dimethylquinoline, thus proving that it consisted of substantially pure 2:7-dimethylquinoline.

This investigation showed that the bulked fractions 7E/6 and 8E/2 contained at least 80% of 2:7-dimethylquinoline, in addition to the amount of this compound which still remained in the liquid residue.

An estimate of the amount of 2:7-dimethylquinoline present in the tar oil was made on the assumption that the bulked fractions 7E/6 and 8E/2 consisted entirely of 2:7-dimethylquinoline, as it was considered that the 2:7-dimethylquinoline content of the neighbouring E-fractions would more than compensate for the impurities in the bulked fractions.

The value found was   0.78% on the total crude wet bases.
i.e. 0.016% on the Benzol Absorbing Oil.

Note - This will be a closer approximation to the true value than was obtained for the previous compounds, as the fractions 7E/6 and 8E/2 were derived from a wider range of D-fractions and there was little chance of any 2:7-dimethylquinoline occurring in any of the other D-fractions.

Fractions/

Fractions 8E/3 - 8E/7.   (169-170.8°C./50mm.)

Isolation of 2:6-Dimethylquinoline.

A solid base has been isolated from the fractions 8E/3 - 8E/7, which has been proved to be 2:6-dimethylquinoline, a compound which has not hitherto been isolated from any natural source.

The solid base which separated from these fractions was filtered off, washed with petroleum ether and recrystallised from petroleum ether to constant melting point.   Finally a product was obtained which consisted of clear needle-shaped crystals with a melting point of 60°C.   This melting point was identical to that of an authentic sample of 2:6-dimethylquinoline prepared according to the method of Doebner and Miller (144) from p-toluidine and paraldehyde, and a mixed melting point showed no lowering.

From the pure base the picrate, styphnate and trinitro-m-cresolate were prepared and recrystallised to constant melting points.   These melting points are listed below together with the literature values of the melting points of these derivatives of 2:6-dimethylquinoline.

Picrate (Ex. absolute alcohol) m.191°C.
Literature value................. 191°C.(86)

Styphnate/

Styphnate (Ex. absolute alcohol) m.199°C.
Literature value.................... 200°C.(86)

Trinitro-m-cresolate (Ex. "cellosolve") m.207°C.
Literature value.......................... 206°C.

The agreement of the above figures, together
with the evidence of the mixed melting point of the
free base, was sufficient to prove that this compound
was 2:6-dimethylquinoline.

Additional confirmation was obtained from
the infra-red absorption spectrogram (Appendix II)
which was found to be identical to that obtained for
the authentic sample of 2:6-dimethylquinoline which
had been prepared.

In order to obtain an estimate of the amount
of 2:6-dimethylquinoline present in the total oil,
a portion of the bulked fractions 8E/3-8E/7 was
subjected to the same treatment as was used in the
evaluation of the 2:7-dimethylquinoline.

In this manner a yield of solid was obtained
which consisted of essentially pure 2:6-dimethyl-
quinoline, and the total liquid residue amounted to
53% of the bulked fractions.

An estimate of the amount of 2:6-dimethyl-
quinoline present in the total oil was made on the
approximation that 50% of the liquid residue consisted
of 2:6-dimethylquinoline, i.e. a total of 73.5% of

the/

the bulked fractions consisted of 2:6-dimethylquinoline.
As a result of this approximation and on account of
the fact that neighbouring E-fractions might have
contained some 2:6-dimethylquinoline, the error in the
value obtained may be as high as $\pm 50\%$.

The value found was 0.36% on the total crude wet bases.
i.e.0.0072% on the Benzol Absorbing Oil.

Fractions 8E/9 - 8E/12.   (173.5-174.2°C./50mm.)

Isolation of 2:4-Dimethylquinoline.

A pure liquid base has been isolated from
these fractions and has been proved to be 2:4-di-
methylquinoline, a compound which has not hitherto
been reported as a coal tar constituent.

As no pure picrate could be isolated from
any of these fractions by fractional treatment with
picric acid and recrystallisation of the resulting
picrate fractions, it was decided to carry out a
fractional acid extraction on the bulked fractions
8E/9 and 8E/10.

This fractional acid extraction was carried
out in a manner precisely similar to that described
on page 28, using as a starting material 200gms. of
the bulked fractions 8E/9 and 8E/10.   The weights
and/

and refractive indices of the ten base fractions,
which were finally obtained by distilling the ether
from the fractions S.6 - S.15 and then distilling the
bases in vacuo, are shown below.

Fraction	Weight	n_D^{25}
F.1	5gms.	1.5965
F.2	16gms.	1.6010
F.3	18gms.	1.6025
F.4	17gms.	1.6035
F.5	21gms.	1.6045
F.6	18gms.	1.6045
F.7	20gms.	1.6045
F.8	19gms.	1.6045
F.9	22gms.	1.6045
F.10	29gms.	1.6022

Owing to their great similarity the fractions
F.5 - F.9 inclusive were bulked together.   A sample
of the bulked fractions was treated with the
theoretical amount of picric acid (calculated for
dimethylquinoline.) as a saturated solution in
boiling 95% alcohol.   This treatment was carried out
in three stages, one third of the total amount of
picric acid being added at each stage and the
                picrate
precipitated filtered and washed after thorough cooling.

In this manner three picrate fractions were
obtained/

obtained which did not differ in either melting point
(189-192°C.), crystalline form (needle-shaped crystals)
or colour (yellow - darkening rapidly on exposure to
light).   The three fractions were therefore bulked
together.   On repeated recrystallisation of these
bulked fractions from "cellosolve" a product was
finally obtained which melted at 196°C.   This melting
could not be raised by further recrystallisation from
"cellosolve" nor by recrystallisation from acetone.
It was considered therefore that a pure picrate had
been obtained.

The free base was regenerated from the pure
picrate by treatment with caustic soda and extraction
with ether.   The ether was distilled from this
extract, after drying over solid caustic soda, and
the free base was distilled at a pressure of 100mm. Hg.

The physical characteristics of this pure
base were determined, and the styphnate and trinitro-
m-cresolate were prepared by the normal methods and
recrystallised to constant melting points.

Below are listed the physical characteristics
of the base and the melting points of its derivatives,
together with the literature values of these constants
for 2:4-dimethylquinoline.

B.p.   174°C./100mm. Hg.

D/

D_4^{20} 1.0515.　　　Literature value 1.0549 (150).

n_D^{20} 1.6075.　　　Literature value 1.6075 (151).

Picrate (Ex. "cellosolve") m.196°C.
Literature value............. 196°C.(86)

Styphnate (Ex. "cellosolve") m.212°C.
Literature value.............. 211°C.(86)

Trinitro-m-cresolate (Ex. "cellosolve") m.212°C.
Literature value......................... 212°C.(86)

　　　　An authentic sample of 2:4-dimethylquinoline
was prepared according to the method of Vaughan (148)
from aniline and acetone via the "acetone anil", and
from this sample the picrate was prepared and recrys-
tallised from "cellosolve" to constant melting point
(196°C.).　A mixed melting point of this picrate
with the coal tar base picrate showed no lowering.

　　　　The agreement of the above figures, together
with the evidence of the mixed melting points of
picrates, was sufficient to prove that this compound
was 2:4-dimethylquinoline.

　　　　Additional confirmation was obtained from
a comparison of the infra-red absorption spectrograms
of the sample isolated from coal tar and the synthetic
sample (Appendix II).

　　　　From the above investigation it can be seen
that the combined fractions F.5 - F.9 consisted almost
entirely of 2:4-dimethylquinoline with only traces
of impurities.　The fractions F.5 - F.9 amounted to
50%/

50% of the combined fractions 8E/9 and 10 and, as it
could be seen from the refractive indices of the other
F-fractions that no other major constituent was present,
it was assumed that the combined fractions 8E/9 and
10 contained at least 75% of 2:4-dimethylquinoline.

An estimate of the 2:4-dimethylquinoline
content of the combined fractions 8E/11 and 12 was
made by means of the m-nitrobenzaldehyde condensation
product.

The condensation product of 2:4-dimethyl-
quinoline with m-nitrobenzaldehyde was prepared
as follows :-

1 Gm. of pure 2:4-dimethylquinoline was
heated with 1 gm. of m-nitrobenzaldehyde in an oil
bath at 130°C. for six hours.   On cooling, the reaction
mixture solidified.   The solid product was washed
with a little alcohol and dried in vacuo.

Yield 1.3gms. (66%% based on formula i)
m.p. 160-162°C.

On repeated recrystallisation of this from
benzene a product was obtained consisting of almost
colourless prisms which melted at 166-167°C.   This
melting point does not agree with the value of 184°C.
given by Spallino and Cucchiaroni (149).   It was
found, however, that on boiling the product for two
hours/

hours with acetic anhydride and cooling, a yellow
powder was obtained which melted at 180-183°C. and
whose melting point was raised to 186-187°C by
repeated recrystallisation from acetic anhydride.

It was considered that the product melting
at 166-167°C. was of the formula -

(i)
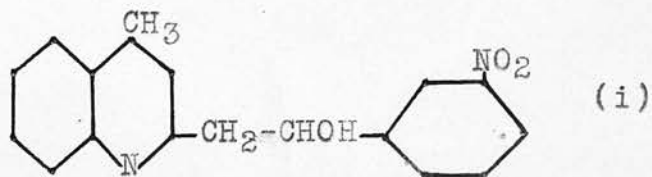
which was dehydrated on boiling with acetic anhydride
to yield -

(ii)
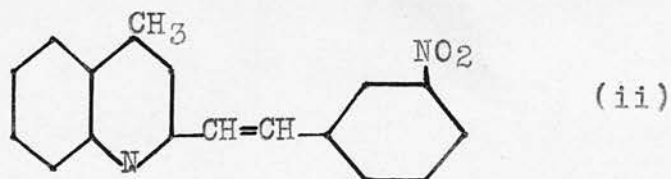
A 10gm. sample of the combined fractions
8E/11 and 12 was heated with 10gms of m-nitrobenzaldehyde
in an oil bath at 130°C. for six hours.   On cooling,
the reaction mixture solidified.   The solid product
was washed with a little alcohol and dried in vacuo.

Yield   12gms. (61.2% on formula i)

m.p. 158-160°C.

This yield was recrystallised from benzene.

Yield   11gms.   m.p. 161-163°C.

This melting point approximates the melting
point of the product obtained in 66.3% yield from pure
2:4-dimethylquinoline, and on repeated recrystallisation
from benzene a product was obtained which melted at
166-/

166-167°C.   The mixed melting point of this product
with that of the same melting point obtained from
pure 2:4-dimethylquinoline showed no lowering, thus
proving the identity of the two compounds.

Summarising the above results :-

1) A crude condensation product which melted
at 160-162°C. was obtained in 66.3% yield from pure
2:4-dimethylquinoline.

2) A crude sample of the same condensation
product, which melted at 158-160°C., was obtained
from the combined fractions 8E/11 and 12 in 61.2%
yield.   Although this melting point was slightly
below that of the corresponding product from pure
2:4-dimethylquinoline, it was raised to a higher level
by one recrystallisation from benzene with a resultant
reduction in yield to 56.1%.

On the basis of these results it was
reasonable to assume that at least 75% of the combined
fractions 8E/11 and 12 consisted of 2:4-dimethyl-
quinoline.

An estimate of the 2:4-dimethylquinoline
content of the total Benzol Absorbing Oil Bases was
calculated on the assumption that the combined fractions
8E/9 - 12 contained 75% of 2:4-dimethylquinoline.

The value found was 1.12% on the total crude wet bases.

i.e. 0.022% on the Benzol Absorbing Oil.

It/

It is possible that the true content of
2:4-dimethylquinoline may have been anything up to 50%
greater than this estimated value.

Fraction 8E/14.   (174-175°C./50mm.)

Isolation of 2:3-Dimethylquinoline.

A solid base has been isolated from fraction
8E/14 which has been proved to be 2:3-dimethylquinoline,
a compound which has not hitherto been reported as
a coal tar constituent.

The solid,which separated from the fraction
on prolonged standing, was filtered off and washed
with petroleum ether.   No more solid could be
separated from the fraction, even on freezing to as
low a temperature as -70°C.   The solid base was
recrystallised to constant melting point from
petroleum ether.   Finally a product was obtained
consisting of clear prism shaped crystals which melted
at 70°C.   This melting point was identical with that
of an authentic sample of 2:3-dimethylquinoline
prepared from isatin and methyl ethyl ketone by the
method of Pfitzinger (145) as modified by Plant and
Rosser (146), and a mixed melting point showed no
lowering.

From the pure base the picrate, styphnate

and/

and trinitro-m-cresolate were prepared and recrystal-
lised to constant melting points.   These melting
points are listed below together with the literature
values for the melting points of these derivatives of
2:3-dimethylquinoline.

    Picrate (Ex. absolute alcohol) m.235°C.
    Literature value.................. 235°C.(86)

    Styphnate (Ex. absolute alcohol) m.242°C.
    Literature value.................... 243°C.

    Trinitro-m-cresolate (Ex."cellosolve") m.248°C.
    Literature value......................... 248°C.

        The agreement of the above figures, together
with the evidence of the mixed melting point of the
free base, was sufficient to prove that this compound
was 2:3-dimethylquinoline.

        Additional confirmation was obtained from
the infra-red absorption spectrogram (Appendix II),
which was found to be identical with that obtained
for the authentic sample of 2:3-dimethylquinoline
which had been prepared.

        No estimate of the amount of this compound
present in the total oil could be obtained, as it
occurred in the last fraction of the E-distillations
and it was to be expected that the greater part of
compound which had been present in the crude bases
would be retained in the residues from the D- and
E-distillations.

DISCUSSION AND SUMMARY.

The starting materials for this investigation were the nitrogenous bases extracted by sulphuric acid from both the Naphthalene Oil and the Benzol Absorbing Oil fractions of vertical retort coal tar.   These bases consist for the most part of pyridine, quinoline and isoquinoline homologues, together with smaller quantities of primary bases.

Each fraction of bases has been subjected to a two-fold fractional distillation, the first of these fractionations having been carried out in a Raschig-ring packed column of efficiency equivalent to 5 - 10 theoretical plates, and the second stages of the fractionations carried out in a "Dixon gauze-ring" packed column of efficiency equivalent to approximately 30 theoretical plates.

From the results of these distillations "weight / temperature of distillation" balances have been drawn up for both fractions of bases.   The distillation "flats" indicated in these distribution graphs correspond well with the boiling points of the bases previously isolated from coal tar, and from the graphs an estimate can be obtained of the relative abundance of the individual components (or groups of components when several boil close together).

The/

The fractions obtained from these two-fold fractional distillations have been studied as follows.

Naphthalene Oil Bases.

A high proportion of these bases distilled at temperatures below 145°C., and quantitative estimates have been made of the individual constituents occurring within this range.

The results obtained were :-

Pyridine................ 2.26% (on total crude wet base

2-Methylpyridine....... 5.73%

3-Methylpyridine....... 3.60%

4-Methylpyridine........1.85%

2:6-Dimethylpyridine... 5.50%

Note - The results obtained for the last three compounds were probably slightly low as some of these bases would have been carried over into the higher cuts which were not examined.

These low-boiling bases have widespread industrial uses and, at the present time, are extracted commercially from the lower boiling tar oil fractions only. There are indications that the present demand for these bases exceeds the supply, and it is possible that the Naphthalene Oils might provide a useful auxiliary source.

A more profitable use for high-boiling tar bases, such as those obtained from the Naphthalene Oils, might be provided by some form of catalytic cracking to pyridine.

Little/

Little work appears to have been carried out
on this possibility, but the Philips Petroleum Co. (152)
have patented a process for conversion of alkyl-pyridines
to pyridine by passing the alkyl-pyridines, with an
excess of benzene or some other alkyl group acceptor,
in the vapour phase over a clay type catalyst at
455-650°C.   The example given, however, refers to
mixed ethylpyridines, and it is doubtful whether the
method would prove satisfactory if applied to the
methylpyridines derived from coal tar.   Prior to the
recent war, however, the I.G. Farbenindustrie (153)
were investigating a process for the conversion of
high-boiling bases into pyridine.   The process
consisted of passing the vapours of the mixed bases,
with hydrogen and a small proportion of hydrogen
sulphide, through a nickel-chrome steel tube at about
860°C.   Although the yield was only about 50% of the
theoretical, the erection of a larger plant had been
considered, but the war caused this plan to be abandoned.

A fraction of the Naphthalene Oil Bases
(b. 131-135°C./100mm. Hg.) has been subjected to a
further fractional distillation in a "Dixon gauze ring"
packed column, of efficiency equivalent to approximately
100 theoretical plates, in the hope of isolating
tetramethylpyridines.   No trace was found of tetra-
methylpyridines but 2:4:5-trimethylpyridine was
isolated from this fraction.

Benzol/

Benzol Absorbing Oil Bases.

From the distribution graph it can be seen
that a high proportion of these bases distilled at
a temperature corresponding with the boiling point
of quinoline, and it is possible that these bases may
provide a useful commercial source of quinoline.

The following fractions of these bases have
been subjected to further fractionation in the "100-
plate" column in the hope of isolating bases not
previously reported as coal tar constituents :-

$126-131^{\circ}C./100mm.$ Hg.	- Distillation 2.E.
$131-137^{\circ}C./$ " "	- Distillation 3.E.
$152-158.5^{\circ}C/$ " "	- Distillation 4.E.
$161-165^{\circ}C./50mm.$ Hg.	- Distillation 5.E.
$165-168^{\circ}C./$ " "	- Distillation 6.E.
$168-170^{\circ}C./$ " "	- Distillation 7.E.
$170-178^{\circ}C./$ " "	- Distillation 8.E.

Eight compounds have been isolated and
positively identified from the narrow boiling range
cuts obtained by these distillations, and, where
possible, approximate estimates of the amounts of
these present have been made.

These compounds are listed below together
with the boiling ranges of the cuts from which they
have been isolated.   The estimates of their content
in the crude wet Benzol Absorbing Oil Bases are
included/

included, together with the possible error involved
in the individual estimations.

Boiling Range	Compound	Content	Possible Error
126.9-127°C/100mm.	2:3:4-Trimethylpyridine	0.34%	+ 100%
131-132.5°C/100mm.	2:3:5:6-Tetramethylpyridine	0.46%	+100%
135-135.2°C/100mm.	2:3:4:6-Tetramethylpyridine	0.26%	+100%
154.8-157°C./50mm.	3-Methylisoquinoline	-	
168.5-169°C./50mm.	2:7-Dimethylquinoline	0.78%	±20%
169-170.8°C./50mm.	2:6-Dimethylquinoline	0.36%	±50%
173.5-174.2°C/50mm.	2:4-Dimethylquinoline	1.12%	+50%
174 - 175°C./50mm.	2:3-Dimethylquinoline	-	

The six compounds underlined in red have not
hitherto been reported as coal tar constituents.

From the distillations 5.E - 8.E inclusive
a more accurate distribution graph has been constructed
for the range distilling between 161 and 175°C./50mm. Hg.

From a study of the results obtained in this
investigation the following notable facts stand out.

1) Of the nineteen possible methyl homologues
of pyridine, seventeen have now been identified in
coal tar.   The remaining two, 3:4:5-trimethylpyridine
and pentamethylpyridine, have neither been isolated
from any natural source nor has either been prepared
synthetically.   The absence of these two compounds
from/

from coal tar has not been proved, however, during
this investigation.

2) Of the dimethylquinolines isolated, all
have been substituted in the 2-position, and in the
boiling range which has been closely examined no trace
                    poly-substituted
has been found of ∧quinolines not substituted in the
2-position, although several such compounds boil
within this range.

It is interesting to note that all the poly-
substituted quinoline homologues isolated from the
mixed petroleum bases have been substituted in the 2-position.

The only claim to the isolation of a poly-
substituted quinoline from any natural source has been
that of Ganguli & Guha (93) to the isolation of 5:8-
dimethylquinoline from coal tar, and some doubt has
been cast on this claim.

3) The percentage of 2:4-dimethylquinoline
found was much higher than that of either 2:6- or
2:7-dimethylquinoline.   Jantzen in his investion of
higher coal tar bases (78) found the following
percentages for the monomethylquinolines.

2-Methylquinoline		......	10.60%
3-	"	"	......	1.79%
4-	"	"	......	5.70%
5-	"	"	......	0.30%
6-	"	"	......	1.80%
7-	"	"	......	1.35%
8-	"	"	......	1.46%

It/

It may be noticed that 2-methylquinoline
was found to be the most abundant, followed by
4-methylquinoline, and that the other methylquinolines
were present to a much smaller extent.

These facts taken together seem to indicate
that the percentages of individual methylated quinolines
present in coal tar bear some relation to the reactivity
of the substituent methyl groups.

ACKNOWLEDGEMENTS.

APPENDIX I.

PYRIDINE, QUINOLINE AND ISOQUINOLINE HOMOLOGUES
ISOLATED PREVIOUSLY FROM COAL TAR.

Pyridine.   First isolated by Williams in 1854 (6)
b. 115.3°C (7); D_4^{25} 0.9776 (8); n_D^{25} 1.5068 (9).
Picrate m.167°C (9);   Chloroplatinate m.268°C (9);
Isolations etc :- (7) - (16) and (18) - (23).

2-Methylpyridine.   First isolated by Anderson in 1846 (2).
b. 129.3°C (9); D_4^{25} 0.9400 (9); n_D^{25} 1.4980 (24).
Picrate m.165.5°C (24), 168°C (25);   Picrolonate
m.212° (24), 214-5°C (25);   Methiodide m.224° (8), 229.5°C (24)
Isolations etc :- (8, 9, 11, 13, 14, 16, 20 and 26)

3-Methylpyridine.   First isolated by Mohler in 1888 (27).
b.144°C (9); D_4^{25} 0.9515 (7); n_D^{25} 1.5038 (9).
Picrate m.149° (8&9), 153°C (25);   Picrolonate m.206-7°C (24);
Chloroplatinate m.208°C (9).
Isolations etc :- (8, 9, 13 and 28 - 52)
Note :- The great amount of literature published on
the isolation of 3-methylpyridine is due to the fact
that it cannot be separated from 4-methylpyridine and
2:6-dimethylpyridine by direct fractional distillation,
and much work has recently been carried out on its
isolation by other means, with a view to its conversion
to nicotinic acid or nicotinamide.

4-Methylpyridine.   First isolated by Ladenburg in 1885 (53)
b. 145.3°C (9)/

b. $145.3^{\circ}C$ (9); D_4^{25} 0.9502 (9); n_D^{25} 1.5029 (9)

Picrate m.167.5-168°C (25); Picrolonate m. 256°(24), 262-3°(25)

Isolations etc :- (9, 13, 27, 29, 32, 35 - 38, 40, 41,
43, 45, 49, 51, 52, 53 and 54)

2:3-Dimethylpyridine First isolated by Ahrens in 1906 (63).

b. $160.8^{\circ}C$ (9); D_4^{25} 0.9419 (9); n_D^{25} 1.5055 (24)

Picrate m. 188°C (9); Picrolonate m.225-226°C (24)

Methiodide m. 206-207°C (24)

Isolations etc :- (9, 55 and 63)

2:4-Dimethylpyridine First isolated by Ladenburg in 1888 (51).

b. $157.9^{\circ}C$ (9); D_4^{25} 0.9271 (9); n_D^{25} 1.4982 (24).

Picrate m182.5-183°C (24); Picrolonate m.209-211°C (24)

Methiodide m.118.5-119.5°C (24)

Isolations etc :- (9, 13, 16, 51, 56, 57, 58 and 60 -62)

2:5-Dimethylpyridine First isolated by Lunge & Rosenburg
in 1887 (56)

b. $157^{\circ}C$ (9); D_4^{25} 0.9261 (9); n_D^{25} 1.4982 (9).

Picrate m.170°C (25); Picrolonate m.171-172°C (25);

Chloroplatinate m.214°C (9).

Isolations etc :- (9, 56, 59, 60, 61, 62 and 64)

2:6-Dimethylpyridine First isolated by Ladenburg in 1885 (54)

b. $144^{\circ}C$ (9); D_4^{25} 0.9183 (9); n_D^{25} 1.4952 (24)

Picrate m.163-163.5°C (24); Picrolonate m.208-9°C(24);

Methiodide m.238°C (24).

Isolations etc :- (8,9,13,16,27,29,32,35-38,40,41,43,
45,51,54,56,60,61,63 and 65-70).

3:4-Dimethylpyridine/

3:4-Dimethylpyridine First isolated by Ahrens in 1896 (71).

b. 178.9°C (9); D_4^{25} 0.9537 (9); n_D^{25} 1.4952 (24).

Picrate m.163°C (9); Picrolonate m.223-226°C (24);

Methiodide m.120-121°C (24)

Isolations etc:- (9, 26, 71 and 72).

3:5-Dimethylpyridine First isolated by Ahrens and
                      Gorkow in 1904 (64)

b. 171.6°C (9); D_4^{25} 0.9385 (9); n_D^{25} 1.5032 (9).

Picrate m.244°C (9); Picrolonate m.239-240°C (24);

Chloroplatinate m.263°C (9)

Isolations etc :- (9, 64 and 73)

2:3:4-Trimethylpyridine First isolated by Komatsu and
                         Mohri in 1931 (61)

B. 192-193°C (8); D_4^{23} 0.9511 (74); n_D^{22} 1.5129 (74)

Picrate m.164.5°C (8); Picrolonate m.239°C (74)

Isolations etc :- (61)

2:3:5-Trimethylpyridine First isolated by Komatsu and
                         Mohri in 1931 (61).

b. 186.8°C (9); D_4^{25} 0.9310 (9); n_D^{25} 1.5057 (9)

Picrate m.184°C (9); $HgCl_2$ compound m.110°C (9)

Isolations etc. :- (9, 60, 61)

2:3:6-Trimethylpyridine First isolated by Eckert and
                         Loria in 1917 (73).

b. 172.8°C (9); D_4^{25} 0.9220 (9); n_D^{25} 1.5057 (24)

Picrate m.148°C (9); Picrolonate m.228-229°C (25)

Chloroplatinate m.220°C (9)

Isolations etc :- (9, 60, 61, 63, and 73) 75)

2:4:5-/

<u>2:4:5-Trimethylpyridine</u> First isolated by Ahrens
in 1896 (71).

b.189.8°C (9); D_4^{25} 0.9330 (9); n_D^{25} 1.5057 (24). 1.5054 (9).

Picrate m.161°C (9);   Picrolonate m.218°C (24);

Chloroplatinate m.192°C (9).

Isolations etc :- (9, 60, 61, and 71) 75)

<u>2:4:6-Trimethylpyridine</u> First isolated by Mohler
in 1888 (27).

b. 170.3°C (9); D_4^{25} 0.9101 (9); n_D^{25} 1.4959 (9).

Picrate m.157°C (9);   Picrolonate m.230°C (24);

Chloroplatinate m.220°C (9).

Isolations etc :- (9,16,26,27,58,63,72,73 and 76)

<u>2:3:4:5-Tetramethylpyridine</u> First isolated by Ahrens
in 1895 (105)

b. 233°C (105)

Isolations etc :- (61 and 105)

<u>2-Methyl-4-ethylpyridine</u> First isolated by Weidel
and Pick in 1884 (77)

b. 179-180°C (9); D_4^{25} 0.9130 (9); n_D^{25} 1.4953 (9).

Picrate m.141-2°C (24);   Picrolonate m.186-7°C (24);

Chloroplatinate m.203°c (8).

Isolations etc. :- (9, 24 and 77)

<u>2-Methyl-6-ethylpyridine</u> First isolated by Jones
in 1950 (106).

b. 160-161°C (106); n_D^{20} 1.4946 (106).

Picrate m.160-161°C (106)

Isolations etc :- (9 and 106)

<u>Quinoline/</u>

Quinoline   First isolated by Runge & Fischer in 1834 (3)

b. 238.05°C (78); D_4^{20} 1.0929 (78); n_D^{20} 1.6268 (78).

Picrate m.203°C (78);   Picrolonate m.219-220°C (25)

Sulphate m.164-164.5°C (78).

Isolations etc :- (3, 42, 78 and 80 - 84)

2-Methylquinoline   First isolated by Jacobsen and
                        Reimer in 1883 (85)

b. 247.6°C (78); D_4^{20} 1.0585 (78); n_D^{20} 1.6126 (78).

Picrate m.195°C (86);   Styphnate m. 219°C (86);

Trinitro-m-cresolate m.223°C (86)

Isolations etc. :- (25, 78, 80, 82, 85 and 88)

3-Methylquinoline   First isolated by Jantzen in 1932 (78)

b. 259.55°C (m.16-17°); D_4^{20} 1.0673; n_D^{20} 1.6172 (78)

Picrate m.190°C (86);   Styphnate m.190°C (86);

Trinitro-m-cresolate m.223°C (86).

Isolations etc. :- (25 and 78)

4-Methylquinoline   First isolated by Pforte in 1925

m. 9-10°C;   b. 264.2°C; D_4^{20} 1.0868; n_D^{20} 1.6206 (78)

Picrate m.220°C (86);   Styphnate m.237°C (86)

Trinitro-m-cresolate m.254°C (86)

Isolations etc. :- (25, 78, 89, 90 and 91)

5-Methylquinoline   First isolated by Jantzen in 1932 (78)

m. 19°C;   b. 262.7°C; D_4^{20} 1.0832; n_D^{20} 1.6220 (78)

Picrate m.223°C (86);   Styphnate m.218°C (86);

Trinitro-m-cresolate m.214°C (86)

6-Methylquinoline   First isolated by Jantzen in 1932 (78)

b.258.6°C/

b. 258.6°C; D_4^{20} 1.0654; n_D^{20} 1.6157 (78).

Picrate m.235°C (86); Styphnate m.234°C (86);

Trinitro-m-cresolate m.238°C (86).

7-Methylquinoline First isolated by Jantzen in 1932 (78)

m. 39°C; b. 257.6°C; D_4^{20} 1.0609; n_D^{20} 1.6150 (78)

Picrate m.242°C (86); Styphnate m.242°C (86);

Trinitro-m-cresolate m.244°C (86)

Isolations etc. :- (25 and 78)

8-Methylquinoline First isolated by Jantzen in 1932 (78)

b. 247.75°C; D_4^{20} 1.0719; n_D^{20} 1.6164 (78).

Picrate m.205°C (86); Styphnate m.202°C (86);

Trinitro-m-cresolate m.199°C (86).

Isolations etc. :- (25 and 78)

2:8-Dimethylquinoline First isolated by Jantzen in 1932 (78)

m. 23.2-23.6°C; b. 225.25°C; D_4^{20} 1.0394; n_D^{20} 1.6022 (78)

Picrate m.183°C (86); Styphnate m.194°C (86);

Trinitro-m-cresolate m.209°C (86)

Isolations etc. :- (25, 78 and 92).

5:8-Dimethylquinoline First isolated by Ganguli and
                        Guha in 1934 (93) ?

Picrate m.186°C (86); Styphnate m.184°C (86);

Trinitro-m-cresolate m.180°C (86).

Note. Ganguli and Guha claim to have isolated this

compound from anthracene oil bases by means of a

crude fractional distillation and fractional crystal-

lisation of the picrates obtained from a fraction

b. 100 - 110°C/2mm./

b.100 - 110°C/2mm. They claim that they obtained a
picrate which melted at 198°C, which is the value
given by Berend (128) for the picrate of 5:8-dimethyl-
quinoline prepared from 2-amino-p-xylene, and that
a mixed melting point of their sample with a sample
prepared according to the method of Berend showed no
lowering. They also claim that a mixed melting point
of the chloroplatinate$_\wedge^s$ of the two samples showed no
lowering from the observed value of 234°C (decompn.).

Manske et alia, however, in a recent and
very reliable work (86), in which they prepared all
the mono- and dimethylquinolines, found that the
melting point of the picrate of 5:8-dimethylquinoline,
prepared from 2-amino-p-xylene, was 186°C.

It is considered that this observation
casts considerable doubt on the claim of Ganguli and
Guha, especially in view of the fact that they give
no physical constants for their base.

Isoquinoline First isolated by Hoogewerf van Dorp in 1885
m. 24.8°C; b. 243.25°C; D_4^{20} 1.0980; n_D^{20} 1.6148 (78)
Picrate m.224-5°C;(25); Sulphate m.209-209.5°C.
Isolations etc. ;- (15,25,17,78,91 and 94-98)

1-Methylisoquinoline First isolated by Jantzen in 1932 (78)
m. 10.1-10.4°C; b.255.25°C; D_4^{20} 1.0777; n_D^{20} 1.6153 (78)
Picrate m.233.4°C;(99); Sulphate m.255.5-256°C (78)

3-Methylisoquinoline First isolated by Jantzen in 1932
m. 64.7°C/

m. 64.7°C (78); b. 252.25°C (78).

Picrate m.197-198°C (25); Sulphate m.154.5-155°C (78)

5 or 7-Methylisoquinoline First isolated by Jantzen
                                in 1932 (78)

m. 76°C (78); b. 264.9°C (78).

Sulphate m.218-219°C (78).

6-Methylisoquinoline First isolated by Jantzen in 1932 (78)

m. 85-86°C (78); b. 265.5°C (78)

Sulphate m.191-192°C (78)

1:3-Dimethylisoquinoline First isolated by Jantzen
                                in 1932 (78)

m. 29.8-30°C (78); b. 262.4°C (78)

Picrate m.180°C (100); Sulphate m.242-243°C (78)

2:4:6-Trimethylquinoline First isolated by Kruber
                                in 1938 (101)

m. 65.5°C (102); b. 286-288°C (101).

Hydrochloride m.268-272°C (103); Hydrobromide m.265-270°C (104)

APPENDIX II.

INFRA-RED ABSORPTION SPECTRA.

During the course of the present investigation
the opportunity was taken of having infra-red absorption
spectrograms prepared for all of the compounds isolated.

The infra-red absorption spectrogram of a
pure compound is unique and cannot be duplicated by
that of any other compound.   Accordingly, such spectra
provide qualitative identification of any unknown
pure compound whose infra-red spectrum has been obtained
previously.

The infra-red spectra of organic compounds
are characterised by absorption bands which occur
repeatedly at specific frequencies.   These have been
correlated empirically with the presence of certain
bonds and atomic groupings.   Thus, even in the
absence of a reference spectrogram for a given compound,
it is generally possible by careful examination of its
infra-red absorption spectrogram to recognise at least
some of the chemical linkages present.   It is also
frequently possible to determine the geometrical
arrangement of the atoms within the molecule by the
presence of certain groups of absorption bands.   Thus
a decision can often be reached as to whether a
molecule is cis or trans, ortho, meta or para, enolic
or ketonic etc.

Benzie/

INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

CM.—¹ WAVE NUMBERS

MICRONS WAVE LENGTH

CM.—¹ WAVE NUMBERS

PERCENT ABSORPTION
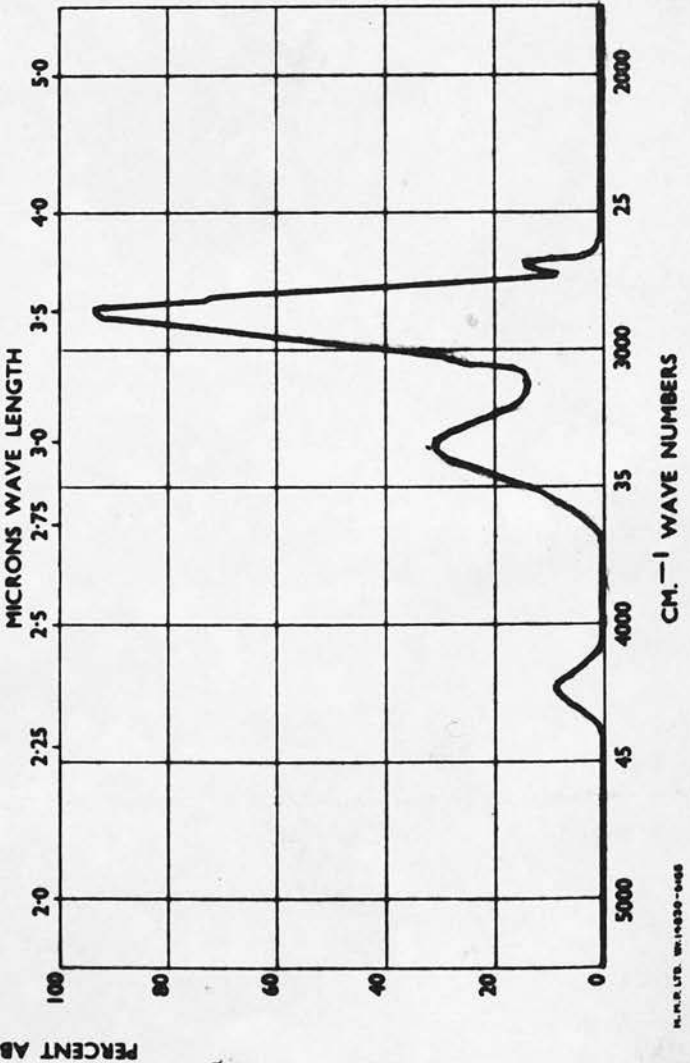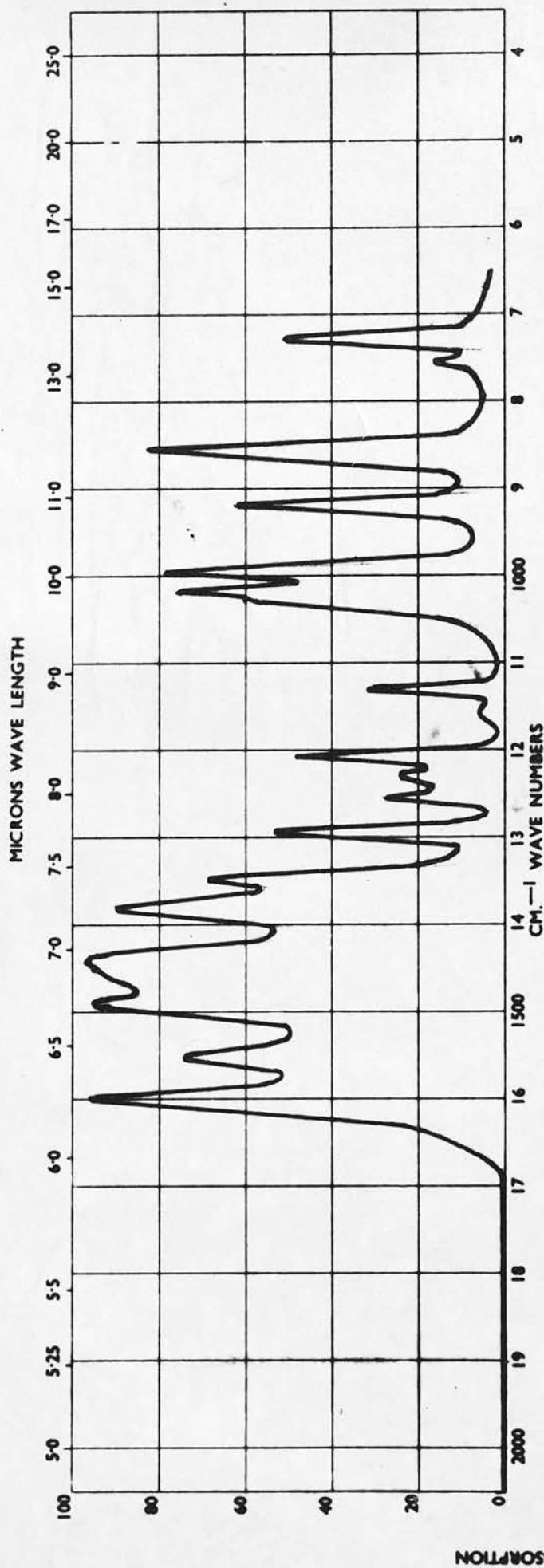
COMPOUND   2:4:5-Trimethylpyridine

SOURCE   Coal Tar

PURITY

STATE   Liquid

CELL LENGTH   0·050mm.

SPECTROMETRIC   Hilger D.209 Double-beam
MEASUREMENT   Spectrometer (Rocksalt Prism)

H.M.R LTD. W.14539-0455

Benzie and Milne (24) have published infra-red absorption spectrograms for three of the compounds investigated during this work, namely 2:4:5-trimethyl-pyridine and 2:3:4:6- and 2:3:5:6-tetramethylpyridines, and in each of these cases excellent agreement was obtained between the spectrograms obtained for the bases isolated during the present work and those published by Benzie and Milne.   In the case of 2:3:4-trimethylpyridine, however, no spectrogram had been published previously, and therefore it was not possible to make any direct comparison.

Unfortunately, no infra-red absorption spectrograms had been published for either 3-methyl-isoquinoline or the dimethylquinolines isolated. In the case of the dimethylquinolines, however, authentic samples of each were prepared, and the spectrograms obtained for these synthetic samples were found to be in agreement with those obtained for the bases isolated from coal tar.

The spectrograms of the nine compounds examined are reproduced together with short notes on each.

2:4:5-Trimethylpyridine.

The excellent agreement with the spectrogram obtained by Benzie and Milne (loc. cit.) confirmed that this compound was 2:4:5-trimethylpyridine.   All the pyridine homologues have an intense, rather broad band/

2:3:5:6 - TETRAMETHYLPYRIDINE   SATURATED SOLN. IN CCl₄ - CS₂ (CORRECTED FOR SOLVENT BANDS)   50μ CELL

% ABSORPTION vs WAVELENGTH (CMS⁻¹)
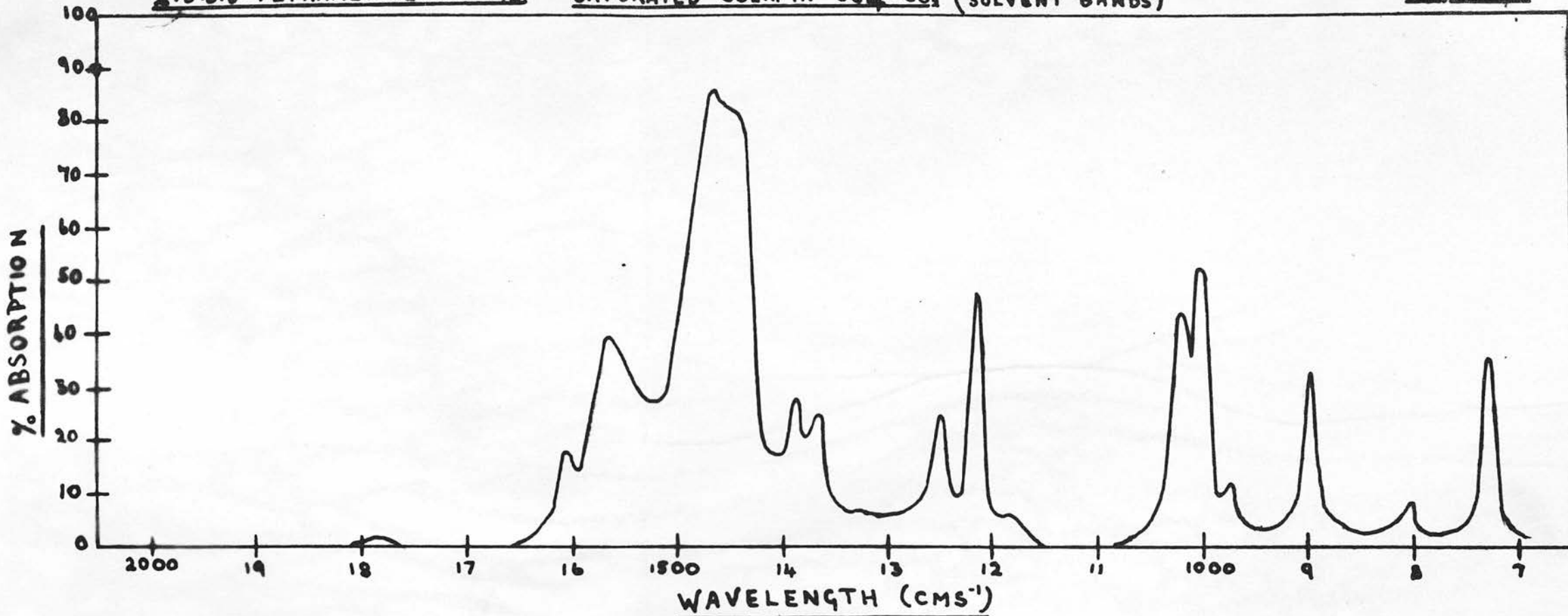
2:3:4:6 - TETRAMETHYLPYRIDINE (LIQUID)   50μ CELL

% ABSORPTION vs WAVELENGTH (CMS⁻¹)

INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH
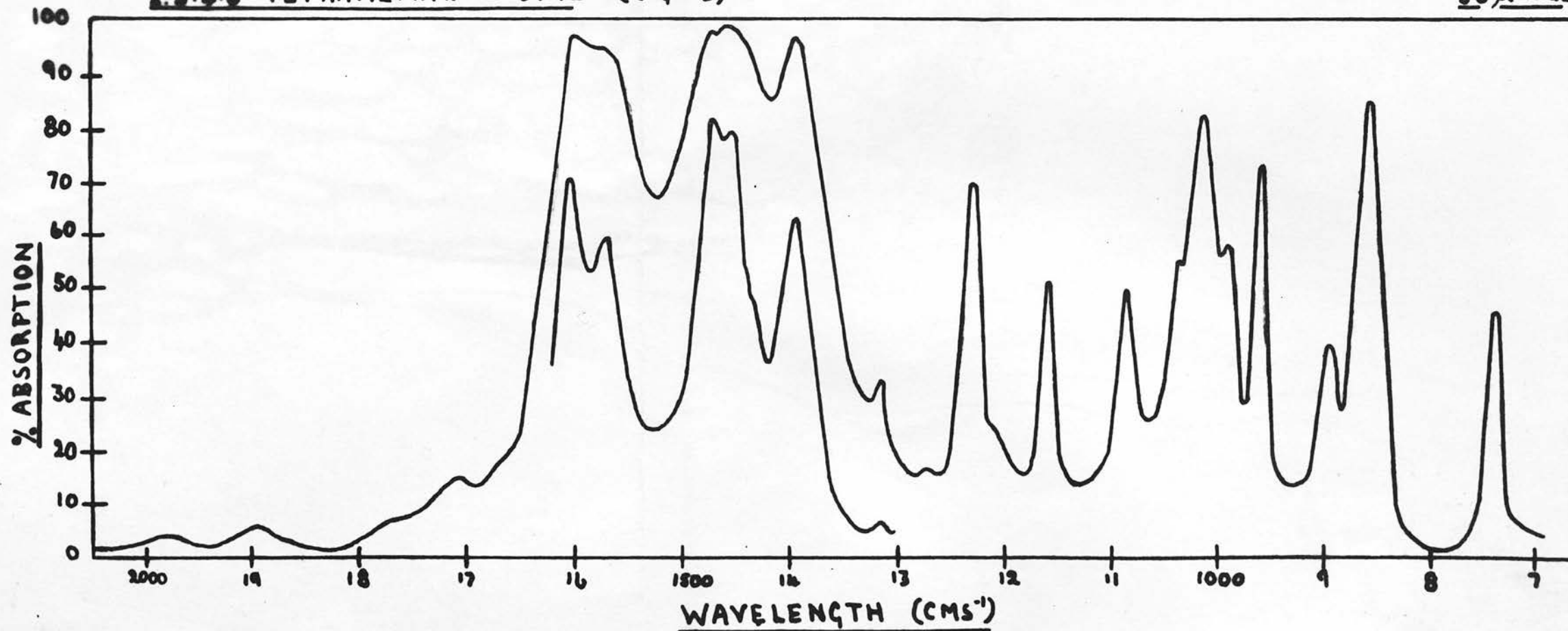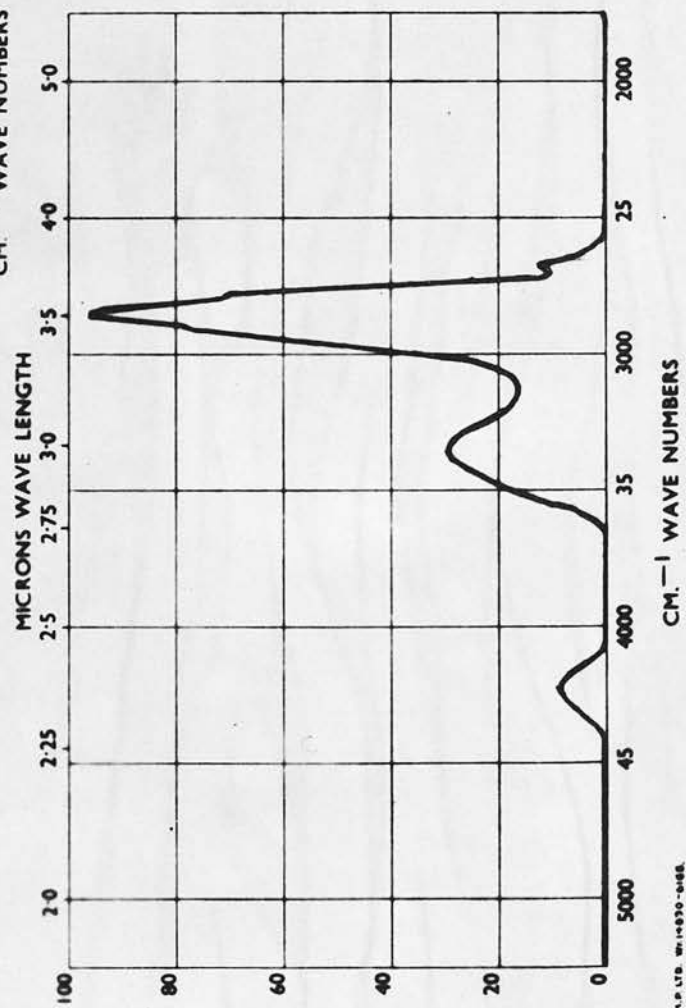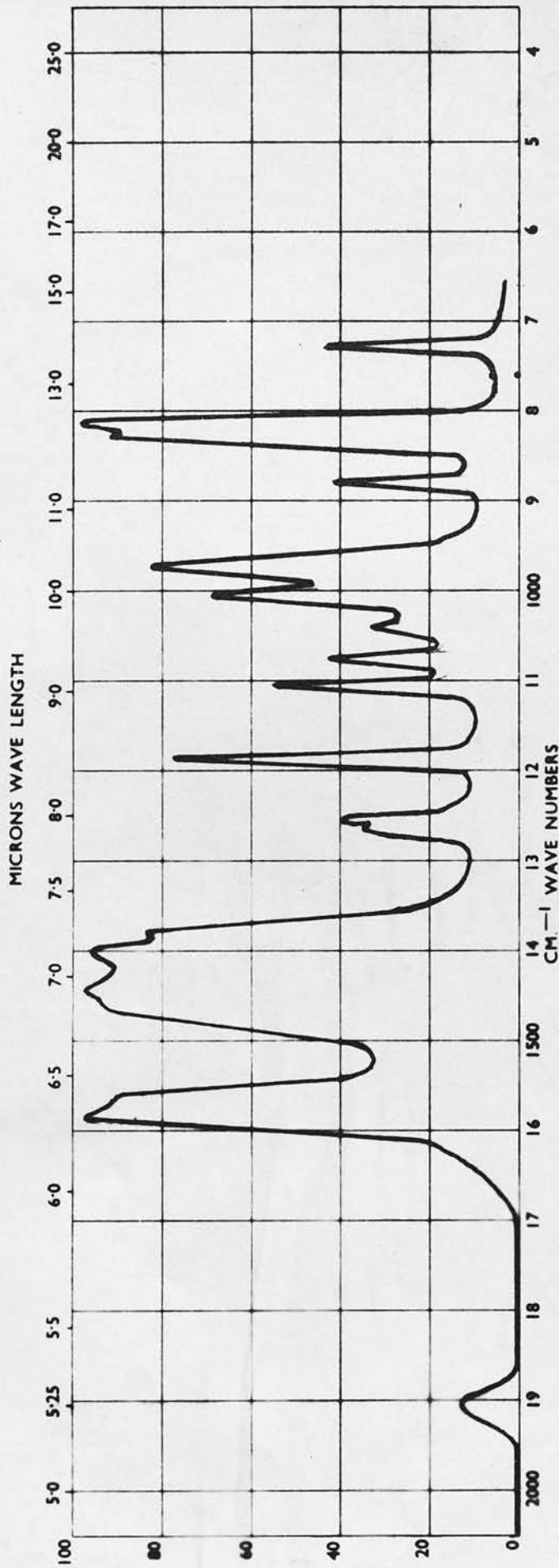
COMPOUND   2:3:4-Trimethylpyridine

SOURCE   Coal Tar

PURITY

STATE   Liquid

CELL LENGTH 0.050 mm.

SPECTROMETRIC Hilger D.209 Double-beam
MEASUREMENTS Spectrometer (Rocksalt Prism)

CM.⁻¹ WAVE NUMBERS

MICRONS WAVE LENGTH

CM.⁻¹ WAVE NUMBERS

PERCENT ABSORPTION

band at 750-855cms.$^{-1}$ which is quite probably due to
ring deformation. In the case of 2:4:5-trimethyl-
pyridine this band occurs at 855cms.$^{-1}$. The band
due to the -C-CH$_3$ deformation which normally occurs
at 1375-1390cms.$^{-1}$ is also strongly marked, while the
band due to -CH$_2$-CH$_3$ (760-780cms.$^{-1}$) is absent.

2:3:4-Trimethylpyridine.

The clean spectrum of this compound indicates
that the sample was pure, while the strong general
resemblance to the spectrograms of 2:4:5-trimethyl-
pyridine and of 2:4:6-trimethylpyridine (154) is in
keeping with the suggestion that the compound had the
formula assigned to it. Unfortunately, no reference
spectrum was available for direct comparison, but the
above notes on the spectrogram of 2:4:5-trimethyl-
pyridine apply very similarly in the case of this
spectrogram and support the view that this compound
was 2:3:4-trimethylpyridine.

2:3:5:6-Tetramethylpyridine.

The spectrum of this compound was found to
be identical to the spectrum obtained for the base
isolated by Benzie & Milne, and to the spectrum obtained
for the sample of 2:3:5:6-tetramethylpyridine prepared
by Smith, thus confirming that this compound was
2:3:5:6-tetramethylpyridine.

2:3:4:6-Tetramethylpyridine./

INFRARED ABSORPTION SPECTROGRAM

No
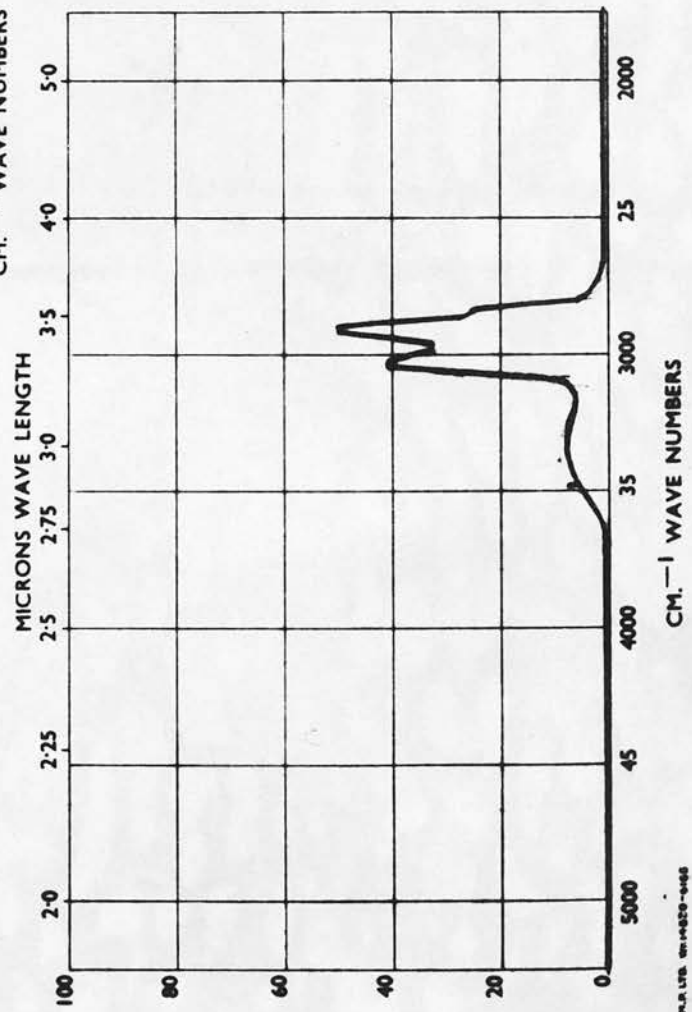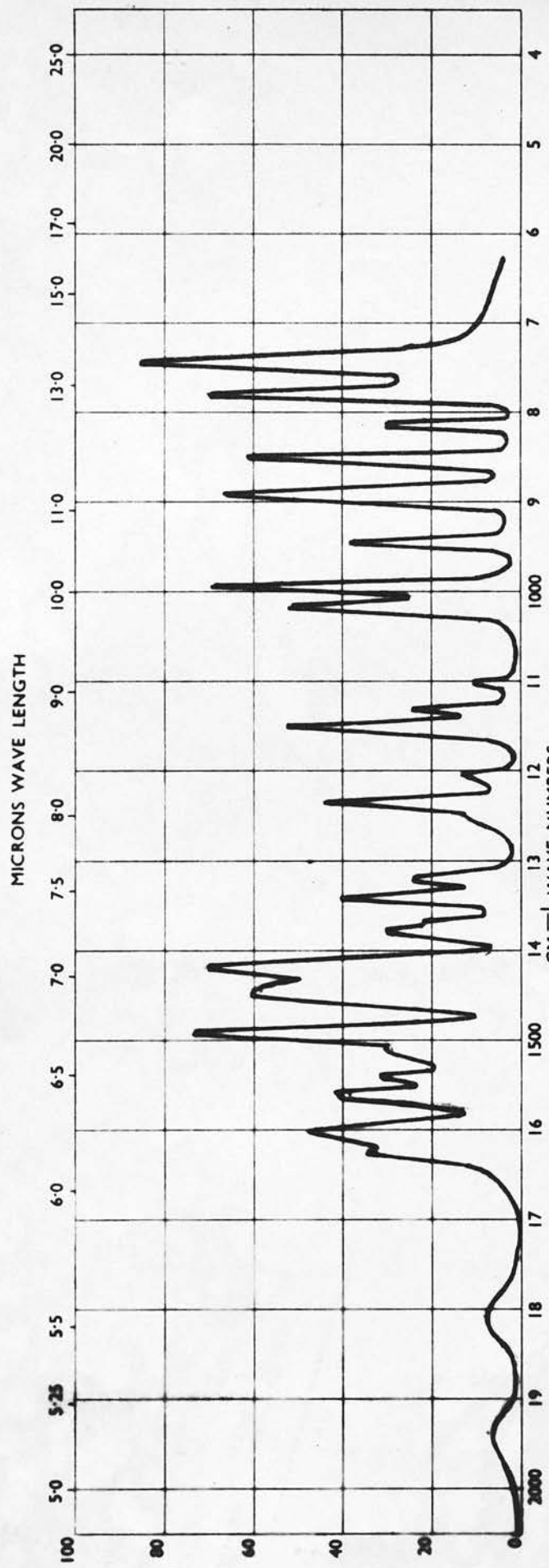
COMPOUND   2,3-Dimethylquinoline

SOURCE   Coal Tar

PURITY

STATE   Satd. Solns. in CS_2 and in CCl_4
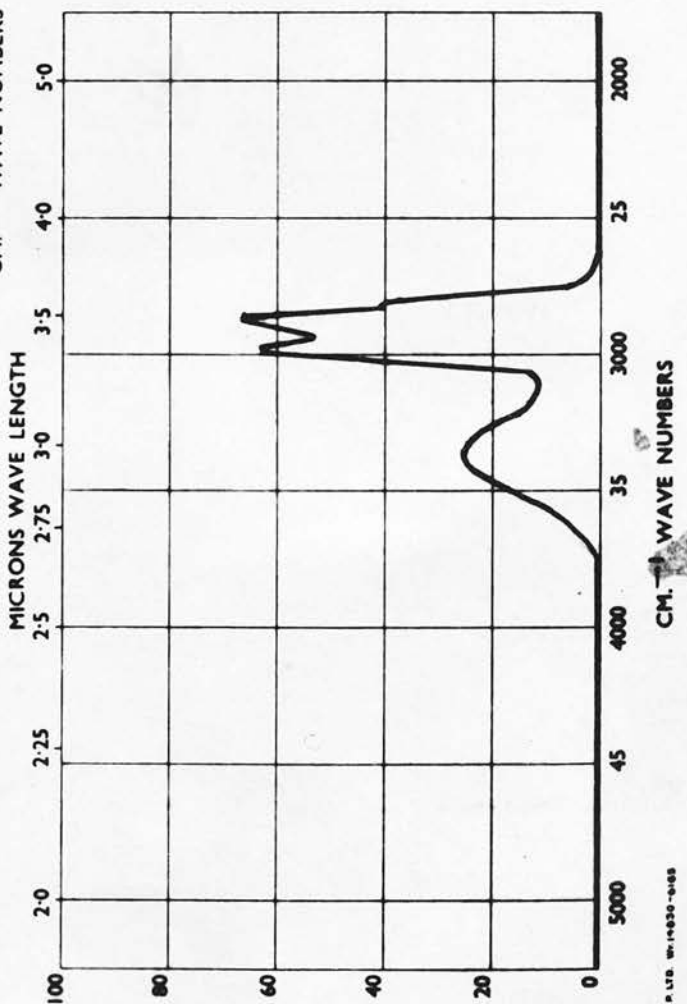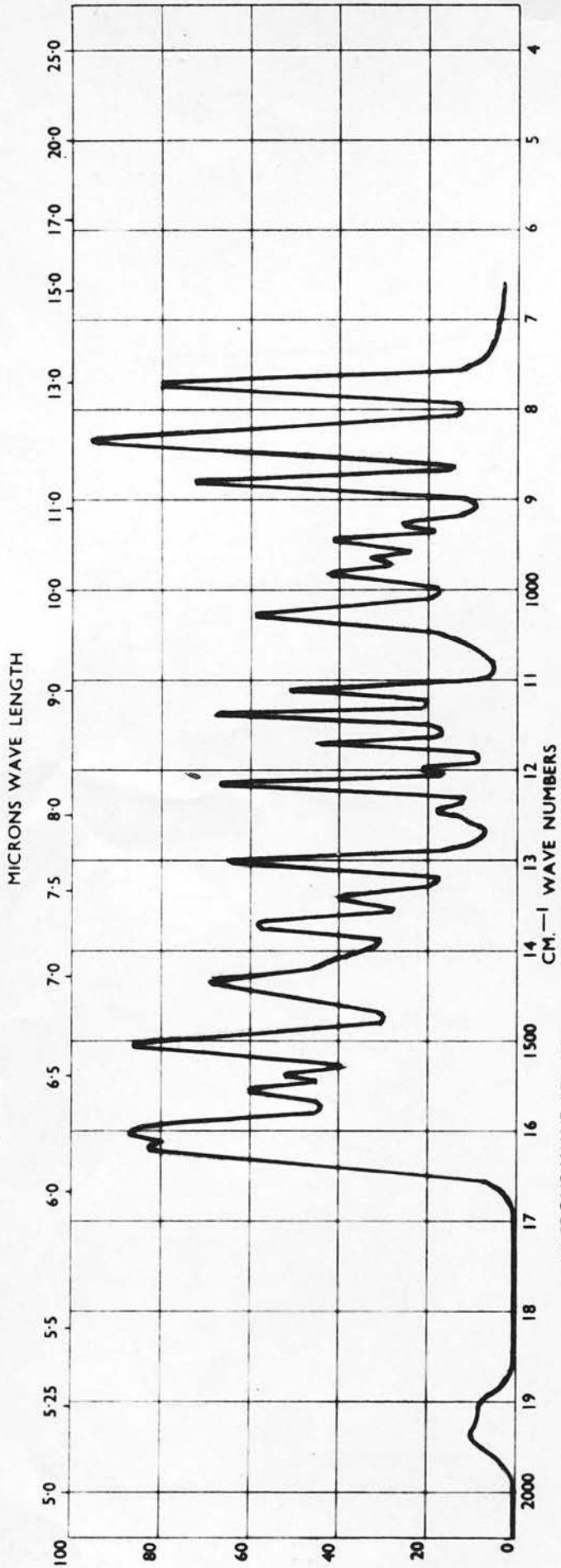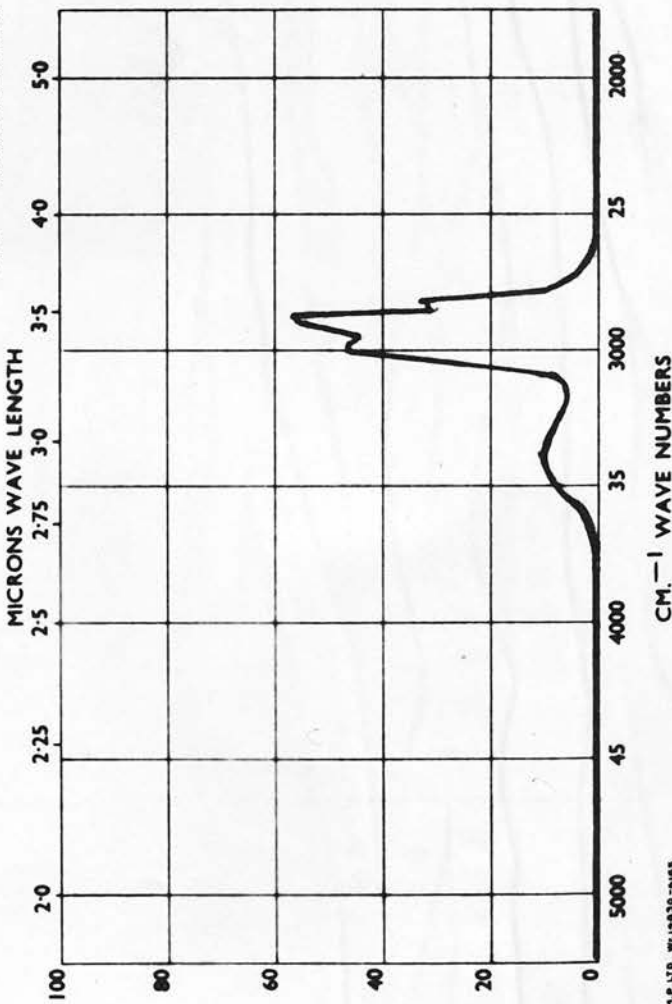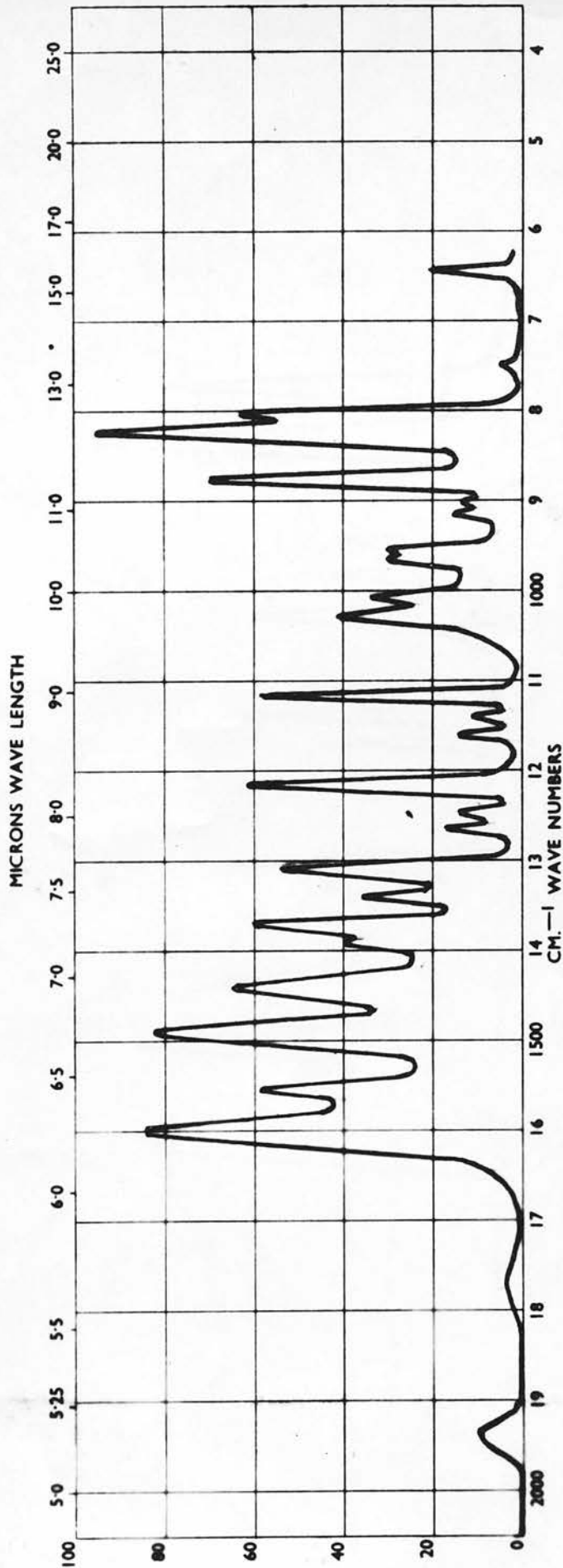
CELL LENGTH   0.050mm.

SPECTROMETRIC   Hilger D.209 Double-beam
MEASUREMENT Spectrometer (Rocksalt Prism)

Corrected for Solvent Absorption

MICRONS WAVE LENGTH

CM.—I WAVE NUMBERS

PERCENT ABSORPTION

INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

CM.—1 WAVE NUMBERS

MICRONS WAVE LENGTH

CM. WAVE NUMBERS

PERCENT ABSORPTION

COMPOUND   2:7-Dimethylquinoline

SOURCE   Coal Tar

PURITY

STATE   Satd. Solns. in CS_2 and in CCl_4

CELL LENGTH   0.050mm.

SPECTROMETRIC   Hilger D.209 Double-beam
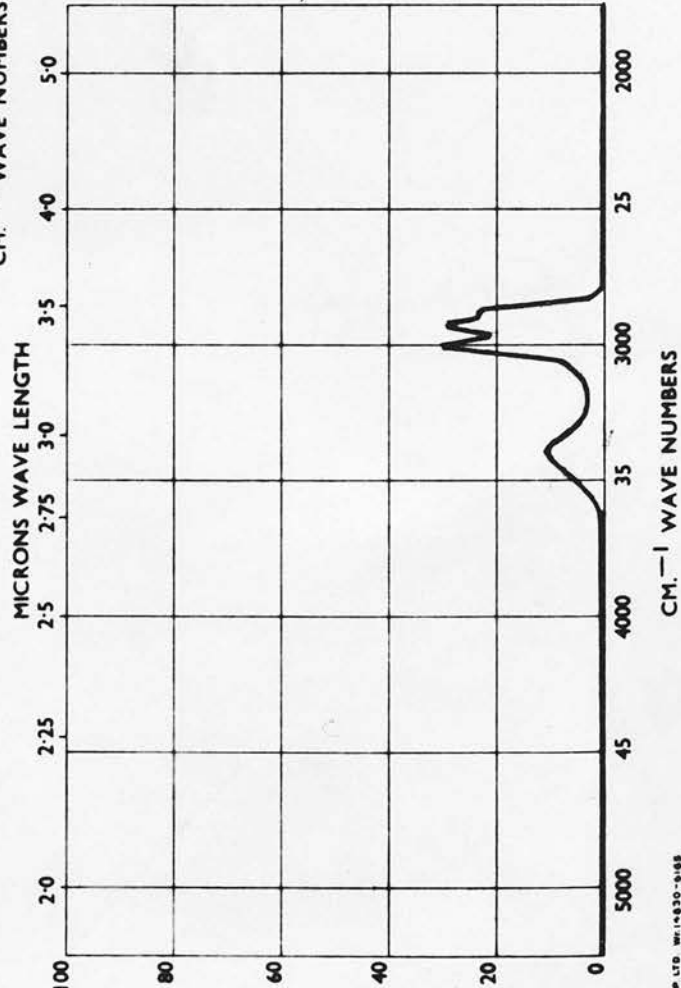MEASUREMENT   Spectrometer (Rocksalt Prism)

Corrected for Solvent Absorption

INFRARED ABSORPTION SPECTROGRAM

No

COMPOUND   2:6-Dimethylquinoline

SOURCE   Coal Tar

PURITY

STATE   Satd. Solns in CS₂ and in CCl₄

CELL LENGTH   0.050mm

SPECTROMETRIC   Hilger D.209 Double-beam
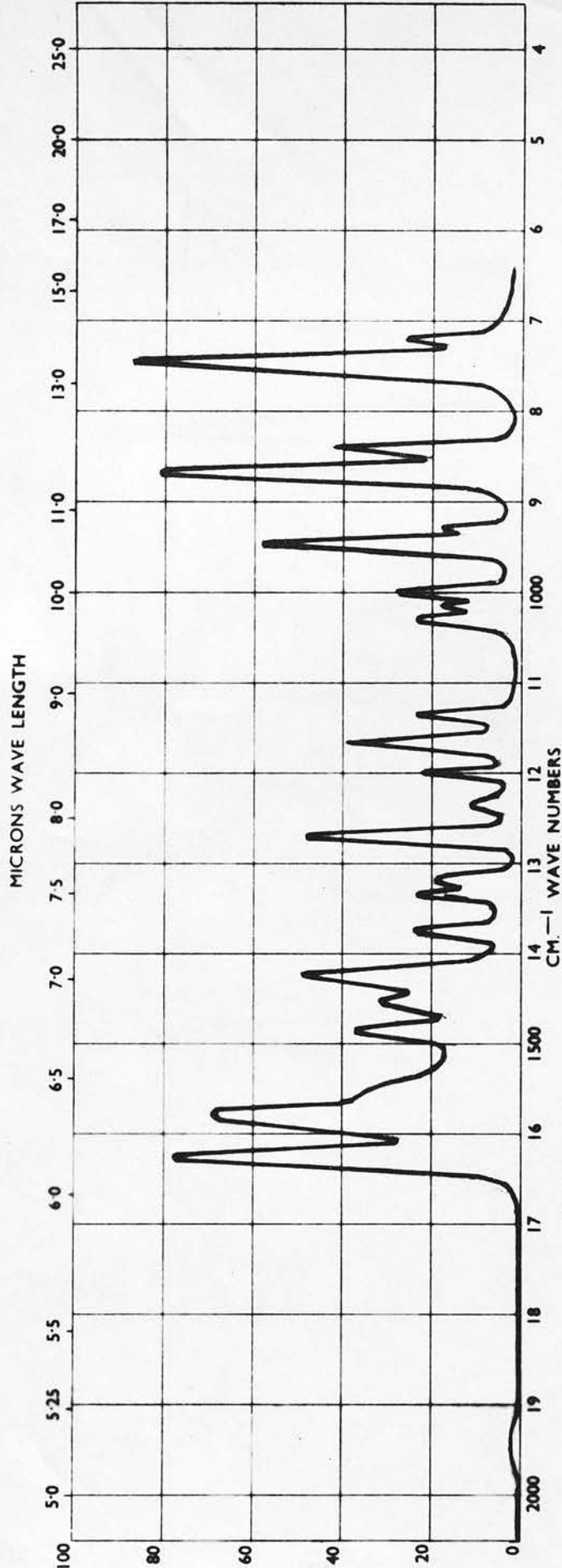MEASUREMENT   Spectrometer (Rocksalt Prism)

Corrected for Solvent Absorption

INFRARED ABSORPTION SPECTROGRAM

No

MICRONS WAVE LENGTH

CM.—I WAVE NUMBERS

PERCENT ABSORPTION

MICRONS WAVE LENGTH

CM.—I WAVE NUMBERS

COMPOUND   3-Methylisoquinoline

SOURCE   Coal Tar

PURITY

STATE   Satd. Solns. in CS_2 and in CCl_4

CELL LENGTH   0.050mm.

SPECTROMETRIC   Hilger D.209 Double-beam
MEASUREMENT   Spectrometer (Rocksalt Prism)

Corrected for Solvent Absorption

DESIGNED BY CHEMICAL RESEARCH LABORATORY, TEDDINGTON MIDDX.
AND PUBLISHED BY H.M.S.O.

M.M.P. LTD. WI.14330-0166

2:3:4:6-Tetramethylpyridine.

The perfect agreement of the spectrogram of this compound with that obtained by Benzie & Milne . confirmed that this compound was 2:3:4:6-tetramethyl-pyridine.

3-Methylisoquinoline.

The infra-red absorption spectrogram of this compound was obtained, but no reference spectrum was available for direct comparison. The general nature of the spectrum, however, is in agreement with the supposition that this compound was 3-methylisoquinoline.

2:6-Dimethylquinoline.

The spectrum obtained for this compound was found to be identical to that obtained for an authentic sample of 2:6-dimethylquinoline, thus confirming that this compound was 2:6-dimethylquinoline.
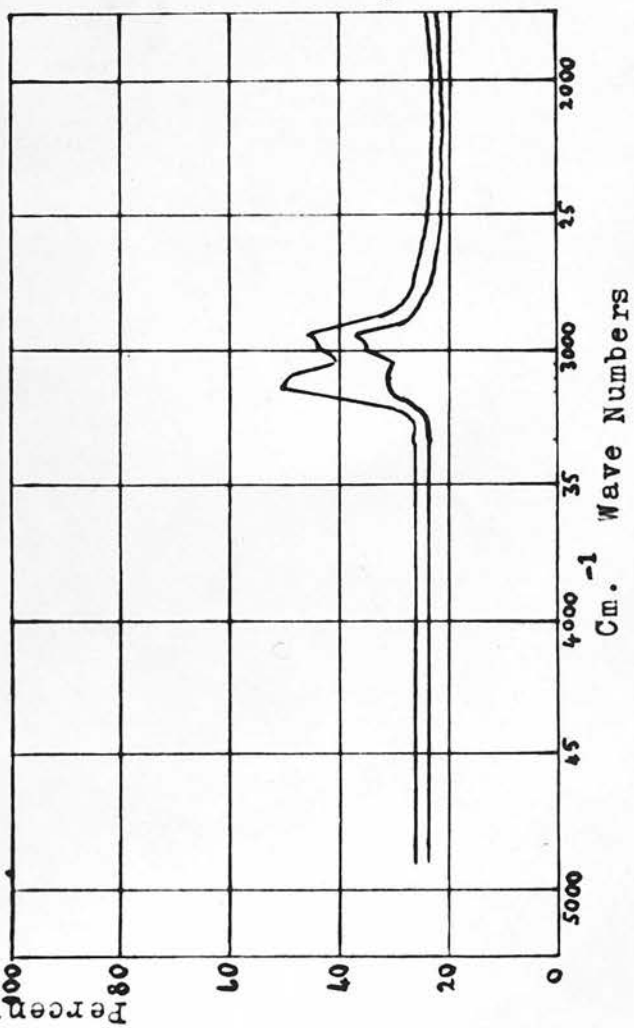
2:7-Dimethylquinoline.

The spectrogram obtained for this compound was found to be identical to that obtained for an authentic sample of 2:7-dimethylquinoline, thus confirming that this compound was 2:7-dimethylquinoline.
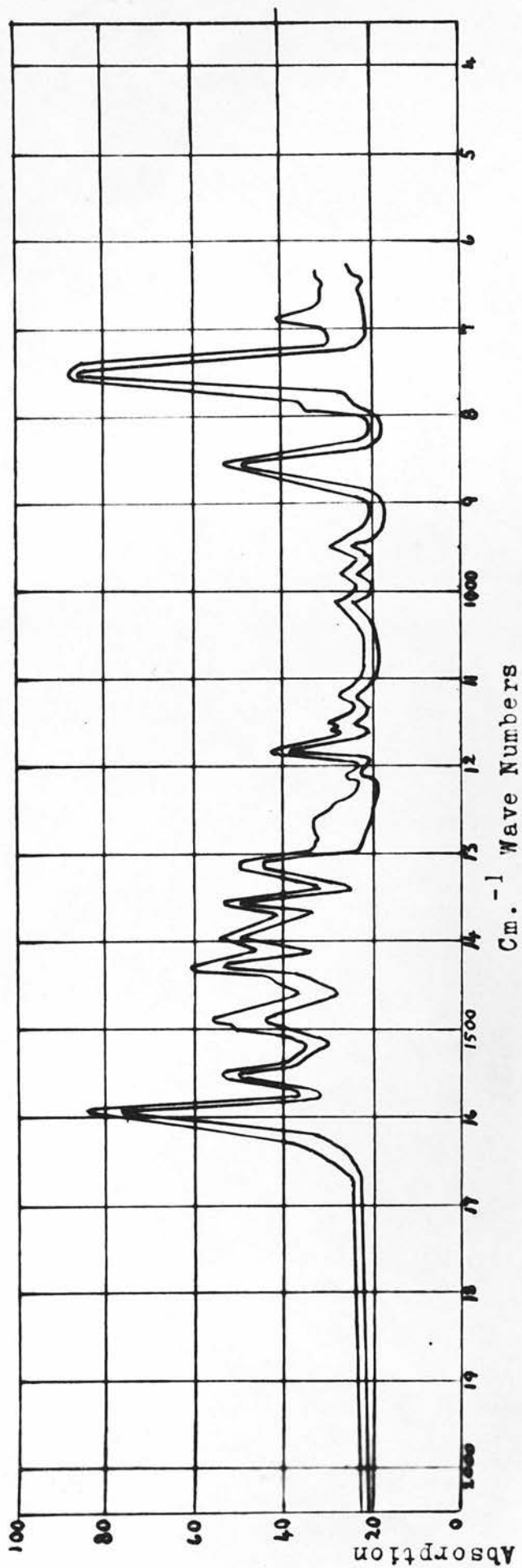
2 3-Dimethylquinoline.

The spectrogram obtained for this compound was found to be identical to that obtained for an authentic sample of 2:3-dimethylquinoline, thus confirming/

INFRA-RED ABSORPTION SPECTROGRAM

Cm. -1 Wave Numbers

Percent Absorption

Compound   2:4-Dimethylquinoline

Sources   Synthetic and Coal Tar

State   Liquid

Cell Length   Capillary Film

• Spectrometric Measurements by the Ministry
of Supply, Chemical Inspectorate, C.36,
Royal Arsenal, Woolwich.

confirming that this compound was 2:3-dimethylquinoline.

Note:- The concentrations used in the measurement of the above four spectra varied as is indicated by the band near 3000cms.$^{-1}$

2:4-Dimethylquinoline

The spectrum obtained for this compound is shown opposite together with the spectrum of the sample of 2:4-dimethylquinoline which had been prepared. The upper graph is that of the synthetic sample. It may be noted that the spectrogram of the synthetic sample contains the following three bands which are not present in the natural sample.

At about 690cm.$^{-1}$ - which is characteristic of mono-substituted aromatic compounds.

At about 1270cm.$^{-1}$ - which is characteristic of aniline.

At about 3300cm.$^{-1}$ - which indicates a hydrogen-bonded NH or OH group.

There is very little doubt that these differences are due to the presence of traces of some impurity in the synthetic material, probably some unreacted aniline, and the overall agreement of the two spectra confirmed that the compound isolated from the tar bases was 2:4-dimethylquinoline.

Most of the above spectrograms were prepared through the courtesy of Dr. E.A. Coulson of the Department of Scientific and Industrial Research and the measurements were carried out by Mr. J.L. Hales at the Chemical Research Laboratory, Teddington. In the cases of the synthetic samples of 2:3-, 2:4-, 2:6- and 2:7-dimethylquinolines and of the natural sample of 2:4-dimethylquinoline, however, the spectra were prepared through the courtesy of Mr. E.T. Osborne of the Ministry of Supply and the measurements were carried out by Mr. L.J. Bellamy at the Chemical Inspectorate, Royal Arsenal, Woolwich.

BIBLIOGRAPHY.

1. Unverdorben, Pogg. Ann., 8, 253-65 & 477-87 (1826)
                       11, 59-74 (1827).

2. Anderson, Ann., 60, 86-103 (1846).

3. Runge, Pogg. Ann., 31, 65-78 & 513-24 (1834),
                       32, 308-333 (1834).

4. Gerhardt, Ann., 42, 310-313 (1842),
                       44, 279-280 (1842).

5. Hofmann, Ann., 47, 37-87 (1843).

6. Williams, Edinr. New Phil. J., 2, 324-331 (1855)

7. Heap, Jones & Speakman, J. Amer. Chem. Soc.,
                       43, 1867 (1921).

8. Hans Maier Bode, Pyridine and its Derivatives (Book).

9. Eguchi, Bull. Chem. Soc. (Japan), 2, 176 (1927)
                       3, 227 (1928).

10. Arndt & Nachtwey, Ger. Patent, 451,956.

11. Wilkie & Shaw, J. Soc. Chem. Ind., 46, 469 (1927)

12. Manners, Chem. Weekbland, 26, 286-290.

13. Rapaport & Kasolapov, Khim. Tverdigo Topliva,
                       4, 585-592 (1933).

14. U.S. Patent, 2,085,287.

15. Tartarini & Samaja, Ann. Chim. Applicata,
                       23, 356-362 (1933).

16. Ochiai & Haginiwa, J.Pharm.Soc. (Japan), 60, 442 (1940)

17. Kruber & Rapper, Ber., 73B, 1178 (1940).

18. Arndt & Nachtwey, Ber., 59B, 448 (1926).

19. Tallantyré, J. Soc. Chem. Ind., 49, 466 (1930)

20./

20. Tartarini & Samaja, Ann. Chim. Applicata,
                          23, 351-356 (1933)

21. U.S. Patent, 1,976,682.

22. Ger. Patent, 605,228.

23. Russ. Patent, 55,844.

24. Benzie & Milne, Ph.D. Theses, Edinr. University, 1949.
    Benzie, Milne & Nisbet, Proceedings of the 2nd.
    International Oil Shale and Cannel Coal Conference.
    (Glasgow, 1950).

25. Hackmann, Wibaut & Gitsels, Rec. Trav. Chim.,
                          62, 229 (1943).

26. Oshima & Ishibashi, J. Soc. Chem. Ind. (Japan),
                          29, 445-451 (1926)

27. Mohler, Ber., 21, 1009 (1888).

28. U.S. Patent, 2,300,741.

29. U.S. Patent, 2,335,823.

30. U.S. Patent, 2,338,571.

31. Brit. Patent, 556,533.

32. U.S. Patent, 2,374,418.

33. Brit. Patent, 561,722.

34. Brit. Patent, 570,427; U.S. Patent, 2,402,667.

35. U.S. Patent, 2,402,158.

36. U.S. Patent, 2,404,167.

37. U.S. Patent, 2,412,649.

38. Brit. Patent, 580,048.

39. Riethof et al., Ind. Eng. Chem.(Anal), 18, 458 (1946).

40. Coulson & Jones, J. Soc. Chem. Ind., 65, 169 (1946).

41. U.S. Patent, 2,420,529.

42. Brit. Patent, 588,277.

43./

43. Lidstone, J. Chem. Soc., 1940, 241.

44. Ger. Patent, 697,759.

45. U.S. Patent, 2,383,016.

46. U.S. Patent, 2,388,499.

47. U.S. Patent, 2,403,949.

48. Lukes, Collection Czech. Chem. Communs., 12, 263 (1947).

49. Brit. Patent, 598,036.

50. U.S. Patent, 2,443,479.

51. Ladenburg, Ann., 247, 1 (1888).

52. U.S. Patent, 2,336,502.

53. Schulze, Ber., 20, 413 (1887).

54. Ladenburg, Ber., 18, 47 (1885).

55. Brit. Patent, 584,148.

56. Lunge & Rosenburg, Ber., 20, 130 (1887)

57. Bacher, Ber., 21, 3071 (1888).

58. Ahrens, Ber., 28, 795 (1895).

59. U.S. Patent, 2,336,502

60. Oparina, Ber., 64B, 562 (1931).

61. Komatsu & Mohri, J. Chem. Soc.(Japan), 52, 722-6 (1931).

62. U.S. Patent, 2,454,019.

63. Ahrens, Chem. Zentr., 1, 510 (1906).

64. Ahrens & Gorkow, Ber., 37, 2062 (1904).

65. Shuster, Ber., 25, 2398 (1892)

66. U.S. Patent, 2,295,606.

67. U.S. Patent, 2,325,880.

68. U.S. Patent, 2,376,000.

69. Grigarovskii & Kimen, J. App. Chem.(U.S.S.R.), 1945, 259.

70. U.S. Patent, 2,430,804.

71./

71. Ahrens, Ber., 29, 2996 (1896).

72. Schutz et al., Ber., 56, 1967 (1923).

73. Eckert & Loria, Monatshefte, 38, 225 (1917).

74. Prelog et al., Helv. Chim. Acta, 25, 1654 (1942)

75. Barnes et al., Ind. Eng. Chem.(Anal), 15, 659 (1943)

76. U.S. Patent, 2,426,442.

77. Weidel & Pick, Monatshefte, 5, 656 (1884).

78. Jantzen, Dechema Monographien, Band 5, Berlin 1932.

79. Decker & Remfry, Ber., 38, 2773 (1905)

80. U.S. Patent, 1,750,082.

81. Lecat, Ann. Soc. Sci.(Bruxelles), 61, 73 (1947).

82. U.S. Patent, 2,408,975.

83. U.S. Patent, 2.456,774.

84. Wibaut & Ahrens, Rec. trav. chim., 60, 119 (1941).

85. Jacobsen & Reimer, Ber., 16, 1082 (1883).

86. Manske et al., Can. J. Research, 20B, 133 (1942)

87. Wyler, Ber., 60B, 398 (1927);

    Brit. Patent, 276,156.

88. U.S. Patent, 2,432,064.

89. Ger. Patent, 468,303.

90. Vanags & Dombrowski, Ber., 75B, 82 (1941)

91. Ger. Patent, 505,320.

92. Perrin & Bailey, J. Amer. Chem. Soc., 55, 4141 (1933).

93. Ganguli & Guha, J. Indian Chem. Soc., 11, 197 (1934)

94. Weissgerber, Ber., 47, 3175 (1914).

95. Harris & Pope, J. Chem. Soc., 121, 1029 (1922).

96. U.S. Patent, 2,391,270.

97. U.S. Patent, 2,432,065.

98./

98. U.S. Patent, 2,432,064.

99. Schittler & Müller, Helv. Chim. Acta, 31, 914 (1948).

100. Witkop, J. Amer. Chem. Soc., 70, 1424 (1948).

101. Kruber, Angew. Chem., 53, 69 (1940).

102. Ger. Patents, 363,582-3.

103. Bahr, Ber., 55B, 1912 (1922)

104. Fischer et al., J. prakt. Chim., 100, 86.

105. Oparina, Zhur. Obschei Khim., 19, 1351 (1949).
     Amer. Chem. Abstr., 44, 1108 (1950).

106. Jones, J. Soc. Chem. Ind., 69, 99 (1950).

107. Lanin & Pozhil'tsova, J. App. Chem.(USSR), 16, 388 (1943)

108. Pott et al., J. Amer. Chem. Soc., 52, 1239 (1930)

109. Bailey & Bratton, J. Amer. Chem. Soc., 59, 175 (1937).

110. Maillard, Compt. rend., 154, 66 (1912).
     155, 1554 (1912).
     157, 850 (1913)

111. Terres, Proc 3rd International Conference on
     Bituminous Coal, 2, 797-808 (1931)

112. Ward, U.S. Bureau of Mines, Technical Paper, 600 (1939).

113. Fay, Ann. Rep. of Chem. Soc., 11, 221 (1943)

114. Stage & Schultze, "Theory, Apparatus and Procedures
     of Distillation and Rectification." Published by
     the Hobart Publishing Co., Washington. (1947).

115. Rose & Rose, " Distillation Literature and Abstracts,
     1941" State College Pa., 1948.

116. Rose, Anal. Chem., 21, 81 (1949).

117. Underwood, Trans. Inst. Chem. Engrs., 10, 112 (1932)

118. Glasgow & Schicktanz, Nat. Bur. Standards J.
     Res., 19, 593 (1937)

119./

119.   Docksey & May,   J. Inst. Petroleum, <u>21</u>, 176 (1935).

120.   Rose,   Ind. Eng. Chem., <u>28</u>, 1210 (1936)

121.   Schicktanz,   Nat. Bur. Standards J. Res., <u>11</u>, 89 (1933)

122.   Fenske,   Ind. Eng. Chem., <u>30</u>, 297 (1938).

123.   Stedman,   Nat. Pet. News, <u>29R</u>, 125 (1937).

124.   Leckey & Ewell,   Ind. Eng. Chem. (Anal.), <u>12</u>, 545 (1940).

125.   Dixon,   J. Soc. Chem. Ind., <u>68</u>, 88 (1949).
                Brit. Patent 578,309.

126.   Birch et al.,   J. Soc. Chem. Ind., <u>66</u>, 33 (1947).

127.   Willingham et al.,   Ind. Eng. Chem., <u>39</u>, 706 (1947).

128.   Berend,   Ber., <u>18</u>, 3165 (1885)

129.   Hunter & Nash,   Ind. Eng. Chem., <u>27</u>, 836 (1935).

130.   Kondo,   "Principles & Practice of Chromatography" Page 233.

131.   Walker,   Austr. J. Sci., <u>13</u>, 26 and 84 (1950).

132.   Jones,   J. Chem. Soc., <u>1950</u>, 1392.

133.   Messrs. I.C.I. Ltd. - Private communication.

134.   Langdon & Tobin,   Ind. Eng. Chem. (Anal.), <u>17</u>, 801 (1945).

135.   Coulson & Warner,   J. Sci. Instruments, <u>21</u>, 122 (1944).

136.   Brit. Patent,   564,512.

137.   Hershberg & Huntress,   Ind. Eng. Chem. (Anal.), <u>5</u>, 344 (1933)

138.   Bromiley & Quiggle,   Ind. Eng. Chem., <u>25</u>, 1136 (1933)

139.   Nisbet & Pryde,   Nature, <u>167</u>, 862 (1951).

140.   Riley & Bailey,   Proc. Roy. Irish Acad., <u>38B</u>, 450 (1929)

141.   Hamer et al.,   Analyst, <u>71</u>, 419 (1946).

142.   Angyal,   Australian Chem. Inst., J. & Proc., <u>14</u>, 12 (1947).

143.   Mills & Smith,   J. Chem. Soc., <u>121</u>, 2724 (1922)

144.   Doebner & Miller,   Ber., <u>16</u>, 2465 (1883).

145.   Pfitzinger,   J. prakt. Chem., <u>66</u>, 263 (1902).

146./

146. Plant & Rosser, J. Chem. Soc., 1929, 1861.

147. British Patent Application, 4491/46.

148. Vaughan, Organic Syntheses, 28, 49.

149. Spallino & Cucchiaroni, Gazetta Chimica Italiana,
     42I, 524 (1912).

150. U.S. Patent, 2,451,610.

151. Campbell & Schaffner, J. Amer. Chem. Soc., 67, 86 (1945).

152. U.S. Patent, 2,504,172.

153. British Intelligence Objectives Sub-Committee
     Surveys, 25, 118.

154. Barnes, Ind. Eng. Chem.(Anal.), 15, 659 (1943)