STUDIES IN NITROGENOUS BASES FROM SCOTTISH SHALE OIL

by

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INTRODUCTION.

The research to be described in this thesis takes the form of an investigation of the Nitrogenous Bases occurring in Scottish Shale Oil, produced by destructive distillation of typical Lothians Shale. These bases, which are produced by the thermal decomposition of the complex organic matter, or "Kerogen", present in the shale, find their way into the oil, and are removed along with other undesirable materials, such as sulphur compounds and phenols, in the normal course of refining, and ultimately find their way into the so called "Acid Tar" which separates out when the various partially refined oil and wax fractions are treated with sulphuric acid in the refinery. This "Acid Tar", which is an extremely complex mixture resulting from the action of the acid on the highly unsaturated crude oil and wax fractions, is subsequently washed with water to recover the free sulphuric acid present in excess, and the resulting dilute sulphuric acid, containing the dissolved bases in the form of sulphates, is ultimately converted to ammonium sulphate, by reaction with ammonia. The weaker bases precipitated by the ammonia form a viscous black "Basic Tar", which is at present recycled and ultimately used as fuel in the refinery. It is this "Basic Tar" which has formed the starting material on which the present investigation has been conducted.

Apart /

Apart from certain preliminary and incomplete examinations carried out in the laboratories of Messrs Scottish Oils, Ltd. and the Anglo Iranian Oil Co. Ltd., details of which will be given, this material has not previously been submitted to any systematic investigation. There is in fact no record in the literature of any investigation of this nature, which has been conducted on a normal refinery waste product, although, some forty years ago, certain specific Scottish Shale Oil fractions were examined for their basic content, and more recently shale oils and petroleums from other sources have been similarly examined. In most of these investigations however, particularly the earlier ones, little use was, or could be made, of the technique of fractional distillation, which in recent years, has been brought to the stage of a fine art, largely at the instigation of the petroleum industry. It is this comparatively recent technique which has throughout formed the mainstay of the work to be described in this thesis, and much of the work has necessarily been concerned with the constructions and operation of efficient fractionating columns.

It will be realised that the time expended on this very necessary part of the work has seriously curtailed the time available for investigation of the products obtained. It is important to bear in mind however, that in a long term investigation, of which this thesis embodies only the preliminaries, such a state/

state of affairs is frequently inevitable.

The subject of this thesis being in the nature of a preliminary investigation, it seems appropriate before describing more relevant details of the technical literature to give a brief historical summary of the Scottish Mineral Oil Industry, and, as far as speculation will permit, an indication of the future prospects of this industry, on which of course, the ultimate value of any investigation of this nature must depend.

SECTION A.

1. Historical Summary of Scottish Mineral Oil Industry.

It is difficult to consider any aspect of the Scottish Mineral Oil Industry without a brief reference to Dr. James Young (1811-1883), to whom the present industry centred in West Lothian owes its inception.

As early as the year 1781, a patent was taken out by the 9th Earl of Dundonald in which a process of extracting or making tar, pitch, essential oils and cinders from common coal is described. (Cannel coal being carefully excluded). In 1830 paraffin was discovered by Reichenbach, and independently by Dr. Christison of Edinburgh, a discovery which was followed by the patents of Butler (1833), Hoempesch (1841), and Du Buisson (1845), in which its manufacture is described.

It appears that Young first took an active interest in the production of mineral oils when, at the instigation of his friend Professor Lyon Playfair, he erected a factory for the distillation of a crude petroleum, obtained from a colliery at Alfreton in Derybshire. With the exhaustion of this supply some two years later, Young returned to Scotland, and in 1851, the works of Messrs J. Young, Meldrum and Binney was set up at Bathgate, West Lothian, for the distillation of Boghead coal, the process being protected by Young's classic patent of 1850. /

1850. With the approaching exhaustion of this rich cannel coal in sight, oil shale, discovered in the Broxburn area some years previously, was adopted as the raw material of the industry in or about 1862 (although Young was not the first to make use of this material).

In this way Young, who apart from being a very competent experimentalist appears to have been gifted with remarkable commercial acumen, laid the foundations of the present industry. An excellent biographical sketch of Young is given by Conacher in the Institute of Petroleum Symposium (1), where a survey of almost every aspect of the industry, in Scotland and elsewhere, is also to be found.

2. Occurrence of Shale Deposits and Future Prospects of Industry.

Extensive deposits of Oil shale are known to occur in many parts of the world including the United States, Canada, Australia, Tasmania, Manchuria, Russia, Czechoslovakia, France, Sweden, Brazil and Estonia, representing in all a vast accumulation of natural wealth, for the most part as yet, untapped. Extensive working of these deposits, apart from that in Scotland, is at present largely confined to the Estonian "Kukersite" deposits, the bituminous shales of France, the Fushun shales of Manchuria and the Swedish shale deposits. The nature of the oils obtained from these shales depends of course, firstly on /

on the fundamental nature of the shale, and secondly, on the method and rate of retorting. Scottish, Australian and Fushun (Manchurian) shale oils, are characterised by the almost complete absence of aromatic compounds in the lower boiling or spirit fractions, while those obtained from Estonian and Tasmanian shale, contain comparatively large amounts of aromatic materials (13-15 per cent). The oils are however, invariably rich in unsaturated compounds, irrespective of the source.

The shale industry has, almost from its inception, suffered severe competition from the petroleum industry. The added costs of mining and retorting the raw material, the greater difficulties of refining the oil to produce marketable products, and the high percentage of inert material, for which there is at present little outlet, place shale oil at a disadvantage which it cannot possibly overcome while a plentiful supply of petroleum exists. The industry in Scotland reached a peak in the year 1913, when some 3¼ million tons of shale were mined, the corresponding figure for 1937 being approximately 1½ million tons. It is interesting to note in this connection that in recent years the average yield of oil and naphtha has been of the order 18 to 25 gallons per ton, as compared with 25 to 45 gallons in the early days of the industry, the richest seams having been largely exhausted at the present time.

It is reasonable to assume that, irrespective of any developments in the fields of nuclear physics, and the production of nuclear energy, the need for liquid and gaseous fuels will continue for many generations to come, and failing the use of such materials as a source of energy, the ever growing demands of industry for the raw materials of organic synthesis will almost undoubtedly persist, and indeed multiply. Similarly, it seems inevitable, although the day be far distant, that ultimately the world supplies of petroleum and coal will dwindle, and finally approach exhaustion. Bearing this in mind, the vast deposits of shale and similar materials, of which those at present being worked in Scotland and elsewhere amount to only an insignificant fraction, represent a vast reservoir of potential raw materials, at present economically unsuited to further development, but apparently destined to meet the needs of future generations of industry. It is significant to note in this connection, that although there is no production of shale oil in the United States at the present day, the United States Bureau of Mines and the United State Geological Survey have conducted a careful survey of the available resources, and a certain amount of experimental investigation has been carried out with a view to ascertaining the type of plant most suited to future development. This work has been summarised by Kraemer (2). It is worthy of note also, that the great oil companies, both in the United /

United States and the United Kingdom, control large interests in the shale bearing areas. Bearing these facts in mind, it is obvious that the examination of any byproduct of the shale industry is not entirely academic.

3. The Nature of Scottish Shale.

It would be out of place here to attempt anything in the nature of a complete survey of the literature on either the geology and chemistry of shale itself, or the production and refining of shale oil. The following summary is an attempt to draw attention to the salient features of the industry, as it is carried on at the present day in the Lothians area of Scotland. Very comprehensive details of almost every aspect of the industry have appeared at various times in the literature, and reference will be made to these sources, on which this summary is largely based.

Typical Lothians Oil Shale is a fine-grained, tough, and often flexible material, black or brownish in colour and minutely laminated; it consists of an inert, inorganic, clayey base containing widely varying quantities of organic matter, to the oil yielding portions of which, the names "Kerogen" and "Pyrobitumen" have been given. Attempts to isolate this organic matter by extraction with solvents have met with little success. (3). McKee and Goodwin (4), found that distillation of certain shales under reduced pressure yields a highly unsaturated polymeric product, /

product, apparently intermediate between "Kerogen" and shale oil, which on further distillation breaks down to give a less unsaturated oil and coke.

The variation in colour of Scottish shales is associated with the oil-yielding qualities, the richer varieties being black, while the poorer quality shales are brown or grey in colour. They are rather fine grained rocks showing little or no structure, although well defined fish remains can be detected in some layers as in the well-known "fish-bed" in the "Curly Shale"at Pumpherston. A rich shale has the characteristic property of curling when cut with a knife, this rather crude test being carried out by the underground workers as a rough guide to the quality.

4. Retorting and Crude Oil Production.

The shale after mining and crushing to a suitable size is fed into continuous vertical retorts (three types are at present in use in Scotland, the Pumpherston retort, the Young's retort and the Broxburn retort), each of which is capable of handling about 3.3 - 3.6 tons of material per day, passage of the shale through the retort taking about 24 hours. Steam, equivalent to about 120 gallons of water per ton of shale, is admitted at the base of the retort and yields an ammonia liquor amounting to about 90 gallons per ton of shale. Some 75-80 per cent of the nitrogen of the shale is thus recovered as ammonia which is used to neutralise the sulphuric acid recovered /

recovered from the refinery tars; giving rise to the "Basic Tar" on which the present research has been conducted.

The crude oil, ammonia liquor and gases on leaving the retort pass to condensers and heat exchangers. After passing through separators, the crude oil and ammonia are run to storage, while the gases, after scrubbing to remove ammonia and naphtha, are used as fuel to heat the retorts. Spent shale amounting to about 75 per cent of the raw shale is discharged at the base of the retort.

5. Refining of the Crude Oil and Origin of the Basic Tar.

Scottish Shale contains approximately 0.6-1 per cent of nitrogen (5). The manner in which this is combined in the shale, and the reactions taking place in the retort have not been sufficiently well investigated for it to be possible to suggest any mechanism by which this nitrogen is converted to ammonia and higher bases. As has already been stated, the production of ammonia accounts for approximately 75-80 per cent of the nitrogen present in the shale, the remainder being accounted for in the spent shale, which contains about 0.15 per cent, in the oil, which contains from 0.5 to 1.00 per cent and (presumably) as free nitrogen in the gaseous products of retorting. According to Beilby (6) the nitrogen content of the crude oil represents about 20-25 per cent of the nitrogen present in the shale, thus /

thus it seems obvious, that although the exact mode of distribution of the nitrogen among the various products of retorting is dependent on too many factors for it to be possible to give anything other than a general indication, it is reasonable to assume that little if any of the nitrogen is set free.

The crude oil as it enters the refinery is a dark green colour and semi-solid. The specific gravity varies from about 0.875 - 0.885 and the setting point from 80 - 90°F. The crude oil is highly unsaturated and in addition to containing nitrogen (0.5-1.00 per cent), contains about 0.4 per cent of sulphur (principally as hydrogen sulphide, mercaptans, thio-ethers and thiophenes) and from 2 to 4 per cent of phenols (principally cresols, xylenols and higher phenols.) It would be outside the scope of this thesis to enter into much detail of the refining, by which the crude oil is converted to finished products, including motor spirit, various grades of kerosene, gas oil and paraffin wax. Briefly, the crude oil is subjected to a preliminary distillation in a conventional pipe still and bubble cap column, by which it is separated into fractions which are then treated with sulphuric acid and caustic soda to remove nitrogenous bases, phenols and other undesirable materials. These fractions are then subjected to further distillation and suitable treatments depending on the products required, the paraffin waxes being separated by freezing and purified by chemical treatment and sweating. The residual oil is /

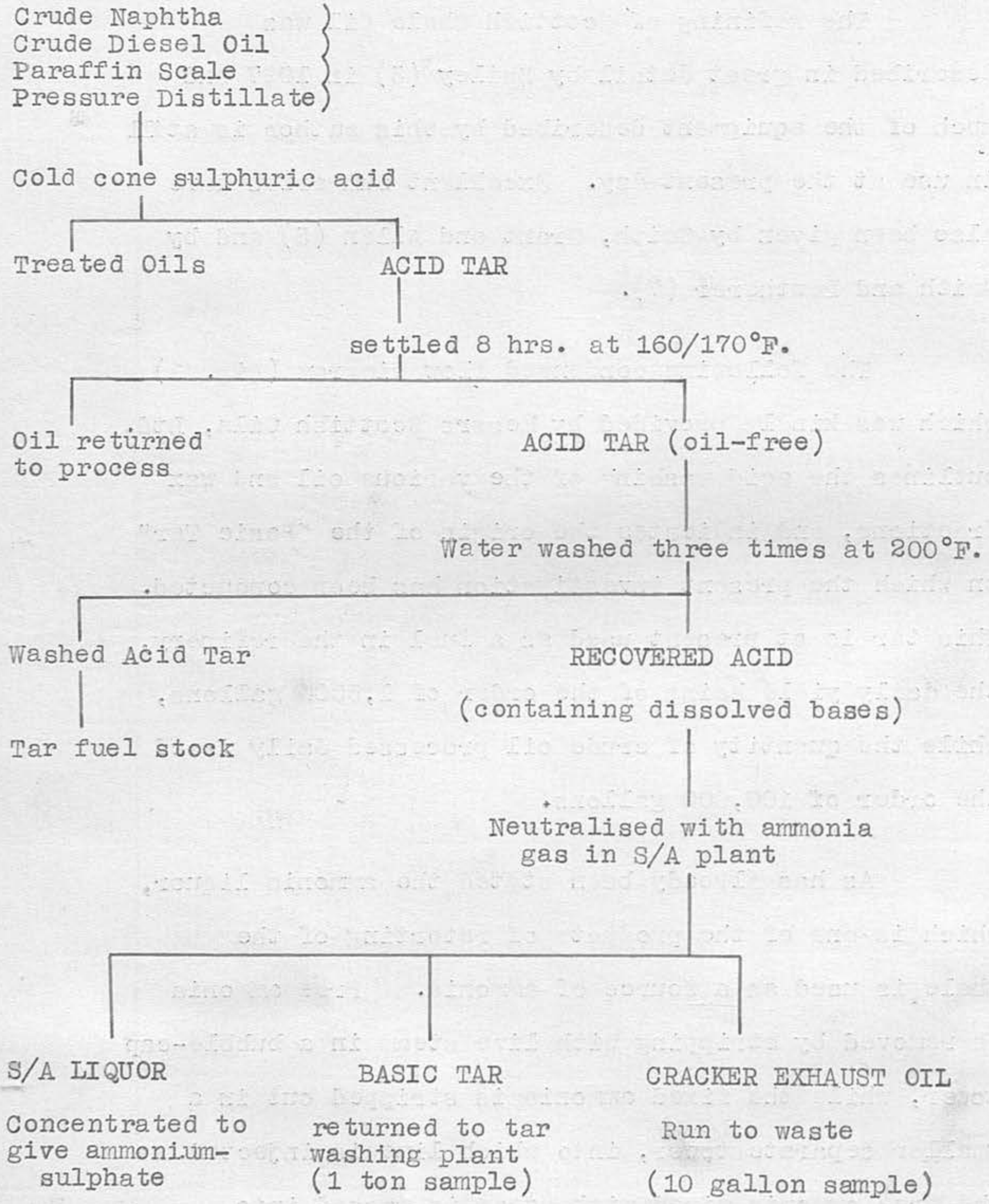
is ultimately taken to coke in batch stills, the oil from this process being returned to the crude feed stock.

The refining of Scottish Shale Oil was described in great detail by Bailey (3) in 1927 and much of the equipment described by this author is still in use at the present day. Excellent summaries have also been given by Smith, Grant and Allan (5) and by Smith and Peutherer (7).

The following condensed flow diagram (Fig. 1) which was kindly provided by Messrs Scottish Oils, Ltd. outlines the acid washing of the various oil and wax fractions, and indicates the origin of the "Basic Tar" on which the present investigation has been conducted. This tar is at present used as a fuel in the refinery, the daily yield being of the order of 1,500 gallons, while the quantity of crude oil processed daily is of the order of 100,000 gallons.

As has already been stated, the ammonia liquor, which is one of the products of retorting of the shale, is used as a source of ammonia. Free ammonia is removed by stripping with live steam in a bubble-cap tower, while the fixed ammonia is stripped out in a smaller separate tower, into which lime is injected. The free ammonia mixed with steam, is passed into large wooden tanks (Crackers), containing the weak acid recovered by water washing of the acid tars produced in the refinery. The more strongly basic ammonia /

FLOW DIAGRAM OF TAR WASHING AND ACID RECOVERY PLANT.



(Simplified Diagram).

FIG. 1.

ammonia liberates the bases dissolved in the acid, and these are separated as "Basic Tar" by passing the resultant ammonium-sulphate solution through separators and finally through sawdust filters.

Steam volatile bases are lost in the exhaust steam from the "Crackers" and are at present run to waste. These steam volatile bases constitute the "Cracker Exhaust Oil" (C.E.O.) of which more will be said in a later section. The yield of C.E.O. is small, amounting to only a few gallons per hour and normally no attempt is made to recover it. (Fig. 1)

It is interesting to note here that Gavin (8) has expressed the opinion, that in the shale oil industry of the future, nitrogen bases may well be of more value to the industry than ammonia, which is at present one of the most valuable by-products. According to the same author, the distribution of the nitrogen in the products of the retorting is a function of the rate of oil production, rapid retorting having a tendency to increase the yield of nitrogen in the oil, so that presumably the yield of "Basic Tar" could be increased at the expense of ammonia, if such a result were to become desirable.

SECTION B.

Survey of Literature on Shale Bases and Allied Subjects.

Before discussing the methods by which an investigation of this complex and intractable material could be undertaken and the reasons for adopting the chosen method of attack, it is logical, at this point, to draw attention to the results of previous investigations. In view of the close analogies between shale oil and petroleum and between shale-tars and coal-tar, some reference has been made to these latter materials, although this summary is not to be regarded as exhaustive.

1. Shale Oil.

One of the earliest investigations of the nitrogen compounds in shale oil was that of Williams, (9) who in 1854 proved the presence of pyridine and pyrrolic constituents in the naphtha fraction of Dorset Shale Oil.

The earliest recorded investigations of Scottish Shale Oil bases are those of Robinson (10) and Robinson & Goodwin (11) who isolated four bases of the so-called "Leucoline" series ($C_nH_{2n-11}N$) viz. $C_{12}H_{13}N$, $C_{13}H_{15}N$, $C_{14}H_{17}N$ and $C_{16}H_{21}N$. from the bases boiling in the range 270-390°C. These combined with amyl iodide, did not form cyanine dyes with alcoholic caustic potash and were presumably isoquinolines. The bases were isolated by a tedious process of repeated distillation and crystallisation /

crystallisation of the chloroplatinates and methiodes. The authors stress the fact that it was extremely difficult to prepare solid derivatives of the crude bases, a fact which, although no doubt partially explained in this case by the presence of impurities, has been borne out in more recent investigations of the higher boiling shale bases (vide infra).

In 1902-1903, Garrett & Smythe (12) examined the bases from the "Green Naphtha" and "Green Oil" fractions of Scottish Shale Oil by extraction with dilute sulphuric acid and subsequent distillation in a rod and disc column. The fractions so obtained were purified by fractional crystallisation of the mercurichlorides. Pyridine and six of its homologues were identified, viz. 2-methyl pyridine; 2:3-, 2:4, 2:5, and 2:6-, dimethylpyridines and 2:4:6-trimethylpyridine.

In 1905, Petrie (13) proved the presence of pyrrole derivatives in the "Torbanite" of New South Wales, by colour reactions, and this has been confirmed more recently in the case of Colorado Shale Oil (14), the bases from which seem to be composed mainly of pyridine homologues, but not quinolines or isoquinolines.

Eguchi (15) has carried out what seems to have been a most careful and thorough investigation of the bases in oil derived from Fushun bituminous shale./

shale. By extraction of the oil fraction of boiling range 220-250°C., with 30% sulphuric acid, he obtained a mixture of bases boiling over the range 100-280°C. Repeated fractionation through a 120 cm. long 20 mm. dia. bead packed column, yielded fractions which were then treated with mercuric chloride or picric acid, the solid derivatives so obtained being fractionally crystallised to constant melting point and reconverted to the pure bases. From the bases boiling up to 220°C. which were so examined, the following compounds were isolated; all the mono and dimethyl pyridines, 2:3:5-, 2:3:6-, 2:4:5-, and 2:4:6- trimethyl pyridines, 2:3:4:6-tetramethyl pyridine, 2-methyl-4-ethylpyridine, 2-methyl-6-ethylpyridine, 2:6-dimethyl-4-ethyl pyridine, and 2:3-dimethyl-6-ethylpyridine. The structure suggested for a further compound isolated (pyrindane) was subsequently established by synthesis (Thompson (16)). In view of the similarity between Scottish and Fushun Shale, it has been interesting to compare the results of the present investigation with those of Eguchi.

Dodonov and Soschestwenskaya (17) have isolated the following compounds from Russian Shale Oil, by means of the mercurichlorides; pyridine, 2- and 3- methylpyridines and 2:4-, 2:5- and 2:6-dimethylpyridines.

Tasmanian Shale Oil has been examined by Cane (18) who isolated 2:4:6-trimethylpyridine and an /

an unidentified trimethylquinoline. Basing his conclusions largely on considerations of refractive index, boiling point and failure to dehydrogenate on heating with selenium, Cane also inferred the presence of "naphthenic" bases and the absence of hydroquinolines. This author also experienced difficulty in preparing solid derivatives of the high boiling bases and noted the toxicity of the vapours.

Kogerman (19) noted difficulty in preparing solid derivatives of the higher boiling bases from Estonian Shale Oil, but remarks that they are pyridines and quinolines.

A sample of "basic tar" from the same source as the material used for the present investigation has been examined in the laboratories of the Anglo-Iranian Oil Company (20) and the following compounds isolated as picrates, quinoline, isoquinoline, 2:4-dimethylquinoline and2:3:4:5-tetramethylpyridine. Electrometric titrations also indicated the presence of bases much stronger than quinoline, and this together with failure to obtain the expected yields of picrates from certain fractions led to the suggestion that long chain aliphatic bases were present. The separation methods used in this investigation included extraction of the tar with acid and fractional distillation under reduced pressure (lowest pressure used, 20 mm. Hg.) The best column used was one of 22-theoretical plates.

Lanin and Pozhil'tsova (21) have examined the bases obtained from "sapropel" of the Karasino lake region (Luga region U.S.S.R.) Primary and secondary bases were absent but the following compounds were separated and identified, 3-methylpyridine, 3-ethyl pyridine, 2-butylpyridine, 2:4-dimethylpyridine, 2:6-dimethylpyridine, 2:4-diethylpyridine, 2-methyl-6-ethylpyridine, 2-methyl-4-ethylpyridine, 4-methyl-3-ethylpyridine, 2:?-dimethyl-5-ethylpyridine and 2:4:6-trimethylpyridine.

A similar "sapropelic" material is found in the Coorong region of Southern Australia in association with the substance known as "Coorongite". This latter material, which is of algal origin, bears some resemblance to asphalt or crude india-rubber and is sometimes regarded as the probable mother-substance of boghead coals and allied materials, and possibly of petroleum. The bases derived from this source are therefore interesting, in that they may be regarded as providing a link between those derived from shale on the one hand and petroleum on the other.

In particular, it is interesting to note that 2-butylpyridine was among the compounds isolated, whereas, with the exception of pyrindane isolated from Fushun shale oil by Eguchi (loc. cit.), all the compounds so far isolated from shale oils have been methyl or ethyl compounds. Pyrindane, being the pyridine analogue of indane, may be regarded as a cyclised derivative of 2- or 3- propylpyridine.

Summarising /

Summarising, it may be said that previous work has shown the lower boiling shale bases to consist almost exclusively of pyridine types, mainly methyl and ethyl derivatives; although pyrroles appear to be present in small amounts there is little or no indication of non-aromatic, primary, or secondary bases.

In the higher boiling ranges, quinolines and isoquinolines are present, but there is also reason to suspect the presence of more complex bases in which the reactions of the pyridine or quinoline ring system, if present at all, are suppressed. Bases of this type have in fact been isolated from certain petroleum distillates. (vide infra).

2. Petroleum.

The literature dealing with the occurrence of nitrogenous bases in petroleum is quite extensive, and it would be outside the scope of this summary to attempt a complete survey. The following briefly indicates the type of work which has been done and the more important results obtained.

Crude petroleum contains complex nitrogen compounds which cannot be extracted with acids but can be concentrated by solvent extraction; according toBailey and his co-workers, these may be pyrrole, indole or carbazole compounds (22). These compounds do not appear to have been examined.

The inevitable slight cracking which occurs during the distillation of crude petroleum leads to the breakdown of these complex materials and small amounts of nitrogen bases are found in straight run distillates, the amount increasing with rising distillation temperature; a large proportion of the nitrogen, however, remains in the form of compounds which are not extracted by acid. As might be expected, cracked distillates contain a larger proportion of simpler bases which appear to be similar to those found in shale oil.

The bases from Californian oil distillates were examined by Mabery and Wesson (23) who obtained a mixture of pyridine polycarboxylic acids by oxidation and concluded that the bases must consist of alkylated quinolines or isoquinolines. No individual compounds were isolated.

Bailey and co-workers have conducted an extensive series of researches on Californian distillates during the period 1928-1942 and these researches constitute in themselves a considerable literature, important not only in the results obtained, but in the methods worked out. Initially, the kerosene fraction was examined (22): In this case, after extraction with liquid sulphur dioxide, (Edeleanu process), the nitrogen bases were extracted with dilute sulphuric acid, which gave a complex mixture of bases boiling within the range 180-335°C. at atmospheric pressure. This mixture could be separated /

separated into aromatic and non-aromatic bases by extraction of the hydrochlorides with chloroform, the hydrochlorides of the non-aromatic bases being fairly soluble while the aromatic base hydrochlorides were sparingly so. This process was subsequently improved and developed into the process known as "cumulative extraction" (24). Aromatic bases are of the alkyl pyridine or quinoline type; non-aromatic bases while possibly still containing a pyridine or quinoline nucleus, have lost their character by the accumulation of heavy side chains, or additional rings, or by hydrogenation of the ring system.

For the isolation of individual bases, large quantities of material were worked up and subjected to repeated fractional distillation using efficient packed columns. Among other separation methods worked out the following may be mentioned, fractional salt precipitation, fractional acid extraction, formation of zinc chloride double salts(which on distillation give the anhydrous base free from water, hydrocarbons and sulphur compounds), fractional degassing of acid sulphites (25), etc.

The following alkylquinolines were isolated from Californian distillates, and it will be noticed that they are invariably substituted in the 2- position.
2:3-, 2:4- and 2:8-, dimethylquinolines (26, 27);
2:3:8- and 2:4:6- trimethylquinolines (28, 24);
2:3:4:8-tetramethylquinoline (29); 2-methyl-8-ethylquinoline (30); 2:3-dimethyl-8-ethylquinoline (31);
2: /

2:4-dimethyl-8-ethylquinoline (32); 2:3:4-trimethyl-8-ethylquinoline (33); 2:3-dimethyl-4:8-diethyl quinoline and 2:3-dimethyl-4-ethyl-8-n-propyl quinoline (34); 2:3:8-trimethyl-4-ethylquinoline (35); 2:3-dimethyl-8-n-propylquinoline (36); 2:4-dimethyl-8-n-propylquinoline (37); 2:3:4-trimethyl-8-n-propylquinoline (38); 2:3:4-trimethyl-8-isopropyl quinoline (39); 2:4-dimethyl-8-sec.-butylquinoline(40) 2:3- and 2:4- dimethylbenzo(h)quinoline (41).

As might be expected, the elucidation of the constitution of the non-aromatic bases has presented considerable difficulty. Bailey examined the non-aromatic base $C_{16}H_{25}N$ over a period of years (28, 42, 43), but it was only in 1942 that the structure was proved to be 2-(2:2:6-trimethylcyclohexyl)-4:6-dimethylpyridine (44). Two further non-aromatic bases $C_{10}H_{15}N$ (45) and $C_{13}H_{21}N$ (42) have been obtained from kerosene diatillates, but their structures have not been determined.

Lochte et al (46) isolated three further bases, also from kerosene distillates, viz. $C_{11}H_{17}N$, $C_{12}H_{19}N$ and $C_{13}H_{21}N$. The C_{13} base was not identical with that obtained by Bailey (42) and the C_{11} compound was shown to be <u>dl</u>-2-sec.-butyl-4:5-dimethyl pyridine. Lochte (47) has also isolated 3- and 4-cyclopentyl pyridines from the same source.

Two bases $C_{15}H_{13}N$ and $C_{16}H_{15}N$ isolated from a transformer oil by Bailey (29) are probably poly nuclear /

nuclear compounds. Their refractive indices are unusually high.

As would be expected, cracked distillates yield a much higher proportion of simpler bases. From a distillate obtained by cracking oil at 454°C and 54-58 atm. Bailey and Bratton (48) isolated 2- and 4- methylpyridines, 2:4-, 2:5- 2:6- and 3:5- dimethylpyridines, 2:4:6- trimethylpyridine, quinoline and quinaldine. These they believed, accounted for all the bases present.

Hackmann and Wibaut (49) on the other hand, examined the bases from a Californian Oil cracked at 500°C. and 30 atm. and presumably of different origin to that used by Bailey and obtained, in addition to all the compounds found by Bailey, a large number of others, including 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 pyridines, 3-, 4-, 7- and 8- methylquinolines, 2:8-dimethylquinoline, isoquinoline and 1- and 3- methylisoquinolines. Several unidentified bases were also obtained.

Although the difference between Wibaut's and Bailey's results may be partially explained by the difference in cracking conditions and feed stock, it is still rather surprising. It is particularly interesting that Bailey found no traces of isoquinoline /

isoquinolines derivatives in either straight run or cracked distillates. Isoquinoline has, however, been found in shale oil (20).

3. Coal Tar.

Coal tar contains some 0.25% of nitrogen bases including pyridine, quinoline, isoquinoline and their homologues. Side chain nitrogen compounds which also occur in coal tar have not been found in either petroleum or shale oil. The early literature on coal tar bases has been summarised by Spielmann (50).

Krüber has published many articles since 1920 on the separation of these compounds, his method consisting generally in distilling large amounts and crystallisation of derivatives. Jantzen in his monograph (51) describes more novel methods including counter current acid extraction.

The following list of compounds known to be present in coal tar is based on the above references and on a list supplied by Dr. J. Idris Jones of the D.S.I.R. Only heterocyclic nitrogen bases of the types which are known to occur in shale oil are included :-

1. Pyrrole (and unidentified pyrrole derivatives),
2. Pyridine, 2,-3 and 4-methylpyridines, 2:4-, 2:5- 2:6- and 3:4-dimethylpyridines, 2:4:6-trimethylpyridine, 2:3:4:5-tetramethyl pyridine.
3. Quinoline, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylquinolines, 2:8-dimethylquinoline, 2:4:6-trimethylquinoline.
4. Isoquinoline, 1- and 3- methylisoquinolines.

The (

The complete list includes a large number of more complex heterocyclic compounds, aromatic primary amines, nitriles, etc.

SECTION C.

1. Nature and Objects of the Present Investigation.

The processes which have been briefly outlined in the introductory section of this thesis are carried out at the Pumpherston refinery of Messrs Scottish Oils, Ltd., where some 100,000 gallons of crude shale oil are processed daily, the daily yield of "Basic Tar" being of the order of 1500 gallons. Apart from its use as a fuel, there is no useful outlet for this material, although experiments carried out by Messrs Scottish Oils Ltd., have shown that it has some value as an inhibitor for the prevention of corrosion in acid pickling and cleaning baths.

Investigation of this material was previously limited to that carried out by Messrs The Anglo-Iranian Oil Company, briefly outlined in the previous section, and there is no record in the literature of any investigation of a similar industrial waste product, although bases extracted from specific oil fractions have been previously examined.

It was shown by Messrs Scottish Oils Ltd. and subsequently confirmed in the present work, that some 30-40% of the tar is distillable below 300°C at atmospheric pressure, the distillate consisting substantially of an extremely complex mixture of heterocyclic bases. Assuming that this represents the percentage of the mixed bases which could be recovered on the commercial scale, the daily yield of mixed /

mixed bases would then be of the order of 600 gallons and although this is only a small amount in terms of modern oil refinery practice, it nevertheless represents a considerable wastage of potentially valuable material, the yield of which could probably be increased if circumstances demanded.

Bearing these facts in mind the principal objects of the present research have been as follows:

(a) The examination of the lower boiling point bases with a view to determining the relative abundance and ease of separation of individual components of commercial value. In this may be included the study of the various separation techniques involved, such as fractional crystallisation of picrates, fractional extraction, etc. and in particular fractional distillation using highly efficient fractionating columns.

(b) Comparison of the results with those of other workers who have examined similar materials from other sources, e.g. shales from other parts of the world, petroleum distillates and coal tar.

(c) The separation of pyridine and quinoline homologues, or more complex substances, which are not readily available from other sources, or by synthetic routes and the compilation of data on these compounds.

Judged from these three standpoints, the conclusions reached have been in general terms, as follows:-

(a) The possibility of separating any single component on a commercial scale is remote. The complexity of the mixture is such that, in the the lower boiling ranges at any rate, no individual component is present in sufficient quantity to make its commercial separation a feasible proposition unless highly specialised methods can be developed. No doubt the difficulty of separation will be even more serious in the higher boiling ranges. The elaborate treatments required also make it difficult to give any but the most approximate indication of the percentage of any given component present.

On the other hand, the research has been a valuable medium for gaining experience in the technique of fractional distillation, although unfortunately the practical difficulties encountered in certain directions have seriously curtailed the time available for the study of other techniques, such as azeotropic distillation, fractional extraction, chromatographic adsorption, etc. It would appear, however, that any commercial outlet for the bases obtained from the tar would have to be for mixed fractions, unless of course the mixture could be considerably simplified by some process such as cracking. Examples of the possible uses to which the mixed bases might be put, include high boiling solvents, inert media for reactions involving the splitting off of acidic by-products (c.f. use of pyridine as a solvent for acylation), preparation of detergents of the quaternary salt type (c.f. "Cetavlon", cetyl trimethyl ammonium bromide), many of which have useful bactericidal properties, etc.

(b) Although time has permitted thorough examination of only a few selected fractions boiling up to 200°C., the results have been in fair agreement with those of other workers in similar fields.

It is almost certain that the lower boiling point bases consist very largely of alkylated pyridines, the alkyl groups present being mainly methyl and ethyl. Refractive index measurements confirm the conclusion that the lower ranges are mainly pyridines, and indicate the presence of quinolines in the higher boiling point bases, although the conclusions of other workers lead to the expectation that more complex substances are also present. Traces of pyrroles (as indicated by colour reactions) appear to be widely distributed throughout.

(c) In spite of the difficulties of separation, the narrow boiling fractions obtained by precise methods of fractional distillation afford a valuable starting point for a comprehensive study of pyridine and quinoline chemistry and the study of separation techniques. At the same time, there is the possibility of obtaining compounds not readily available by synthetic routes, many of the syntheses in this branch of organic chemistry being rather tedious and at the same time unsatisfactory from the point of view of yield and /

and availability of starting materials.

A study of the literature reveals a surprising amount of contradictory data, and frequently a complete lack of data regarding the physical properties of even the simpler alkyl pyridines and quinolines, which must be largely explained by the relative inaccessibility of many of these compounds, particularly the alkyl pyridines. Any source of these substances, therefore, even as difficultly separable mixtures, can be regarded as a subject quite worthy of investigation, both from the point of view of the materials separated and the evolution of the necessary techniques.

It is significant in this connection that there has been in recent years, a revival of interest in the compilation of reliable physical and thermodynamic data on known compounds of established purity. This important task is well illustrated by the work of the U.S. Bureau of Standards and the Department of Scientific and Industrial Research. Many of the large industrial concerns are also participating in this work, and much attention has recently centred on the heterocyclic nitrogen bases, presumably because of their physiological importance.

2. Separation Methods and Identification of Components.

The problem inherent in the present investigation divided itself naturally into three distinct phases: (a) separation of the volatile bases from the "Basic Tar" and removal of non-basic matter such as sulphur compounds, etc. (b) separation of the bases into individual components or mixtures suitable for examination by chemical methods and (c) identification of individual components.

Of /

Of these, the first and last stages involved only consideration of well known and well tried methods. In the case of the former, the choice of methods was largely dictated by the scale on which the operation was to be conducted and the apparatus available. In point of fact, these limitations so reduced the number of possibilities that one only, namely straight vacuum distillation, was considered suitable. The reasons for this are discussed in the "Experimental" section. Identification of the individual components was again largely a matter of the application of standard methods, including analytical determinations, preparation of derivatives and determination of physical constants such as boiling point, refractive index, molecular refractivity, infra-red absorption spectra, dissociation constant, etc.

The major part of the work centred around the second of the three stages, that is to say, separation into individual components, or simple mixtures, suitable for chemical examination and since the problem was one of separating mixtures of chemically similar materials, the methods employed were largely of a physical nature, including fractional distillation, fractional acid extraction and fractional crystallisation of derivatives. Other methods which were considered, but not extensively applied in the present work owing to limitations of time, included azeotropic distillation and chromatographic /

chromatographic adsorption.

The literature of these subjects is extensive and has been studied carefully during the course of the present work. A review of the literature of fractional distillation, which formed part of a report submitted to the Department of Scientific and Industrial Research at the end of the first year of the present work, has now been expanded to include the remaining methods cited above: However, to avoid any discontinuity in the main topic under discussion, this has been included in the form of an "Appendix" to this thesis.

SECTION D.

Apparatus.

Much of the work having been concerned with the construction, testing and operation of efficient distillation equipment, this has been described in some detail. The following is a list of the apparatus used in the present work, in the order in which it was employed :-

1. The 16-litre Gas Heated Vacuum Still,
2. The 14-Plate Eyelet Packed Column
3. The 100-Plate I.C.I. Gauze-Ring Packed Column.
4. The 30-Plate I.C.I. Gauze-Ring Packed Column.

Additional apparatus, constructed or tested during the course of the work, but not extensively used, includes :-

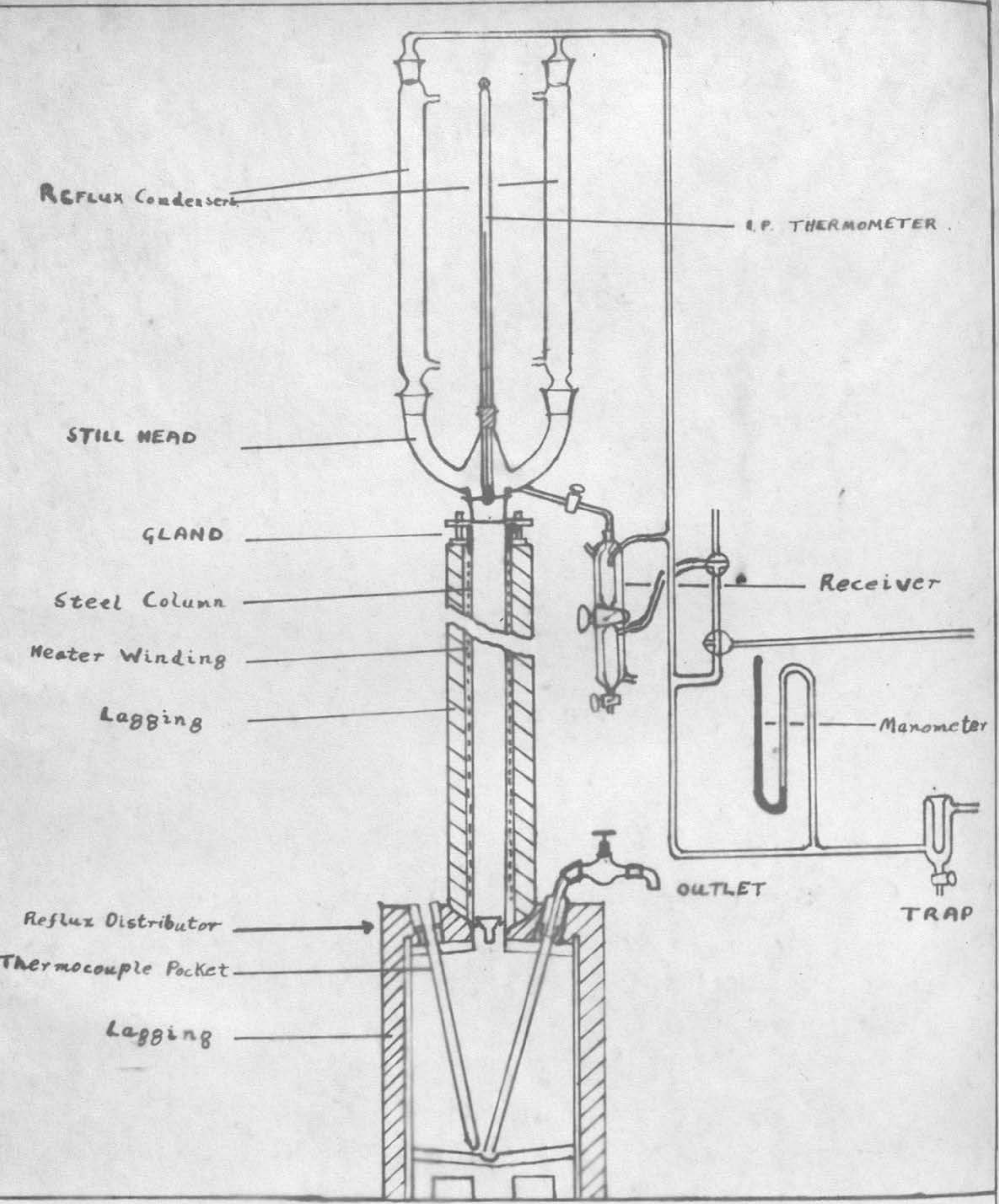
5. The 40-Plate Fenske Helices Column,
6. The 14-mm. I.C.I. Gauze-Ring Packed Column,

and 7. A Rotary Fractional Extraction Apparatus.

This equipment, plus certain auxiliary apparatus, is described below.

1. The 16-litre Gas Heated Vacuum Still (Fig. 2)

This still, the property of Messrs Scottish Oils Ltd., and situated at their Central Laboratory, Uphall, was placed at the author's disposal by the courtesy of the Chief Chemist, Dr. Smith, and was used for the preliminary distillation of the Basic Tar and subsequent redistillation of the crude bases. It should be stated at the outset, that the still was neither intended for, nor suited to the purpose for which it was used, but since no more suitable apparatus /



16 LITRE STILL

FIG. 2.

apparatus was available, it offered the only possible solution to the problem in hand, and in the circumstances, stood up remarkably well to the drastic treatment to which it was necessarily subjected. The following is a brief description of the still and associated equipment.

The boiler consists of a cylindrical mild steel vessel of 16-litre capacity with a dished bottom. To the flat top of the boiler are connected the following :

(a) A 2 inch diameter mild steel pipe, 5 ft. in length forming the fractionating column,
(b) A stand pipe reaching to the bottom of the boiler and fitted with a $\frac{1}{2}$ inch outlet valve,
(c) An inlet pipe and valve (not shown in Fig. 2),
(d) A mild steel thermocouple pocket.

At the base of the column, where it joins the boiler, a graduated sight-glass is fitted. Vapour passes into the column through a short upriser, while reflux is returned by a separate line at the base of the sight-glass, fitted with a 3/8th inch valve. When this valve is closed, reflux accumulates behind the graduated sight-glass and the whole thus forms a simple type of reflux meter. This reflux meter has not been shown in Fig. 2, since in practice it could not be used owing to the accumulation of tar-spray in the base of the column.

The top of the column is connected by the normal type of gland fitting to a short length of wide bore glass tubing with a B.45 standard joint for connection to the still head and condenser assembly.

A /

A simple weir type of total reflux variable liquid take off still-head is used, the rate of take off being controlled by a grooved stop-cock. The still head carries twin condensers, the upper ends of which are connected to the vacuum system.

The receiver assembly consists of two 250 ml. graduated vessels connected in series through a stop-:cock and connected to the vacuum system through a system of stop-cocks, so that the lower receiver can be brought to atmospheric pressure, emptied and re-evacuated,without disturbing the pressure in the upper receiver or the still.

Vacuum is maintained by a Speedivac Pump (Type 2), which is connected to the system via a large trap containing solid sodium hydroxide, a ten gallon buffer vessel, and a variable air leak. The pressure in the system is indicated by a mercury U-tube manometer and controlled by manual operation of the variable leak. Pressure fluctuation, under normal conditions of operation,is surprisingly small, due to the presence of the buffer vessel, although there is of course, a tendency for the pressure to drift slowly.

For distillation at atmospheric pressure a diaphragm gauge (0-25" water) can be connected to the inlet pipe of the still pot, for observation of the back pressure in the still.

The still pot is heavily lagged with magnesia-:asbestos pipe lagging and supported by a thin metal casing which raises it from the ground sufficiently to allow a gas ring-burner to be used for heating.

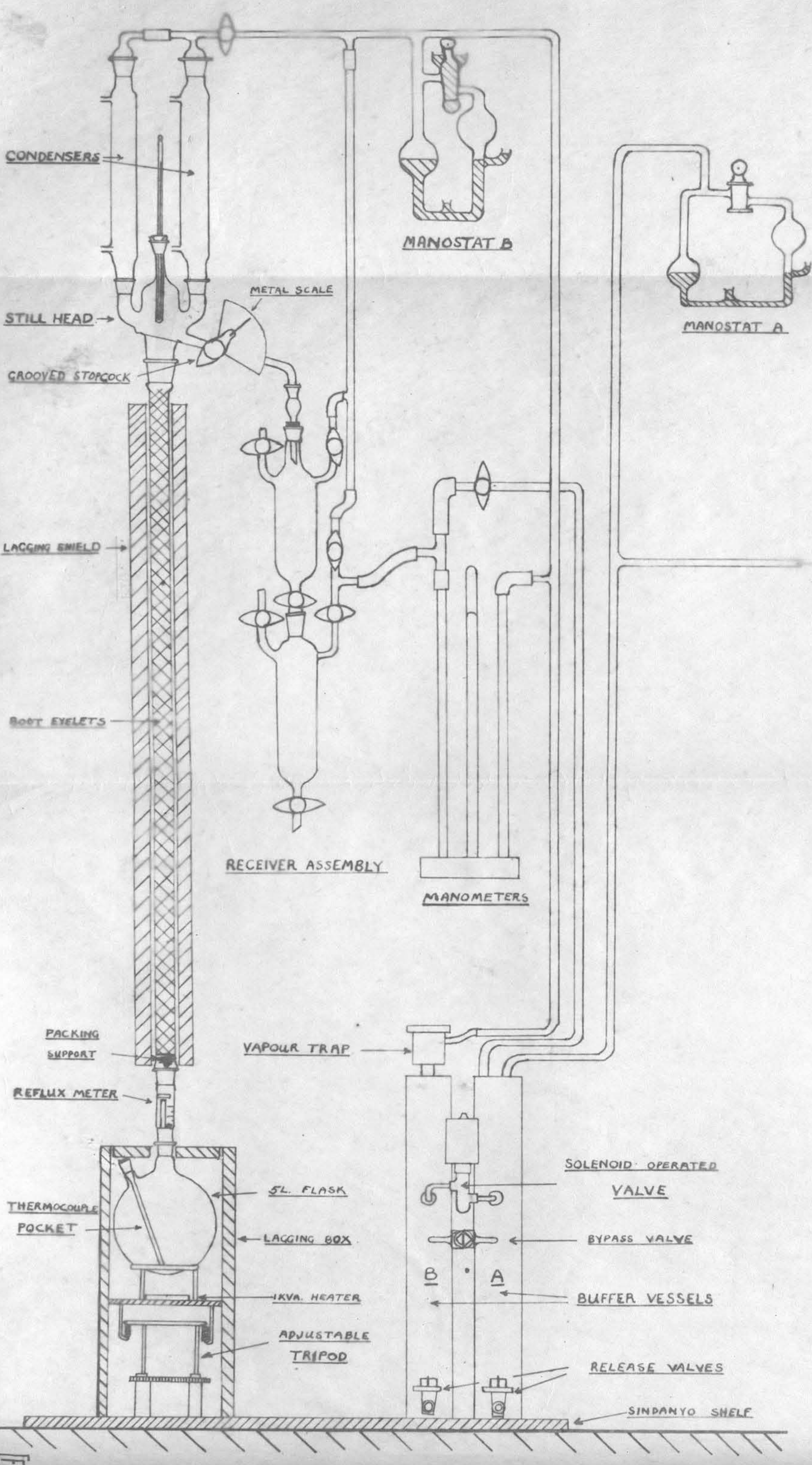
The column itself is wound in three separate sections with resistance wire, each heating circuit being controlled separately by a sliding resistance with an ammeter in series. Three iron-constantan thermocouples, spaced evenly, are screwed into the column wall, one at the centre of each heater winding. These, plus a fourth couple which fits into the well in the still pot, are connected through a system of switches to a direct reading "Cambridge" pyrometer. The column and heaters are also heavily lagged with magnesia-asbestos, and both column and still pot are painted with aluminium paint to further reduce heat losses. Overhead temperatures are measured with an ordinary mercury in glass thermometer.

The column is packed for a length of 4'6" with boot eyelets, its efficiency calculated on the figures obtained with the 14-plate column (vide infra) being of the order of 7 - 8 plates at a boil up rate of about 5 l per hour, on total reflux.

The boot eyelets used in this column for the present work were actually those tested and used in the 14-plate column and are described below.

2. <u>14-Plate Column (Fig. 3 and Plates 1, 2 and 3)</u>.

This apparatus, based on similar types in use in the laboratories of the Anglo-Iranian Oil Co. Ltd. and /



[FIG

14-PLATE STILL

and on Institute of Petroleum specification 25/44, was supplied as a complete unit by Messrs Griffin & Tatlock, Ltd. Before it could be put into operation however, extensive alterations were required, and in particular, the vacuum system was completely re-designed. The modified version of the apparatus is described below and it was used in this form for the present work, when it proved a most valuable and versatile piece of apparatus, its greatest virtues being large capacity combined with rapid throughput and relatively high efficiency.

The still pot is a 5 l heavy-walled flask with a B.34 joint on the neck and a B.19 radial neck into which a thermocouple pocket fits. The flask is supported by a ring wound with asbestos rope which in its turn is supported by three short legs bolted into a heavy Sindanyo shelf which also carries a 750 watt circular boiling-ring element, symmetrically placed so as to lie directly below, but not in contact with, the bottom of the flask. The shelf and heater are supported by three stout springs carried by a tripod, the three legs of which may be simultaneously lengthened or shortened by means of a chain and screw mechanism. (Plate 3).

The entire still pot and heater assembly is enclosed in a double-walled, asbestos lined, sheet iron box, the space between the walls of which is packed with glass-wool. The back of the box is rigidly fixed /

fixed to the framework of the apparatus while the remaining three sides can be removed in one section. The lid is divided into two sections and the bottom is formed by a very stout Sindanyo shelf, to which the angle-iron framework supporting the apparatus is bolted.

The neck of the flask where it projects from the lagging-box is connected by the B.34 joint to a reflux-meter of the type designed in the laboratories of the Anglo-Iranian Oil Co. Ltd. It consists simply of a short graduated measuring chamber, into which the vapour upriser projects. Reflux is prevented from returning through the vapour upriser by means of a flat glass cap fused on to the wall of the measuring chamber, and normally returns to the still through a small hole close to the lower end of the vapour upriser. When it is desired to measure the rate of reflux, this hole can be closed by a steel ball operated by an external magnet and the rate at which the measuring chamber fills can then be measured with a stop-watch. (Plate 3).

The column itself is a heavy-walled glass tube, 36 mm. internal diameter with a B.34 cone at the lower end and B.45 socket at the top. The overall length is 4' 6" (packed length 4'), and the tube is supported at the lower end by the reflux meter which is held in a clamp attached to the main framework, and at the upper end by a loose fitting ring /

ring immediately below the cone joint and similarly attached to the main framework.

The still head, which is a simple weir type, is supported by the column itself and has twin condensers of the internal spiral type, the upper ends of which are connected to the vacuum system. Take off is controlled by a grooved stop-cock, fitted with a pointer and scale to facilitate repetition of the setting. The thermometer is supported by a pocket which fits into a B.14 socket in the still head so that the lower end is completely immersed in the vapour stream. (Plate 2)

The distillate leaves the still head by a short side arm carrying a B.12 cone at its lower end, this connects with a B.12 socket with a long stem which in its turn is connected to the receiver assembly by a close fitting rubber bung. This arrangement serves to impart some degree of flexibility to the assembly, while at the same time exposing the distillate to the smallest possible chance of contamination from the rubber.

The receiver assembly consists of two 250 ml. graduated vessels connected in series with connections from each to the vacuum system. Stop-cocks on the receivers and vacuum lines, make it possible to empty the lower receiver and re-evacuate it without disturbing the pressure in the remainder of the system. (Plate 2).

For /

For measurement of the pressure, two manometer tubes and a simple barometer are mounted in a common mercury reservoir. One manometer indicates the pressure in the still and upper receiver, while the other is used to indicate the pressure in the lower receiver when re-evacuating after removal of a fraction. Pressures are measured by the difference in the level of mercury in the barometer and manometer tubes, a sliding cursor and scale being provided to facilitate measurement. (Plate 2).

Heat losses from the column are balanced by enclosing it in a brass tube wound in three sections with resistance wire and provided with thermocouples as in the case of the 16 l. gas heated still. The heat losses are further reduced by a layer of Versil glass-wool pipe lagging over the heater windings. The thermocouples from the column lagging and still pot are brought, via a cold junction bath, to a multi-point switch and thence to a millivoltmeter. Heat inputs to the three column sections and still pot are separately controlled by Variac transformers. The flask lagging box and column compensating lagging are painted with aluminium paint to reduce loss of heat by radiation. When the apparatus is in operation the still head is lagged by winding it with a layer of asbestos rope, while the reflux meter is heavily lagged with glass cloth. (Plate 2).

Vacuum System.

Unlike the 16-litre gas heated still, pressure control on the 14-plate column is fully automatic, and apart from very gradual drifts, mainly due to the effect of the ambient temperature on the mercury manostat, the pressure remains substantially constant when once set. The sensitivity of control varies somewhat according to the pressure at which the apparatus is being worked; at 100 mm. for example, it is of the order of ± 0.5 mm.Hg., and could no doubt be reduced further by suitable thermostatic control of the manostat, which has in fact been done with the 100-plate column described later. Day to day pressure drifts, exceeding the normal limits of error, are readily corrected by hand.

The system of control is substantially that described by Coulson and Warne (52) and operates as follows (Fig. 3).

The cylindrical steel buffer vessel A (Fig.3) which has a capacity of about 5 litres, is connected to a mercury manostat A and a Speedivac pump. (Type 2 not shown in Fig. 3). The pressure in this vessel is reduced until it is about 20 mm.Hg. below that at which it is desired to operate the apparatus, and the tap on the manostat A is then closed. Further reduction of the pressure changes the level of the mercury in manostat A and breaks the control circuit of a "Sunvic" relay (not shown in Fig. 3) which controls /

controls the operation of the pump. The slight time delay characteristics of the "Sunvic" relay, cause the pressure in buffer vessel A to fluctuate within certain limits, but this has no effect on the ultimate pressure in the still and in fact is an advantage, serving as it does to protect the pump from too frequent stopping and starting. The pressure in buffer vessel B and the remainder of the system is then reduced to the desired value by operation of the bypass valve which links buffer vessels A and B. When the pressure in the still has been finally adjusted to the desired value the mercury-sealed stop-cock on manostat B is closed, sealing off in the closed limb of the manostat a volume of air at the desired operating pressure. Any leakage of air into the apparatus will now cause the mercury in manostat B to complete a circuit which causes a momentary operation of the solenoid valve linking buffer vessels A and B, and since A is at a slightly lower pressure than B, the pressure in vessel B and the remainder of the system is reduced until the mercury in manostat B is restored to its proper level, breaking the circuit and closing the solenoid valve.

The solenoid valve (British Thermostat Co. Ltd.) operates on 230 volts A.C. and to avoid the fouling of the mercury in manostat B by the inductive sparking its operation is controlled through the medium of an electronic valve relay of the type described by Coulson and Warne (52). This operates a /

a miniature telephone type of relay which in its turn operates a heavier battery relay which controls the supply of current to the solenoid valve. By this means only an infinitesimal current is carried by the mercury in the manostat, and consequently there is no fouling of the contacts. The electronic relay assembly is shown in Plate 4.

It will be seen that, once set, the pressure in the system cannot vary unless the pressure in the closed limb of manostat B varies, and since leakage is virtually eliminated by the mercury-sealed stopcock, pressure variations in this bulb and hence the remainder of the system are substantially limited to those produced by changes in the ambient temperature.

Packing Characteristics and Efficiency.

The packing originally intended for this column was glass Raschig rings. Since however, the boot-eyelet packing from the 16 l. gas heated still was available, this was used instead.

Data on the two types of packing were kindly supplied by the Anglo-Iranian Oil Co. who found that, using a column of the same dimensions as that described, the efficiency obtained with glass Raschig rings was 7 theoretical plates as opposed to the 14 theoretical-plates obtained using boot-eyelets. The boot-eyelets were also found to have almost double the surface area per unit volume and about 20 per cent more free space than the Raschig rings when packed in tubes of similar dimensions.

The following data for the two types of packing are taken from the figures supplied by the Anglo-Iranian Oil Company (Table 1).

TABLE 1

Characteristics of Raschig Ring and Boot Eyelet Packings

Dimensions	Raschig Rings	Boot Eyelets
Outside Dia. (mean)	0.295"	0.180"
Inside Dia.	0.21"	0.163"
Length	0.32"	0.145"
Rim Dia.	-	0.260"
Thickness (mean)	-	0.014"
Weight (average)	0.40 gm.	0.10 gm.
Surface Area	0.00398 sq.ft.	0.2319 sq.in.
Free Space cu/ft./cu/ft. of packing	0.71	0.904
Surface Area sq/ft./ft^3 of packing	206	395
Number/litre	1830	8750
	in 4.7 cm. diameter tube	in 3.81 cm. dia. tube

The eyelets used in the 16-litre still were made of thin brass, with a flange at one end, and were identical in form with those commonly used in boots and shoes. When new, they were plated, and substantially identical with those referred to in the above table. On removing them from the 16 l. still, after /

after distillation of the basic tar and re-distillation of the crude bases, it was found, however, that the plating had been completely stripped off; many of the eyelets were badly distorted, and all were heavily coated with a coke like deposit resulting from decomposition of the tar. Before use in the 14-plate column, they were cleaned by shaking for several hours with sand, etching with dilute acid and copious washing with water. All faulty eyelets were removed by hand picking. Fortunately, it was found that the now unprotected brass was not seriously attacked during subsequent distillations of the bases, and the characteristics of the packing appeared to be substantially unchanged.

Before putting the column into service, the plate efficiency under total reflux at atmospheric pressure was determined over a range of boil up rates, using the test mixture benzene-carbon tetrachloride. This mixture, although not suitable for efficient columns, has the advantage that the components are readily available in a pure state and gives reasonable accuracy with columns of less than about 20 theoretical plates. Analysis is simply and accurately carried out by determination of the refractive index, and the disadvantage of the constant boiling mixture containing 91.8 mol. per cent carbon-tetrachloride, can readily be avoided by calculating a suitable composition for the still charge.

It /

It should be emphasised at this point that measurement of the efficiency of a column in terms of the number of theoretical plates to which it is equivalent, is influenced by the choice of the test mixture. Where possible, the test mixture should be similar in nature to the materials for which the column is to be used, and where this is not possible, as in the present case, the results are only valuable as an indication of the approximate efficiency to be expected. (Ward(53))

The tests were carried out as follows.

Benzene and carbon-tetrachloride (A.R. quality) were purified by careful fractionation taking a heart cut, which in each case, had a refractive index in exact agreement with the value given by Ward (53). The test mixture was made up on the assumption that the column would have an efficiency of about 20 theoretical plates, and the composition adjusted so as to ensure working, as nearly as possible, on the centre portion of the vapour-liquid equilibrium curve.

The thermocouple pocket of the 5 l. flask was replaced by a capillary sampling line leading into a sampling tube to which gentle suction could be applied, and the receiver assembly was disconnected.

To carry out a determination, the boil up rate was adjusted to the required value and the column lagging jacket set at the appropriate temperature /

:ure to ensure adiabatic conditions. After running for several hours to establish equilibrium conditions, a sample was drawn from the still pot by first blowing a few bubbles of air through the sampling line to clear it of stagnant liquid, and immediately afterwards applying gentle suction so that about 1 cc. of liquid was drawn into the sampling tube. While this was being done, three samples of a few drops each were taken from the still head, the first few drops being discarded. As soon as the samples were taken the boil up rate was measured.

The refractive indices of the samples were measured on the Abbé refractometer, the mean value being taken for the overhead samples (agreement was invariably within 1 or 2 units in the 4th decimal place.) The mol. percentage of carbon tetrachloride was estimated from the figures given by Ward (53), which are based on these given in the International Critical Tables (54) and checked with the data of Rosanoff and Easley (55), and the plate efficiency was calculated from Fenské's equation (56)

$$n+1 = \log \frac{x(1-y)}{y(1-x)} \div \log \alpha$$

where n = number of theoretical plates in column
x = mol. percentage of carbon tetrachloride in overhead
y = mol. percentage carbon tetrachloride in still pot
α = relative volatility.

The value of α was calculated from the equation given by Langdon and Tobin (57) viz.

Should be
1+0.00238

$$= 1+0.000238\,(91.8-\bar{x})$$ where $\bar{x}$ is the arithmetic mean of x and y.

Cf. Burgess
p. 22

The same authors give a table of plates versus composition for this mixture, and results determined from this table, which is based on Fenskés equation, agree closely with those calculated directly. The results of the tests are summarised in Table 2.

TABLE 2.

Efficiency of Eyelet Packed Column used in Present Work

B.U.R. mls/hr.	Time before sampling (hours)	Refractive Index		CompMol. %CCl_4		No. of Plates
		Over-head	Still pot	Over head	Still pot	
940	3	1.4680	1.4758	74.5	55.0	13.8
940	3	1.4682	1.4755	74.0	55.8	13.0
1980	2	1.4678	1.4758	75.0	55.0	14.5
2120	3	1.4682	1.4761	74.0	54.6	13.4
3000	5	1.4681	1.4760	74.3	54.8	13.7
3000	8	1.4682	1.4760	74.2	54.8	13.7
4780	3	1.4682	1.4764	74.1	53.8	13.9
8030	4	1.4679	1.4780	74.6	50.0	16.4
8030	2	1.4678	1.4780	74.8	50.0	16.5

The average value for the plate efficiency of the column, excluding that at a boil up rate of 8 litres per hour, which is close to the flood point, is 13.7, giving an H.E.T.P. of 3.5 inches. The packing was pre-flooded before carrying out the plate tests, although it is known that the efficiency of this type of packing is not appreciably influenced by any pre-flooding technique (20).

Since the still pot heater (750 watt) was insufficient to raise the boil up rate to the flood point, /

point, flooding was carried out by adjusting the boil up rate to the maximum obtainable, and then momentarily reducing the pressure in the still until flooding took place. The flood point and column hold-up were not measured, but figures supplied by the Anglo-Iranian Oil Co. Ltd. for a column of identical measurements, using the same packing are given below.

TABLE 3

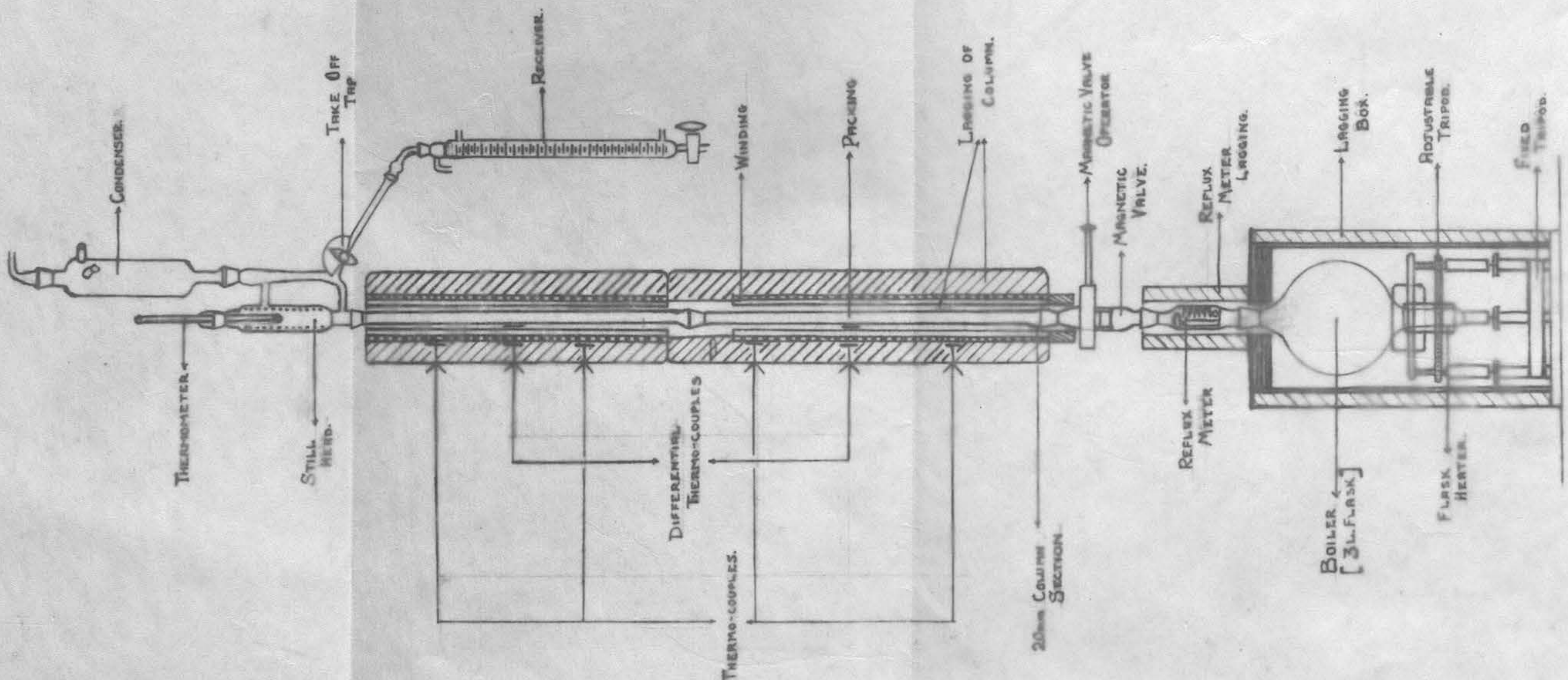
Hold-up and Pressure Drop of Anglo-Iranian Eyelet Packed Column

<table>
<tr><td colspan="2">Static Hold up</td><td colspan="2">7.8 mls.</td></tr>
<tr><td colspan="2">Flood Point</td><td colspan="2">7.0 l./ hour (calculated)</td></tr>
<tr><td colspan="2">Hold-up Factor</td><td colspan="2">4.7/ml./plate/ml./sec.</td></tr>
<tr><th>B.U.R.ml/hr. after pre-flooding</th><th>Pressure Drop (inches of water)</th><th>Dynamic Hold-up (ml.)</th><th>Total Hold-up (ml.)</th></tr>
<tr><td>1390</td><td>0.35</td><td>51</td><td>59</td></tr>
<tr><td>1730</td><td>0.65</td><td>53</td><td>61</td></tr>
<tr><td>2450</td><td>0.85</td><td>62</td><td>70</td></tr>
<tr><td>3360</td><td>1.50</td><td>69</td><td>77</td></tr>
<tr><td>4250</td><td>2.60</td><td>75</td><td>83</td></tr>
<tr><td>5000</td><td>2.70</td><td>82</td><td>90</td></tr>
<tr><td>6200</td><td>5.10</td><td>115</td><td>123</td></tr>
</table>

It should be pointed out that the above figures were determined with petroleum ether (b.p. 60°C), and therefore do not apply directly to the benzene-carbon tetrachloride test mixture, or the bases used in the present work, they are however, an indication of the characteristics of the column.

FIG. 4

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



3. The 100-Plate I.C.I. Gauze-Ring Packed Column (Fig. 4 and Plates 1, 5, 6, 7 and 8)

This column was almost entirely constructed in the laboratory although a few of the component parts (e.g. boiler, lagging box and adjustable tripods) were kindly supplied by the Anglo-Iranian Oil Company. The design is partly based on that of similar columns used by the Anglo-Iranian Oil Company and use has been made of the highly efficient gauze packing recently developed by Messrs I.C.I. Ltd. (58) who were good enough to supply data on this packing and on the construction and operation of their own stills. (59). The general lay-out of the column and auxiliary apparatus is shown in Plates 1, 5, 6, 7 and 8, and the detailed construction is shown in Fig. 4. The vacuum system which was fitted at a later date is similar in construction and operation to that used on the 14-plate column, (although following more closely the designs of Coulson and Warne (52)) and has not been shown in Fig. 4.

The apparatus and auxiliary equipment is supported by a rigid framework of $\frac{3}{4}$" gas piping, firmly bolted to the floor and wall, and extending to within a few inches of the roof, the overall height of the apparatus being about 10 ft. 6 in. For ease in attaching the usual laboratory clamps and boss-:heads a $\frac{1}{2}$" mild steel rod is rigidly clamped to the cross pieces of the framework and supports the column, reflux-meter/

reflux-meter, magnetic valve, receivers and still head.

The column itself consists of two sections of 20 mm. precision bore Pyrex tubing fitted with B.24 cone and socket joints, the overall length of each section being 93.5 cm. Each section is packed for a length of 82.5 cm. with 1/16" X 1/16", 100 X 100 mesh, square weave, Staybrite gauze Lessing rings. The two sections are mounted one on top of the other, giving a total packed length of 165 cm. The packing is supported at the bottom of each column section by a spiral of nichrome wire resting on a slight constriction of the column wall, with a few glass Raschig rings to prevent the smaller gauze rings from slipping out between the turns of the spiral. The packing is similarly held in position at the top of each section by a ring of Staybrite gauze sprung into position immediately below the top cone joint, and held in place by a few glass Raschig rings.

Each column section is provided with an electrically wound compensating lagging, consisting of a length of 1¼" bore Fibreglass steam pipe lagging ¾" 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, the total resistance of each winding being about 250 ohms.

To /

To compensate for end losses, the turns of the winding are more closely spaced towards the top and bottom ends of the upper and lower lagging sections respectively. 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 Fibreglass lagging 1½" in thickness, outside diameter 6". The column is thus insulated by a double layer of Fibreglass approximately 2¼" in thickness with a concentric heater winding at a distance of about 1" from the column wall. An unheated extension of the lower lagging section accommodates the junction of the two column sections, so that only the upper and lower joints are exposed. When in operation any exposed parts of the column are protected by removable laggings of Fibreglass or asbestos rope. (Plate 5).

Each lagging section is provided with two copper-constantan thermocouples at distances of 11" from the ends. The hot junctions of these couples are immediately over, but insulated from, the windings. In addition, there is at the centre of each lagging a differential thermocouple, consisting of two copper leads joined by a short constantan lead. One junction is attached to a small 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 /

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thermal contact with, but insulated from the winding. In practice, only these differential thermocouples are used during a distillation, and with a sensitive galvanometer, any lateral heat flow is immediately evidenced by a deflection, the direction of which indicates whether heat is flowing to or from the column. This type of couple has been found ideal for the close maintenance of adiabatic conditions and simulates current practice in adiabatic calorimetry.

The laggings are independently controlled by Variac transformers, supplied with either 110 or 230 volts, A.C., and normally, heat input is adjusted so that there is a slight but insignificant loss of heat from the column.

The boiler consists normally of a 3 l. heavy walled, Pyrex flask (smaller sizes of flask are available) with a B.24 joint on the neck and a boiling tube extension at the bottom, over which a removable heater, consisting of a nichrome wound aluminium tube, insulated on the outside with a layer of fireclay cement, may be fitted. The flask and heater are supported on an adjustable tripod with a sprung seating, which rests on a smaller fixed tripod. The boiler assembly is efficiently insulated by a lagging box (Plate 6) similar to that on the 14-plate eyelet packed column, although smaller in size. Heat input to the boiler is controlled by a Variac and ammeter.

Between the boiler and the bottom of the column there is a reflux-meter with removable lagging and a magnetic valve. (Fig. 4). The former is identical in design with the reflux-meter on the 14-plate column, but of a smaller capacity, while the magnetic-valve, designed by Messrs I.C.I. Ltd. for use with their gauze-ring packing, consists simply of a short length of tubing with a B.24 joint at each end, in which there is situated a simple type of plate valve, coupled to a short bar magnet and operated by an external system of movable magnets. Its sole purpose is to limit the return of reflux when flooding the column, prior to carrying out a distillation. Thus, when the valve is closed, reflux builds up from the bottom of the column until the entire packing is submerged in a column of liquid and completely wetted by the liquid. On cracking the valve open, the reflux drains back at a controlled rate and the column is ready for running to equilibrium.

Still Head.

Alternative types of still head are available for this column. In Fig. 4 and Plate 5 there is shown a simple type of total-reflux variable liquid take off head. Take off is adjusted by means of a grooved stop-cock, fitted with a pointer and scale for ease of setting. The vapour-upriser is surrounded by a vacuum-jacket to avoid excessive condensation and temperature fluctuations due to draughts. /

draughts. This type of still-head suffers from the disadvantage that the take off rate rarely remains steady for long periods, and this is especially noticeable at low take off rates of the order of 10 ml. per hour. The solvent action of the bases also makes lubrication of the stop-cock difficult and attempts to find a satisfactory insoluble lubricant have been unsuccessful. (Apiezon-M is the grease generally used; Silicone grease was found to be unsatisfactory).

An alternative type of still head, which has been used and found very satisfactory, both at atmospheric pressure and under reduced pressure, is shown in Plate 7. This is the tipping bucket still head designed in the laboratories of the Anglo-Iranian Oil Co. Ltd. (60). It also is a total-reflux, variable liquid take off head, The reflux after returning from the condenser, passes via a small auxiliary condenser to a small glass bucket, the overflow from which is returned to the column. At intervals, an external solenoid is energised, attracting a small counterweight to which the bucket is attached and ejecting a measured volume (0.5 ml.) of distillate. The rate of take-off is thus determined by the setting of the timer, which controls the supply of current to the solenoid. Although highly satisfactory in operation, since it enables a predetermined rate of take-off to be maintained over long periods without attention, this type of still head /

head suffers from the theoretical disadvantage of returning cold reflux to the column. This may result in slight loss of fractionating efficiency in the top few inches of packing due to the disturbance of equilibrium conditions.

The tipping bucket still head is very well suited to vacuum operation, since it avoids the use of a stop-cock. Unfortunately, owing to the difficulty of construction, the still head shown in Plate 7 was only available during the last stages of the present work. It is shown fitted with a fibre-:glass lagging to prevent excessive condensation of vapour, and for use with high boiling fractions a heater winding and differential thermocouple are provided.

With both types of still head an efficient, double-surface, spiral reflux condenser is used. This is provided with an unsilvered vacuum jacket to prevent excessive condensation of moisture on the outer walls. For atmospheric pressure operation, a water jacketted burette is used as a receiver.(Fig.4)

Packing Characteristics and Efficiency.

The efficiency of this column is such that the more readily available test mixtures, such as benzene-carbon tetrachloride and benzene-ethylene dichloride are quite useless, since the degree of separation obtained would be so great that small errors in the determination of the composition would produce disproportionately /

disproportionately large errors in the results.

Of the test mixtures commonly used, only the system n-heptane-methylcyclohexane is suitable for columns with an efficiency of more than about 50 theoretical plates. Unfortunately, pure n-heptane is not readily available and although specimens from several sources were subjected to the most efficient fractionation, it was found to be impossible to isolate a fraction of the required degree of purity (as determined by measurement of Refractive Index). Very pure methylcyclohexane, on the other hand, was readily obtained by careful fractionation of the commercial product, and possibly this could have been used in conjunction with one of the inseparable mixtures of isomers obtained from commercial heptane. It was decided, however, that the expenditure of time in re-determining the analytical data for such a system would not have been justified. The possibility of synthesising pure n-heptane by ketonisation of n-butyric acid and Clemmenson reduction of the di-n-propyl ketone so obtained was similarly dismissed.

Quite recently, the test mixture benzene-thiophene has been proposed by Coulson and Herington (61), and although it is not certain that this system would be suitable for columns of the order of 100 theoretical plates, it offers a possible solution to the problem. By the time this method was published however, /

however, the column was in daily use and it was not expedient to carry out tests.

Fortunately, Messrs I.C.I. Ltd. were good enough to provide full information of their own experiments with this packing (59) and from the data supplied it was possible to make what is probably a fairly reliable estimate of the characteristics of the column used in the present work.

The I.C.I. gauze-packing, which is in the form of Lessing rings fabricated from fine mesh square weave gauze has been described in the patent literature (58) and possesses some rather unique properties. In particular, its efficiency varies markedly with boil up rate, increasing rapidly as the boil up rate is reduced. This characteristic is shown to a lesser extent by other gauze packings, such as the Stedman and Lecky and Ewell types. The packing has a large surface area per unit volume and comparatively small hold up. The increase of efficiency with decreasing ring size is more than proportional to the increase of surface area, while the increased hold up is less than proportional to the increase of surface area. The pressure drop through this type of packing is fairly small, making it suitable for use at reduced pressures. In many respects therefore, this packing may be said to be one of the most valuable which has yet been described and as far as efficiency is concerned, in terms of H.E.T.P. /

H.E.T.P. it is unsurpassed.

The column which has been used in the present work is packed with 1/16" X 1/16" rings, fabricated from 100 X 100 mesh square weave Staybrite gauze. (The ring size is based on the dimensions of the forming tool on which the rings are made and does not represent the actual dimensions of the rings which are as follows: Length (mean) 0.067"; Diameter (mean) 0.086".) When freely packed there are approximately 102,200 rings per litre, corresponding to 2,895,000 per cubic foot.

The following data for the column used in the present work are calculated from the figures provided by Messrs I.C.I. Ltd.

Static hold up = 21.2 gm.

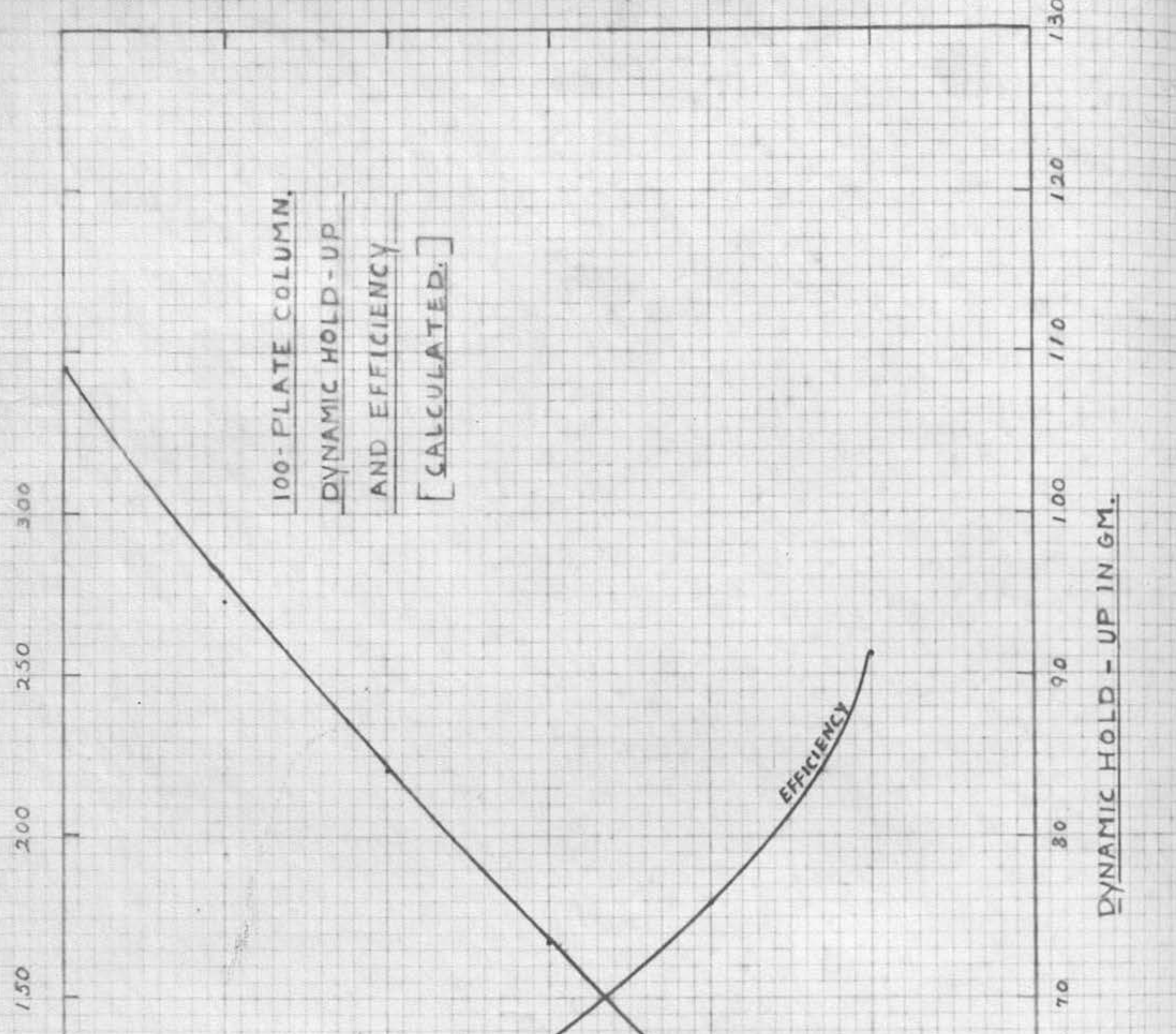
This is based on data given for hold up of 100 gm. of 1/16" 100 mesh Staybrite gauze rings, measured with 2; 2;4-trimethylpentane after 10 minutes draining.

Dynamic hold up.

The variation of dynamic hold up with boil up rate is given in Table 4 and Graph 1.

TABLE 4

Boil up rate (gm/hr.)	Dynamic hold up (gm)
200	44.1
400	54.1
600	64.2
800	73.4
1000	84.0
1200	94.5
1400	109.1


100-PLATE COLUMN.
DYNAMIC HOLD-UP
AND EFFICIENCY
[CALCULATED.]
EFFICIENCY
HOLD-UP
0
50
100
150
200
250
300
1400
1200
1000
800
600
400
200
B.U.R. IN GM./HR.
40
50
60
70
80
90
100
110
120
130
DYNAMIC HOLD-UP IN GM.

GRAPH. 1.

These figures are based on data given for 1/16" 100 mesh phosphor-bronze gauze rings. The determinations were carried out in a column of ¾" bore, 2'3" long, using 2; 2; 4-trimethylpentane (drainage time 10 minutes). Allowance has been made for the difference in the diameters of the columns, but no correction could be made for the difference in gauze material, the effect of which is probably very small.

Theoretical Plates.

The effect of boil up rate on the number of theoretical plates is shown in Table 5 and Graph 1.

TABLE 5

Efficiency of 100-Plate Gauze Packed Column.

Boil up rate (gm./hr.)	Theoretical Plates
400	255.8
600	178.3 column
800	136.4
1000	112.0 preflooded
1200	95.0
1400	82.8

The figures were obtained by extrapolation of data given for 1/16" 100 mesh, phosphor-bronze gauze rings in a ¾" bore column 12" long. Allowance was made for the difference in diameters, making use of the fact that for small changes

Efficiency $\propto \frac{1}{(\text{Diameter})^2}$. It was assumed that efficiency was directly proportional to length, although this is not strictly true, since increase of column /

column length follows the law of diminishing returns. No allowance could be made for the difference in gauze material, but the effect of this is known to be small. The tests were carried out using the mixture n-heptane-methylcyclohexane.

It will be observed from Graph 1. that the efficiency increases rapidly with decreasing boil up rate. The limiting factor with this type of packing is apparently the boil up rate at which the reflux is insufficient to maintain a complete liquid seal in the interstices of the gauze, on which the efficiency of the packing apparently depends. It is for this same reason that thorough preflooding of this type of packing is particularly important, hence the use of the magnetic valve at the base of the column.

During the present work a boil up rate of 900-1000 ml. per hour has generally been used, giving an efficiency of the order of 112-120 theoretical plates and providing more than sufficient reflux to ensure thorough wetting of the packing.

It should be borne in mind that, although plate efficiencies determined with a hydrocarbon mixture are probably applicable to other mixtures of hydrocarbons, they may not be applicable to such widely different materials as pyridine bases, and therefore serve only as an indication of the order of efficiency of the column, so far as the present work is concerned. It is interesting to note in this connection that Döstrovsky and Hughes (62) use a column 12 ft. long 20 mm. in diameter packed with 1/16" phosphor-bronze rings for concentration of the heavy isotopes of oxygen in water. From the separation achieved they estimate the efficiency as being about 450 theoretical plates, at a boil up rate of 500 ml. per hour. This is rather lower than might be expected, but it must be remembered that in this case, the relative volatility is exceptionally low, and the high surface tension of water may interfere with the proper wetting of the packing.

Constant Voltage Supply.

During the earlier stages of work with this column, it was soon noticed that the boil up rate fluctuated in an irregular manner, and sometimes there was a total stoppage in the flow of reflux with consequent loss of equilibrium and draining of the packing. The fault was soon traced to variations in the mains supply voltage, sometimes amounting to as much as ±15 per cent.

The problem was ultimately solved by feeding the power supply through a constant voltage transformer (Advance Components, Ltd.), the output of which remains substantially constant at 230 V. ± ca. 1 per cent, throughout a wide range of input voltages.

Operation under Reduced Pressure.

The 100-plate column has been used in the present work for the close fractionation of narrow boiling cuts obtained from earlier distillations carried out under reduced pressure. During the earlier stages of the work it was found quite satisfactory to operate this column at atmospheric pressure and in spite of the long period of time required for a distillation (a charge of say 1800 gm. requiring about a week of continuous operation), there was no evidence of appreciable decomposition, although the residues from the still pot were usually very dark and occasionally slightly tarry. It was felt, however, that with higher boiling fractions, the risk of thermal decomposition might become more serious. In addition, it was observed that with high boiling fractions (b.p. 190-200°C), there was a marked tendency for the overhead temperature to fluctuate and ultimately it became difficult to maintain a steady boil up rate. The apparatus was also observed to become extremely susceptible to slight draughts in the region of the still head. It was decided, therefore, that before any further distillations could be carried out, the apparatus would have to be converted to vacuum operation. The change over was accomplished without great difficulty and the results more than justified the labour involved in the conversion. Fluctuation of the overhead temperature was

completely/

completely eliminated, susceptibility to draughts became negligible and the advantages of avoiding decomposition, and working at a fixed steady pressure, which is independent of the atmospheric pressure,more than outweigh the slight disadvantages of reduced pressure operation. Moreover, it has been possible to instal a safety cut-out device so that should any part of the vacuum system fail while the apparatus is unattended, all power is automatically cut off.

The useful working range of the vacuum system is from about 20 mm Hg. up to several hundred mm.Hg. Below 20 mm. Hg., the pressure drop due to the column cancels out the advantage of working at low pressure, and at high pressures, the sensitivity of the vacuum control system is somewhat reduced.

There is comparatively little in the literature to indicate the effect of pressure on the efficiency of fractionating columns. According to Docksey and May (63), however, there is no marked effect down to about 10 mm. Hg.

The vacuum system has not been shown in Fig.4. but since it is very similar to that used on the 14-plate column, it is only necessary to draw attention to the points of difference.

Vacuum System.

Like the vacuum system of the 14-plate column, the pressure control is again carried out in two stages /

stages and follows very closely the system described by Coulson and Warne (52). The low pressure buffer vessel A (Fig. 3) is shared in common with the 14-plate column and avoids duplication of the manostat A (Fig. 3) and Speedivac pump. If the two stills are to be operated simultaneously at different pressures, the pressure in A is maintained about 20 mm. Hg. below the pressure in whichever of the two stills is operating at the lower pressure.

The place of buffer vessel B is taken by a 10 l. bolt-head flask, enclosed for safety in a sheet-iron casing (Plate 5). The solenoid valve is replaced by a simple type of flap valve, operated by a small electromagnet, the whole valve assembly being attached to a glass tube drawn out to a jet, which is normally closed by the flap valve. The valve assembly is mounted inside the 10 l. bolt-head flask and supported by a rubber bung through which the glass tube passes, the other end of the tube being connected directly to buffer vessel A. Vacuum connections to the still head condenser and receiver system pass through the rubber bung closing the 10 l. flask, which is maintained at the still operating pressure. To protect the flap valve from damage in case of accidental flooding, or overflow of the receivers, a 2 l. bolt-head flask, which serves as a catchpot, is connected in series between the 10 l. flask and the still (Plate 7). The effective volume of the apparatus /

apparatus is thus increased by about 12 l., all of which is maintained at the still operating pressure, and effectively reduces the influence of leakage and minor pressure changes in the still. Manostat B is replaced by a sulphuric acid manostat of the type described by Hershberg and Huntress (64), containing sulphuric acid of density about 1.7, which greatly increases the sensitivity of the system. For ease in making minor adjustments, this manostat is mounted on a pivot and can be rotated through a small arc by means of a screw mechanism. The sulphuric acid manostat is connected via a small safety trap to the 10 l. flask.

To eliminate the effect of ambient temperature on the sulphuric acid manostat, it is mounted inside a wooden box fitted with a simple bi-metallic thermostat (Sunvic type T.S.3.) and a heater consisting of a 25 watt lamp. (Plate 5). The box is thus maintained at an arbitrarily chosen temperature, a few degrees above room temperature, and although temperature control inside the box is not close, fluctuating in a regular manner over a range of 1 or 2°C, the period of the system is so rapid that, in effect, the air enclosed by the manostat is maintained at a substantially constant temperature.

Operation of the system is as follows. Any rise of pressure in the still alters the level of the sulphuric acid in the manostat, causing it to break contact /

contact with a tungsten electrode, the point of which is normally in contact with the surface of the sulphuric acid. This electrode, and another which is below the surface of the acid, form part of the grid circuit of a simple triode amplifier ((52)Plate 4). The change in grid potential causes an increase in the anode current which is sufficient to operate a miniature telephone type relay, and this in turn operates a 40 V. local battery circuit, energising the coil of the flap valve inside the 10 l. flask. Air then passes from the 10 l. flask to buffer vessel A (Fig. 3) reducing the pressure in the 10 l. flask and the still, until the status quo is restored. The sensitivity of the system is of the order of 0.1 - 0.2 mm. Hg. (at 100 mm. Hg. operating pressure).

A set of manometers and a barometer, similar to the assembly on the 14-plate column, indicates the pressures in the still and receivers (Plate 8). As with the 14-plate column, two receivers in series are used, a tap manifold making it possible to drain and re-evacuate the lower receiver without disturbing the pressure in the rest of the system. The receivers are connected to the tipping bucket still head by a long wide bore tube, so that they are at a convenient level for emptying. Liquid hold-up in the connecting tube is negligible.

During long periods of operation there is a gradual pressure drift, usually of the order of 0.5 mm. Hg. /

Hg. in twelve hours. This is readily corrected by hand as necessary.

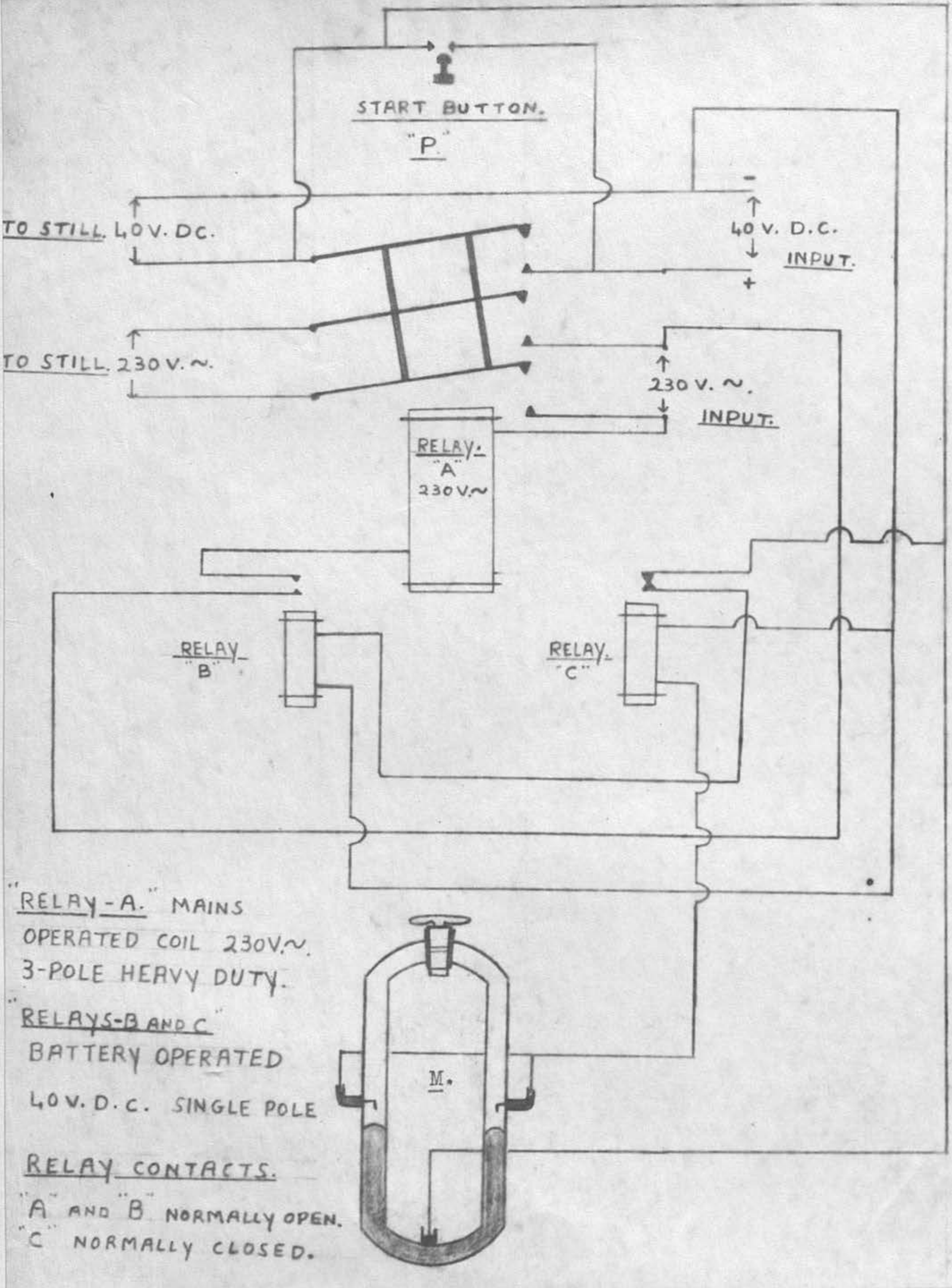
Flask Heater.

The normal type of heating arrangement, consisting of a tubular heater which fits over a boiling tube extension on the base of the flask, is not suitable for vacuum operation owing to the risk of bumping and the danger of the flask collapsing. A plain 3 l. heavy walled round bottomed flask with a B. 24 neck is therefore used. The tubular heater is replaced by a 750 watt cylindrical bowl-fire element suspended from the adjustable tripod. (Plate 6).

Safety Cut-out.

Since the 100-plate column requires to be run under total reflux for a period of approximately ten hours in order to establish thermal equilibrium after starting up, it is obvious that for it to be of any practical value it must be operated continuously night and day. During the earlier stages of the work this difficulty was overcome by arranging the work of the laboratory on a shift basis, so that the still was never unattended for more than a short period. In the later stages of the work the still was frequently allowed to operate over-night on total reflux, and, with the advent of the tipping bucket still head, it was sometimes possible, when operating on a flat part of the distillation curve, to arrange for distillation

to /



"RELAY-A." MAINS OPERATED COIL 230V.~. 3-POLE HEAVY DUTY.

"RELAYS-B AND C" BATTERY OPERATED 40V. D.C. SINGLE POLE

RELAY CONTACTS.

"A" AND "B" NORMALLY OPEN.
"C" NORMALLY CLOSED.

SAFETY MANOSTAT AND CUT-OUT FOR 100-PLATE COLUMN.

FIG. 5.

to be continued over-night without attention. When operating under reduced pressure however, the slight risks involved in this procedure became positive hazards, and it was considered advisable to arrange for automatic cutting off of the power supply in the event of a failure in the vacuum system. This has been done as follows.

One side of a small and rather insensitive mercury manostat M (Fig. 5 and Plate 7) is connected to the catch-pot and maintained at the operating pressure of the still. When the apparatus is left unattended the tap on this manostat is closed, any change in pressure then results in a rise in the mercury level in one or other of the limbs, depending on whether the pressure in the system rises or falls. The mercury levels are so adjusted that if this rise exceeds 1 or 2 mm. a circuit is closed, irrespective of whether the change in levels is due to a rise or fall of pressure in the system. This manostat is connected to a relay set, the circuit diagram of which is shown in Fig. 5. Operation is as follows: A is a three pole heavy duty relay, the contacts of which are normally open but close when the coil is energised, the coil operates on 230 V a.c. Relays B and C are single pole battery operated relays, the contacts of B are normally open, those of C normally closed, these conditions being reversed when the respective coils are energised.

It will be seen from the circuit diagram that when the push button P is pressed, relay B is energised by the 40 V. local battery supply. This in turn energises the coil of relay A, which in turn short circuits push button P and connects the mains and battery supplies to the still. The relays A and B are then mutually self energising and self holding. Any movement of the mercury in manostat M completes a circuit momentarily energising relay C, the contacts of which open, releasing relay B and hence releasing relay A and cutting off both mains and battery supplies. Conditions cannot then be restored until the manostat circuit has been broken, and the push button P pressed again. Obviously a temporary failure in the mains or battery supply will have the same effect.

The degree of latitude allowed in pressure control may be altered by varying the level of mercury in manostat M. Normally this is adjusted so that a change of about 1-2 mm. Hg. is sufficient to operate the cut out, and since this is well beyond the normal limit of sensitivity of the vacuum system, there is little danger of an accidental cut out.

Operation.

After charging the flask, re-greasing and making up the joints, the system is tested for leaks, if operating under reduced pressure. Any serious leaks /

leaks are attended to by re-greasing the appropriate joints or taps and the pressure is then set at the required value and the electronic relay set switched on. If all is well there will be no detectable change in the pressure, as indicated by the manometers, and the electromagnetic flap-valve will operate regularly, at intervals of not less than about twenty seconds. The frequency of operation usually decreases to about once per minute or even less, when the system has been in operation for some time.

The heating circuits to the boiler and column laggings are then switched on and the voltages adjusted to appropriate values depending on the boil up rate required and the boiling point of the charge. When a steady reflux appears at the still head the column lagging jackets are set to the correct temperature to ensure adiabatic conditions and the boil up rate brought to the required value. During this heating up period, it is often convenient to switch off the electronic relay, and by opening the appropriate taps, operate the entire system at the pressure of buffer vessel A. (Fig. 3), which is usually about 20 mm. Hg. below the normal operating pressure of the system. This avoids too frequent operation of the electromagnetic valve due to the expulsion of the expanding air in the still.

The column is then flooded by closing the magnetic /

magnetic valve (Fig. 4) until a column of liquid reflux builds up from the base of the fractionating column, and finally appears immediately below the still head. The column is then deflooded by cracking open the valve and allowing the liquid to drain back slowly into the boiler. This operation requires some skill when operating under reduced pressure, as there is a tendency for a seal of violently boiling liquid to form near the top of the packing, while the lower portion drains more or less completely.

After flooding, final adjustments are made to bring the pressure to the desired value and when all conditions are stable, the column is run to equilibrium for a period of about 10-12 hours, or until there is no further drop in the overhead temperature.

Take off is then started by either opening the tap on the still head, or if the tipping bucket still head is used, by switching on the timer which controls the solenoid at the still head.

Normally a boil up rate of 900-1000 ml/hour is used at a reflux ratio of approximately 100:1. The take off rate is, therefore, of the order of 9-10 ml. per hour. A charge of say 2000 ml. requiring approximately 180 hours for complete distillation, after allowing for column hold-up and a reasonable volume /

volume of residue.

Automatic Vacuum Distillate Take-off.

An automatic vacuum distillate take-off was constructed to the design of Brown and Coles (65) and fitted to the 100-plate column. This apparatus consists essentially of a glass bell-jar sealed to a brass plate with six-holes, each of which communicates with a separate receiving flask. Distillate is directed to each of the holes in turn through a movable delivery tube mounted in a bearing and sealed into the neck of the glass bell. Rotation of the delivery tube is controlled by a small bar-magnet which aligns itself between the poles of three pairs of external electromagnets, each pair being energised in turn by a timing device. The net result is that six fractions may be collected without any attention to the apparatus, the distillate being directed to each of the six receivers in turn at predetermined intervals.

Unfortunately, this apparatus was not available until a late stage in the present work. It was also found to be rather uncertain in action and subject to leakage under vacuum. Unfortunately, also, its fitting coincided with the appearance of a solid fraction in the distillate from the 100-plate column, so that its use had to be discontinued almost immediately and it was not replaced.

A /

A study of this apparatus, showed that there is a real need for some simple and reliable form of automatic fraction cutting device suitable for vacuum work, but unfortunately, it was not possible to pursue this matter further during the present work.

4. 30-Plate I.C.I. Gauze-Ring Packed Column.

During the interim period, while the 100-plate column was being converted to vacuum operation, distillation work was almost at a standstill, since all the bases had already been fractionated in the 14-plate eyelet packed column. As a temporary measure, this column was re-packed with ¼" X ¼" I.C.I. Staybrite gauze rings of 60-mesh square weave gauze. This provided a column of efficiency and throughput intermediate between those of the 14-plate and 100-plate columns, which, while lacking the resolving power of the 100-plate column, made it possible to continue fractionation of the higher boiling bases. The packed length was retained at 4 ft. and since no alterations were made other than the change in packing, no description of the apparatus is necessary.

Packing Characteristics and Efficiency.

The static hold-up has been estimated from figures provided by Messrs I.C.I. Ltd. (59) for 2:2:4-trimethylpentane, and is approximately 3 gm. No figures are available from which the dynamic hold-up can be calculated, but this is believed to be correspondingly /

correspondingly small.

Efficiency tests were carried out at atmospheric pressure using the test mixture benzene-carbon tetrachloride, the results of which are given in the following table (Table 6).

TABLE 6

Efficiency of 30-Plate Gauze Packed Column.

B.U.R. (ml/hr.)	Overhead Mol% CCl_4	Still-pot Mol% CCl_4	Theoretical Plates (from Table of Langdon and Tobin (57))
5200	64.16	16.94	20.0
3600	67.31	17.44	22.0
2180	73.20	17.44	27.7
2000	71.75	16.92	26.2
1500	76.10	13.08	33.5
765	84.52	16.92	48.8
			By extrapolation

The column was preflooded by sudden temporary reduction of the pressure before carrying out the above tests and brought to equilibrium by running for several hours on total reflux.

It will be noticed that, as with the 100-plate column, efficiency increases rapidly with decreasing boil up rate. The anomalous result for a B.U.R. of 2000 ml./hr. was probably due to imperfect pre-flooding of the packing. Although a high efficiency can be obtained by operating at a boil up rate of less than 1000 ml./hr. this is probably approaching /

approaching the point at which the rate of reflux is barely sufficient to keep the packing wet.

This column has normally been operated during the present work at a boil up rate of 1500 ml./hr. and a reflux ratio of ca. 30:1. The column is thus referred to in this thesis as the 30-plate column, since this is the approximate efficiency to be expected under these conditions.

5. <u>40-Plate Fenske Helices Column</u>.

This was supplied as a complete unit by Messrs Griffin & Tatlock and is based on designs of the Anglo-Iranian Oil Company Limited. Its general design closely resembles that of the 100-plate column although it lacks many of the refinements of the latter.

The main differences are in the packing, which in this case consists of single turn glass Fenske helices (internal diameter 0.125") and the absence of a magnetic valve, which is not required with this type of packing. The column lagging again consists of a double-layer of Fibreglass with a compensating winding. Heat input is controlled in a step-wise manner by a series of fixed resistances which may be switched out in turn, increasing the temperature of the lagging jackets by fixed steps to a series of pre-selected temperatures. The column may thus be run under approximately adiabatic conditions, although, since the /

the lagging is thinner than in the case of 100-plate column, heat losses tend to be excessive at high temperatures. Thermocouples were not fitted to the lagging jackets as supplied, but were fitted at a later date.

This column has so far found little application in the present work as its efficiency is considerably less than that of the 100-plate column, although its operating rate is consequently higher. It has been of some indirect use for the purification of solvents, etc.

Tests carried out using the mixture benzene-carbon tetrachloride, showed, as was expected, that the efficiency remained substantially constant over a wide range of boil up rates. The tests also showed that pre-flooding of the packing caused an increase of 5-6 theoretical plates in the efficiency.

It was intended that this column might be used for azeotropic-distillations using as azeotrope formers, aliphatic carboxylic acids which seem to attack the Staybrite gauze packing. Time however, did not allow these experiments to be carried out.

6. 14-mm. I.C.I. Gauze-Ring Packed Column.

For small scale experiments, a 14-mm. column packed for a length of 120 cm. with 1/16" I.C.I. Staybrite gauze Lessing rings was constructed.

The /

The design is simple, still pot and still head assemblies being essentially the same as on the 100-plate column, although a smaller still pot (750 ml.) is used. The column lagging takes the form of a glass jacket, 2 cm. I.D. wound in two equal sections with nichrome tape. A thermometer is attached to each section of the heater winding, the thermometer bulbs being midway between the centre and ends of the lagging jacket. The whole is mounted inside an outer glass jacket 38 mm. I.D. so that the column, packing, and lagging jacket thermometers are visible when the apparatus is in operation.

This column was intended for azeotropic experiments, but owing to the corrosion problem to which reference has been made, it was not put into service.

7. Fractional Extraction Apparatus.

A simple type of rotary liquid-liquid extraction apparatus, similar to that described by Lochte and co-workers (66) was set up in the laboratory, and some preliminary experiments were carried out, the results of which were discouraging.

The apparatus, which can be seen to the right of the 100-plate column (Plate 5), consists essentially of two bulbs connected by a vertical glass tube in which a rapidly rotating rod is suspended, connections being provided for the inlet and outlet of solvents, acid and alkali, etc.

The essential feature of the apparatus is that the clearance between the rotor and the walls should be small, so that ascending drops of liquid are flattened into a continuous spiral, presenting a large surface for interchange. Great difficulty was experienced in finding a glass rod of the correct diameter, which was sufficiently straight to enable a high speed of rotation to be used. This difficulty was eventually overcome by using a Staybrite rod turned down to the required diameter.

Unfortunately, preliminary experiments using petroleum ether water mixtures showed that successful operation of the apparatus was dependent on a number of critical factors and its use was abandoned in favour of multiple extraction in separating funnels, using the scheme of Jantzen. (51)

SECTION E.

Experimental.

Owing to the intractable nature of the starting material the initial stages of purification involved a considerable expenditure of time. For reasons which will be given, it was decided that the only practicable method of separating the bases from the high-boiling or non-volatile pitch was by vacuum distillation, as opposed to such methods as solvent or acid extraction. This preliminary distillation, while affording no information of any value, was a tedious, but at the same time very necessary preliminary, the difficulties of which it is impossible to over emphasize.

The volatile bases thus isolated were subjected to a further distillation, a preliminary fractionation and ultimately a precise fractionation using a highly efficient column.

While these distillations alone were insufficient to separate pure components, they constituted in fact the major part of the work done. Efficient fractional distillation is necessarily a slow and painstaking procedure and in the absence of elaborate automatic control gear, one which requires almost continuous supervision, and if a reasonable throughput is to be maintained, continuous operation, night and day. For this reason a large part of the work to be described has been of a joint nature.

The time consumed in this part of the work unfortunately curtailed the time available for examination of the final fractions and identification of the components, and for the same reason several of the projected separation methods were examined only superficially. It is nevertheless felt that the work which has been carried out both in the construction of the apparatus and the separation of the starting material into fractions suitable for further investigation constitutes an appreciable step forward and should provide impetus for subsequent work in this field.

For convenience the experimental work has been divided into four parts.

a. Examination of the "Basic Tar"
b. Possible methods of working up the starting material
c. Distillations
and d. Examination of the narrow boiling fractions.

a. <u>Examination of the "Basic Tar"</u>

The "Basic Tar", as has already been explained, originates in the sulphate of ammonia plant, by neutralisation with ammonia of the recovered acid containing dissolved bases. As it comes from the sulphate of ammonia plant, the "Basic Tar" is a viscous, black, evil smelling, tarry liquid. It is known that the composition shows irregular day to day variations, and that the amount of entrained water is variable. However, it is reasonable to assume that the same bases are always present in the tar, although the /

the percentage composition may vary within certain limits.

For the present investigation, a 1 ton sample of tar from a typical day's run was put aside to be used as required, and formed the stock on which all the present work has been carried out.

The tar sample was given a preliminary examination in the laboratory and found to contain 7.8% of water(Dean and Stark). An analysis carried out on the wet material showed it to contain 4.6% of nitrogen and 3.8% sulphur.

On attempting to distil a 150 gm. sample of the wet material at atmospheric pressure, trouble was experienced with frothing, until most of the water had been removed after which the tar distilled smoothly until about 40% of volatile material had been taken over (including water). At this stage decomposition became serious and distillation was discontinued, the final temperature reached being 310°C. The apparatus used consisted simply of a large distilling flask (500 ml.) fitted with a thermometer and a simple air condenser. The distillate was collected in a graduated cylinder, the whole forming a modified Engler distillation apparatus.

The crude bases obtained from this distillation formed a dark yellow-brown oily liquid with a characteristic "sooty" odour (c.f. Robinson (10,11)) and /

and amounted to about 33% of the tar sample. The residue was a hard glossy black friable pitch. Subsequent experiments on the larger scale showed that removal of the water alone, is sufficient to convert the tar to a solid pitch.

The results of this distillation are summarised in Table 7.

TABLE 7

Distillation of Basic Tar at Atmospheric Pressure.

Temperature	Per cent distilled (including water)
-250°	10.2
-300°	16.6
-310°	40.8
Weight Balance	
Water	7.7%
Insoluble Bases	33.1%
Residue (Pitch)	55.0%
Loss (decomposition)	4.2%
TOTAL	100.0%

The crude bases from this modified Engler distillation were redistilled in vacuo after separating from the water and it was found that about 75% came over below 150°C at 4 mm.Hg. The distillate was not examined further, but the two distillations indicated that it should be possible to obtain at least a 25% recovery of crude bases from the tar and this /

this was in fact the approximate figure achieved on the larger scale. The difficulties involved, however, were considerably greater than had been anticipated.

b. Possible Methods of Working Up the Starting Material

There appeared to be little point in wasting further time in examination of the crude "Basic Tar" and it was at this stage that all possible methods of separating the volatile bases were considered. These included batch distillation at atmospheric or reduced pressure, flash distillation, steam distillation at atmospheric or reduced pressure, and extraction with acids or solvents.

Flash Distillation.

Flash distillation, that is to say pumping the hot tar under pressure into an evacuated flash chamber, from which the vapour and pitch could be drawn off separately, appeared on the face of it to be an ideal method of handling this rather difficult material. Further consideration however, showed that the construction of a suitable apparatus which would handle the very viscous pitch would have presented very great difficulty. The experiment was tried of running the tar into a sloping tube furnace, the vapours being drawn off from the top, while the pitch flowed out at the bottom, the whole being maintained at a low pressure by means of a rotary vacuum pump. While the method showed some promise, the

throughput /

throughput of the apparatus was very small and there was great difficulty in maintaining the flow of the viscous pitch. The method was therefore abandoned without further investigation.

Steam Distillation.

Steam distillation was obviously out of the question on the laboratory scale owing to the viscous nature of the material, and the difficulty of handling any reasonable volume. It was unfortunately impossible for technical reasons to arrange for this operation to be carried out in one of the Pumpherston refinery coking-stills, although if this could have been done it would no doubt have yielded an excellent clean product and the entire batch could have been treated in one operation.

A proposal to have the initial distillation carried out in a local coal-tar distillery was similarly abandoned, since the size of the plant would have required a batch of about ten tons for successful operation.

Solvent Extraction.

Acid or solvent extraction had to be dismissed since there was no suitable plant of the requisite size available.

There was therefore no alternative but to carry out the initial purification by batch vacuum distillation /

distillation using the largest apparatus which could be adapted to the purpose. This was the 16 l. Gas Heated Vacuum Still, and some fifty litres of crude bases were isolated with the aid of this apparatus. These bases were then worked up by a series of distillation processes and ultimately by chemical means.

c. Distillations.

The distillations now to be described divide themselves naturally into four series and it has been found convenient to designate these the A, B, C and D distillations, the significance of these terms being as follows.

A-Distillations.

Distillation of the crude "Basic Tar" and separation of the crude bases.

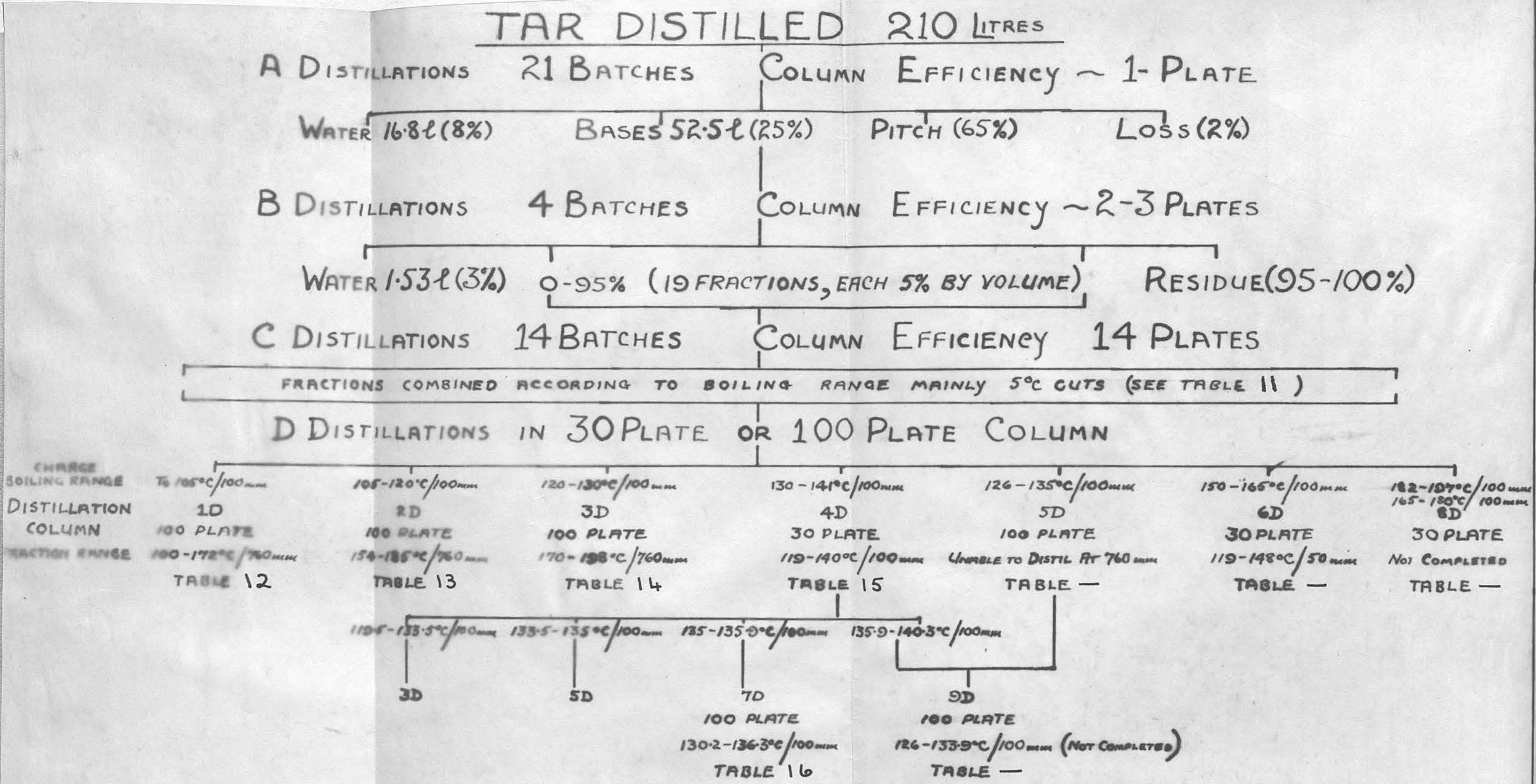
B-Distillations.

Re-distillation of the crude bases and separation into five per cent fractions by volume.

C-Distillations.

Initial fractionation of the five per cent volume fractions, and separation into narrow boiling-range cuts. (5°C. cuts).

D-Distillations. /


TAR DISTILLED 210 LITRES
A DISTILLATIONS 21 BATCHES COLUMN EFFICIENCY ~ 1-PLATE
WATER 16·8ℓ (8%)
BASES 52·5ℓ (25%)
PITCH (65%)
LOSS (2%)
B DISTILLATIONS 4 BATCHES COLUMN EFFICIENCY ~2-3 PLATES
WATER 1·53ℓ (3%)
0-95% (19 FRACTIONS, EACH 5% BY VOLUME)
RESIDUE (95-100%)
C DISTILLATIONS 14 BATCHES COLUMN EFFICIENCY 14 PLATES
FRACTIONS COMBINED ACCORDING TO BOILING RANGE MAINLY 5°C CUTS (SEE TABLE 11)
D DISTILLATIONS IN 30 PLATE OR 100 PLATE COLUMN
CHARGE BOILING RANGE
DISTILLATION
COLUMN
FRACTION RANGE
To 105°C/100mm
1D
100 PLATE
100-172°C/760mm
TABLE 12
105-120°C/100mm
2D
100 PLATE
154-185°C/760mm
TABLE 13
120-130°C/100mm
3D
100 PLATE
170-198°C/760mm
TABLE 14
130-141°C/100mm
4D
30 PLATE
119-140°C/100mm
TABLE 15
126-135°C/100mm
5D
100 PLATE
UNABLE TO DISTIL AT 760mm
TABLE —
150-165°C/100mm
6D
30 PLATE
119-148°C/50mm
TABLE —
182-197°C/100mm
165-180°C/100mm
8D
30 PLATE
NOT COMPLETED
TABLE —
119·5-133·5°C/100mm
133·5-135°C/100mm
135-135·9°C/100mm
135·9-140·3°C/100mm
3D
5D
7D
100 PLATE
130·2-136·3°C/100mm
TABLE 16
9D
100 PLATE
126-133·9°C/100mm (NOT COMPLETED)
TABLE —

FLOW SHEET

D-Distillations.

Final fractionation of the narrow boiling-range cuts and further separation into narrow boiling-range fractions (1°C. cuts.)

The scheme of distillations is shown in the appended flow sheet (Fig. 6) and the experimental details are given below.

A-Distillations.

These distillations were carried out in the 16 l. gas-heated still at the laboratories of Messrs Scottish Oils Ltd. and it is impossible to over-emphasise the difficulties which were involved.

The tar was supplied in 40 gallon barrels and owing to its high viscosity transfer was difficult. This was solved by storing the barrels in a large electric oven, the warm tar being taken to the still in 1 gallon tins and heated over a gas ring before attempting to charge the apparatus. During the initial stages of the work the tar was poured into the cold still, but it was soon found that some trouble could be saved by maintaining the still pot at a temperature of about 100 - 150°C. while the tar was slowly added in stages. The column lagging was also switched on during the charging operation and as much as possible of the water was removed at this stage. Unfortunately, it had been found impossible to dehydrate the tar before distillation, and the water /

water remaining after the charging operation had to be removed very slowly and carefully by gentle heating at atmospheric pressure. At this stage frothing was a very serious problem, and although partially solved by keeping the column temperature at about 150 - 200°C the removal of the water usually required three or four hours of very slow distillation with constant attention. The back-pressure, as indicated by the still pot manometer, was a useful guide to the amount of frothing taking place, but as the line to this was frequently blocked by tar, there was often little or no warning until, as frequently happened, the tar foam reached the still head, dislodging the packing and choking the condensers.

When most of the water had been removed, the pump was switched on and the pressure reduced very slowly until the last traces of water were removed and the distillate consisted entirely of oily bases. The pressure was then gradually reduced during the remainder of the distillation until the best possible vacuum (usually about 5 mm.Hg.) was obtained. Distillation was usually much easier when all water had been removed, but it was still necessary to proceed with some care in order to avoid splashing of the tar. The reflux meter was invariably obscured by tar foam, so that it was impossible to check the boil-up-rate and this had to be judged from the rate of distillation, the take off tap always being kept fully open so that reflux was reduced to a minimum./

minimum. If, as sometimes happened, the boil-up-rate became too high there was a sudden rush of tar which completely blocked the still-head and often the vacuum lines and receivers. Usually the only thing to do when this happened was to shut down, dismantle the still-head and receiver assembly and remove the solid tar. Usually this could only be done by washing with hot aniline, since the partially distilled tar resisted all the common solvents. A shut-down of this nature often meant that distillation was stopped for several hours, and it was sometimes necessary to abandon the charge, since if the tar was allowed to solidify in the still pot it could only be re-melted with great difficulty. The drastic cleaning operations frequently resulted in breakage of the glass parts, and it was often necessary to carry on with makeshifts until repairs could be made.

A further difficulty was the solvent action of the mixture of water and bases on all the usual stop-cock greases. No really satisfactory solution to this problem was found and it was necessary to shut-down at intervals while the taps were re-greased. Audco grease No. 656 was found to be satisfactory for the ground glass joints, but unfortunately this grease was not suitable for taps.

As distillation was continued, the colour of the distillate changed from pale yellow to dark yellow and then orange-yellow. The viscosity also increased until /

until when the still pot temperature reached about 200°C the distillate was very oily and dark orange-yellow in colour. At a still pot temperature of about 200°C. decomposition also became appreciable and it became more difficult to maintain a steady pressure. Drops of water usually appeared in the distillate at this stage owing to the decomposition of the tar and ultimately a hazy fog of decomposition products appeared in the still head. As soon as these symptoms were observed, which was almost invariably at or near a still pot temperature of 250°C., distillation was stopped.

During distillation the column was always maintained at about 50-100°C. above the overhead temperature in order to break the foam. Owing to the continuously changing conditions of pressure and heating, the overhead temperatures were never steady and no attempt was made to achieve fractionation. The apparatus was used simply as a pot still, the column serving no purpose other than to act as a foam breaker and arrest the tar spray.

Immediately a distillation was completed it was essential to empty the still pot, otherwise the residual pitch solidified in the stand-pipe and could only be re-melted with great difficulty. The still was emptied by blanking off the condenser and receiver assembly and applying pressure to the filling orifice. The pitch was extremely viscous even at 250°C. /

250°C. and the external parts of the still pot stand-pipe and the outlet valve had to be continuously heated with a hand blow-pipe during the process of emptying. The hot pitch gave off dense choking fumes, so that it was almost impossible to carry out this operation without wearing a respirator.

As soon as one batch was completed, the next, previously warmed, was charged without delay into the hot still pot, heating being continued so that the temperature of the tar was maintained at about 120°C. during the charging operation.

The residual pitch set on cooling to a glossy black friable solid with a strong odour of hydrogen sulphide when crushed.

Further difficulties encountered during these distillations included the following:-

(a) Owing to the method of heating (gas ring burner) it was rather difficult to maintain a steady rate of heat input.

(b) The manometer was often blocked by small globules of tar or bases splashed into the vacuum lines and the mercury surfaces were fouled by the presence of hydrogen sulphide in the gases given off. Thus, it was often impossible to obtain more than a rough indication of the operating pressure.

(c) A coke-like deposit gradually collected on the column /

column packing, causing it to bind together and ultimately choking the column. On two occasions it was necessary to strip the entire column and remove the packing for cleaning.

(d) Owing to the decomposition of sulphur compounds and to a lesser extent of the bases and other nitrogen compounds, the exhaust gases were nauseating, highly toxic and extremely corrosive and appeared to contain hydrogen sulphide, hydrogen cyanide, nitriles, ammonia, etc. In spite of the presence of two traps and a large buffer vessel, volatile decomposition products and corrosive gases passed into the Speedivac pump. This was particularly the case during the early stages of a distillation when volatile compounds were driven off and towards the end when decomposition became appreciable. The corrosive properties of these gases caused the pump to seize frequently, and on more than one occasion it had to be completely stripped for cleaning.

The exhaust gases from the pump were carried out of the laboratory by a stand-pipe passing through the roof, but until this arrangement was adopted it was often impossible to work without a respirator.

As will be seen from the analytical figures in Table 9 (p.95) the decomposition at this stage was largely confined to the sulphur compounds present in the tar,

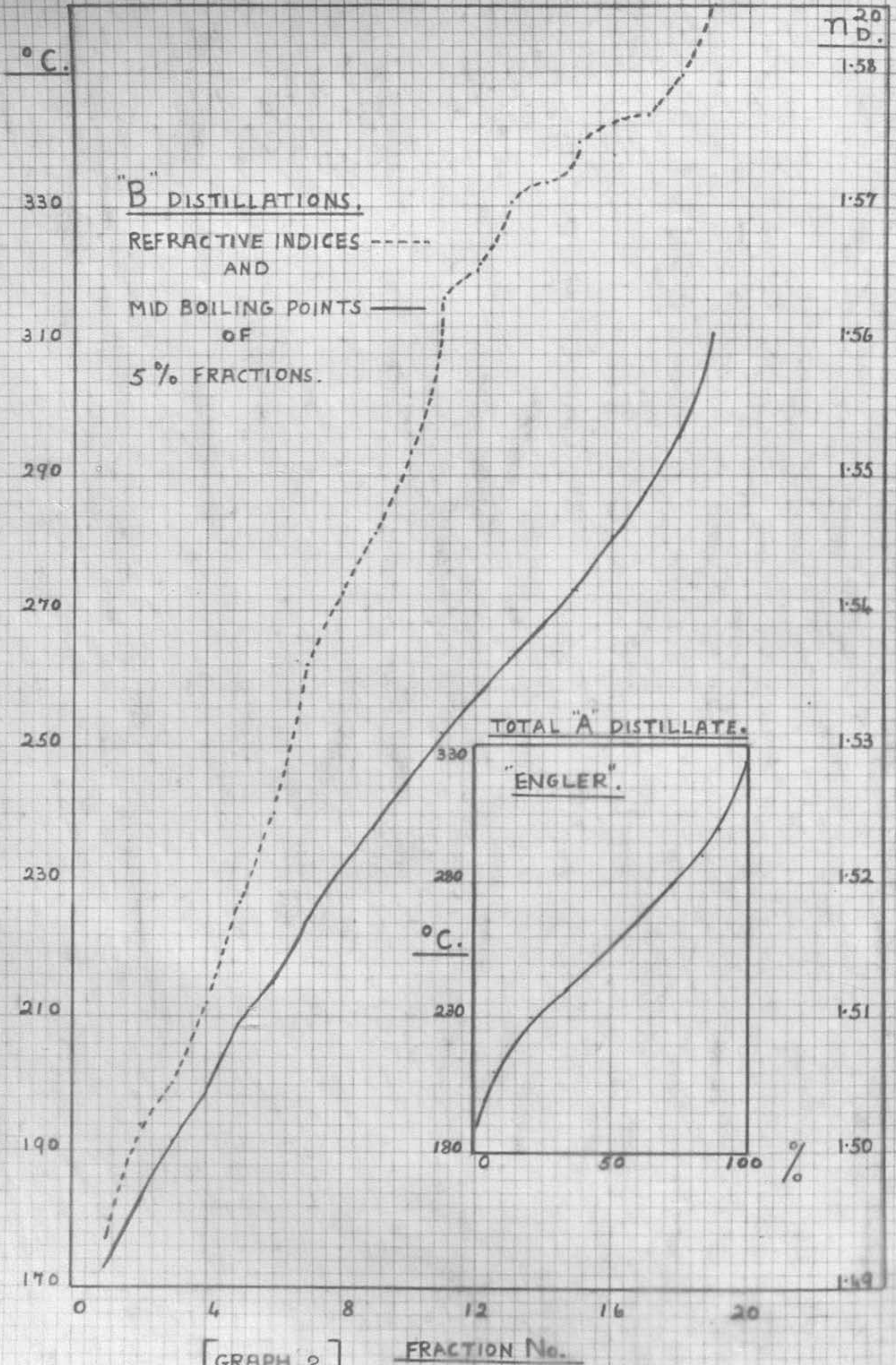
This /

This had the useful effect of eliminating much of the sulphur, while the remainder tended to accumulate in the residual pitch. This was extremely fortunate since removal of the sulphur compounds might otherwise have been rather difficult.

In all twenty-one batches were processed: Of these, the first was a total loss owing to flooding of the tar into the condensers and receiver system. Of the remainder, four were not completed owing to various mishaps, and the rest were completed with varying degrees of success. The size of the batches, at first about ten litres, was later increased to about 12.5 litres (ca. 2½ gallons). Weight balances were carried out on the first six batches, but owing to difficulties in the charging and emptying operations, it became impossible to continue this practice with any reasonable degree of accuracy and it was abandoned. An overall estimate of the tar used and the products obtained was however made. In all some 53 l. of bases were obtained from approximately 210 l. of tar (25.2% vol./vol.) or if four incomplete batches are excluded, some 49 l. of bases were obtained from approximately 167 l. of tar. (29.3% vol./vol.)

The weight balance for a typical good batch is given in Table 8.

TABLE 8. /


°C.
n_D^{20}
"B" DISTILLATIONS.
REFRACTIVE INDICES -----
AND
MID BOILING POINTS ———
OF
5% FRACTIONS.
330
310
290
270
250
230
210
190
170
1·58
1·57
1·56
1·55
1·54
1·53
1·52
1·51
1·50
1·49
0
4
8
12
16
20
FRACTION No.
TOTAL "A" DISTILLATE.
"ENGLER".
°C.
330
280
230
180
0
50
100
%

[GRAPH 2.]

TABLE 8.

Weight Balance for Typical A-Distillation

Product	Wt. %
Bases	27.6
Water	8.1
Pitch Residue	62.1
Traps	0.5
Loss	1.7
Total (tar)	100.0%

Since there was no fractionation intended during these distillations, the bases were collected as one fraction, and after settling, the water was separated and the batches bulked for charging to the B-Distillations.

Examination of Crude Bases from A-Distillations.

The crude mixture of bases from the A-Distillations was a dark, yellow brown, evil smelling, oily liquid, density 0.998 gm./ml. at 15°C. n_D^{15} 1.5480. The water content as determined in a Dean and Stark apparatus was 1.9%,but water equivalent to 2.7 per cent was recovered during the B-Distillations. The results of an Engler distillation on the dried material are given in Graph 2 (inset) which shows the high percentage of substances boiling between 210-310°C.

Sulphur and nitrogen estimations on the original /

original "Basic Tar", the total distillate from the A-Distillations, and the residual pitch showed clearly that the nitrogen compounds had been concentrated in the distillate, while the sulphur compounds escaping decomposition into gaseous products, were either non-volatile or had been polymerised during distillation and remained in the pitch.

A few simple experiments were carried out with a view to finding the percentage of non-basic material present in the distillate, and the possibility of removing this together with the remaining sulphur compounds, either by treatment with strong alkali or by solution of the bases in acid and subsequent re-precipitation with alkali.

The effect of both acid and alkali treatments on the sulphur content was disappointing, although acid treatment was the better of the two. Addition of cresylic acid during the alkali treatment made little or no difference. (Solutizer process (67)). Acid treatment was successful in removing the non-basic material, which appeared to consist largely of unsaturated hydrocarbons, but the amount of this was comparatively small (ca. 2 per cent), and its complete separation required the use of relatively large volumes of acid, followed by either solvent extraction or steam distillation. As no plant of a suitable size for treatment of the entire stock of bases /

bases was available, the experiments were discontinued and the crude bases re-distilled without any treatment.

The following Table (Table 9) shows the distribution of the nitrogen content of the original "Basic Tar" between the distillate and the residual pitch. The effect of acid and alkali treatments on the A-Distillate is also shown.

TABLE 9

Distribution of Nitrogen and Sulphur (A-Distillations)

Material	N%	S%
Basic Tar (undried 7.8% water)	4.70	3.80
Pitch residues from A-Distillations (not representative sample)	3.16	5.72
Crude bases from A-distillations (dried)	8.21	0.37
Crude bases after removal of non-basic material by acid treatment	8.43	0.24
Crude bases after treatment with alkali	8.30	0.34
Crude bases after treatment with alkali and cresylic acid	-	0.36

The nitrogen estimations were done by the micro-Dumas method, sulphur was estimated by direct oxidation to sulphate in the bomb-calorimeter.

B-Distillations.

These distillations were also carried out in the 16-litre gas-heated still. The bases, which contained some dissolved water, were fed to the still without /

without drying and a total of 52,860 ml. of crude wet bases was distilled under vacuum in four batches, each of 12.5-14 litres.

During these distillations it was again almost impossible to achieve anything in the way of true fractionation of the material. The apparatus was not provided with any means of pressure control other than a manually operated variable air-leak in the vacuum line, and being gas heated it was difficult to maintain steady operating conditions. The main objects of these distillations were (a) to divide the material roughly into five per cent fractions of narrower boiling range than the crude material, and of a size convenient for working up in the 14-plate eyelet packed vacuum column, (b) to separate as much as possible of the dissolved water present in the bases, and (c) to eliminate the small amount of entrained tar and high boiling material carried over in the previous distillations.

The distillations were carried out as rapidly as possible using a low reflux-ratio (approximately 3 to 1), and the highest possible boil-up-rate. It has been estimated that under these conditions the column would have an efficiency of only about two theoretical-plates. The crude bases were charged to the still in batches of 12.5 or 14 litres and heated gently at atmospheric pressure until the water began to distil slowly. Most of the water was then taken over at atmospheric pressure, the pressure being reduced slowly to remove the final traces. Although there was some tendency for the charge to froth, this was not a serious difficulty, as in the case of the original tar. The bases steam distilling with the water were reckoned as part of the first five per cent fraction, the size of the fractions being estimated on the volume of the charge, after making allowance for the volume of the recovered water.

When no further water appeared as a separate layer in the distillate, the pressure was reduced to 50 mm.Hg. and the bases were taken over. When 25 per cent of the charge had been distilled, the pressure was reduced to 30 mm.Hg. and at 65 per cent, the pressure was dropped to 20 mm.Hg. and thereafter reduced slowly to 10 mm.Hg.

In the case of the first two batches, only 90 per cent of the charge was distilled. In the case of batch 3 however, a 90-95 per cent fraction was collected, its volume being based on the total volume of batches 1, 2 and 3. A 90-95 per cent fraction was also taken from the fourth and final batch. Each fresh batch was charged on top of the residues remaining from the preceding batches and the residual 95-100 per cent fraction from all four batches was collected as a still-pot residue. The corresponding fractions from the four charges were combined.

The difficulty of controlling operating conditions during these distillations made it virtually impossible to maintain steady overhead temperatures, so that although regular readings were taken, the results were of little or no value. Since fractions were collected and combined by volume, this was not of great importance. The approximate range over which the 95 per cent distillate collected was from 100°C at 50 mm.Hg. to 170°C. at 10 mm.Hg. The final still pot temperature was about 240°C. but there was no evidence of any decomposition.

Weight Balance.

In all, 52,860 gm. of crude wet bases were charged to the still. From this there was recovered 1,530 gm. of water (2.7%) and of the remaining 51,330 gm. of crude bases, 48,100 gm. was recovered as 19 fractions, each of very nearly 5 per cent by volume, representing in all, a recovery of 94 per cent of the crude dry bases. The still-pot residue, which was very viscous and black, probably consisted of polymerised material, high boiling bases and traces of entrained tar. There were no appreciable losses during these distillations.

Examination of 5 per cent Fractions from B-Distillations (Fractions B1-19)

The colour of the freshly distilled fractions varied from pale yellow up to 25 per cent, to dark brown above 60 per cent. A pronounced bluish fluorescence /

fluorescence was noticeable in the range 15-35 per cent, and the colour changed from yellow to apple-green in the range 25-60 per cent. All fractions darkened rapidly on standing and ultimately all became dark brown in colour. Above 60 per cent the fractions were noticeably more viscous and oily than the lower fractions.

Engler distillations were carried out on the 19 fractions and the mid-boiling points are plotted in Graph 2. The Engler distillations showed that only a slight separation had been achieved. The boiling ranges of the fractions varied from 20°C to 30°C and there was considerably overlapping of adjacent fractions. As might be expected, fraction 1 (0-5 per cent), containing a considerable amount of steam distilled material, had a very wide distillation range.

The refractive indices of the fractions are also shown in Graph 2, showing the gradual increase of refractive index in passing from the range of pyridine derivatives (N_D^{25}1.5) into the quinoline range (N_D^{25}1.6) and suggesting the continued presence of pyridine derivatives or other substances of low refractive index even in the higher fractions.

Although the B-Distillations achieved very little in the way of separation, they did provide charges of a suitable boiling range for more careful fractionation, enabling the 14-plate eyelet packed column /

column to be used to better advantage: They also ensured that the charges for the next series of distillations (C-Distillations) followed each other in a logical order of increasing boiling point and consequently simplified the work of combining the corresponding fractions obtained from these distillations.

Cracker Exhaust Oil.

Reference has previously been made to the cracher exhaust oil, a ten gallon sample of which was collected for examination. This crude mixture of bases was rather similar in appearance to the crude bases obtained from the A-Distillations, but had a more penetrating unpleasant odour. On standing it appeared to become more viscous, and that some change had taken place is shown by the fact that, whereas with a fresh sample, some 80 per cent distilled below 150°C. at 50 mm.Hg., in the case of a sample which had been stored for five weeks, only 55-60 per cent distilled below this temperature.

In the hope that time would permit an examination of this oil, three batches of 14-litres were distilled in the 16-l. gas heated still as soon as the B-Distillations were completed.

The distillations were carried out under very much the same conditions as the B-Distillations, freshly collected material was used and an 80 per cent /

cent distillate was collected in 5 per cent fractions by volume. The earlier fractions had a strong nitrile like odour and subsequent examination has shown that they contained a high percentage of non-basic material.

Unfortunately it has not been possible to examine any of the fractions systematically, or submit them to efficient fractionation, although this work is now in hand.

C-Distillations.

The five per cent fractions from the B-Distillations were dried by standing over solid sodium hydroxide and after the preliminary examination, details of which have already been given, were charged to the 14-plate eyelet packed column and carefully fractionated under reduced pressure. The boiling ranges of these fractions being of the order of 20-30°C (Engler Distillation), they provided excellent charges for this still and being graded in order of boiling point, it was convenient to charge each batch on top of the residues from the previous batch.

Initially each 5 per cent fraction was used as a separate charge, but since the still-pot had a capacity of 5 litres and the 5 per cent fractions were only about 2500 ml. each, operations were speeded up by bulking some of the later charges.

Thus, the 19 five per cent fractions (95 per cent B-distillate) were fractionated in 14 batches.

In spite of long standing over sodium hydroxide, a small amount of water was always present at the beginning of each distillation. This invariably caused some frothing in the still head during the early stages of the distillation and until the water was removed the overhead temperatures tended to fluctuate. This difficulty was largely obviated by bleeding off the water and a small quantity of bases, during the process of running the column to equilibrium. The water and bases were then separated and the bases returned in the next batch. This water has been included in the weight balance given below and has been reckoned as part of the base fractions, the total amount being quite small. The lists of fractions given later however, includes only those dry fractions which were collected after removal of all water, when the column had been brought to equilibrium.

The distillations were carried out at a pressure of 100 mm.Hg., until the overhead temperatures reached 195°C./100 mm.Hg. At this stage, which was first reached during the distillation of the 9th of the 5 per cent fractions (e.g. 40-45 per cent of total B-distillate), the pressure was dropped to 50 mm.Hg. and when the overhead temperature reached 200°C/50 mm.Hg., which first happened in the distillation/

distillation of the 16th five per cent fraction (e.g. 75-80 per cent of total B-distillate) the pressure was dropped to 20 mm.Hg. The overall boiling range in the whole series of distillations was from 60°C/100 mm.Hg. to 192°/20 mm.Hg. Only a very small amount of the total bases (ca. 0.5 per cent) distilled below 80°C./100 mm.Hg.

The general procedure adopted during these distillations was as follows. The charges were weighed into the five litre flask, and after making up the joint between the flask and the reflux meter, using Audco grease No. 656, the receiver taps were re-greased with Apeizon grease M and the take off tap with either Apiezon M or Audco 365. The pressure was then reduced to the approximate value required and the charge refluxed for 2-3 hours to bring the column to thermal equilibrium. During the first part of this period, any water present was removed by careful operations of the take off tap; The pressure was adjusted to the exact value desired; heat input to the column was adjusted so as to give a steady temperature gradient between the still head and the still pot, and the boil-up-rate was brought to the required value, which was generally 2-3 litres per hour.

When the overhead temperature reached a steady minimum value, take off was started and the rate set so as to give a reflux ratio of at least 20 to /

to 1. Fractions were collected over five degree ranges and were combined with corresponding fractions from previous distillations at the same pressure.

After weighing the distillation residue, the next batch was charged on top of it and the process repeated until all the bases had been separated into 5°C cuts, thus providing suitable charges of narrow boiling range for further and more efficient fractionation in the 100-plate column.

Weight Balance.

Individual weight balances on the fourteen C-distillations showed that losses generally were remarkably small, and probably consisted mainly of handling losses on the many small fractions.

An overall weight balance is given below (Table 10), the difference between the total weight of bases charged (47,873 gm.) and the total weight obtained from the B-Distillations (48,100) is due almost entirely to absorption of water and bases by the sodium hydroxide over which the 5 per cent cuts were stored. The small gain in weight of the charcoal traps on the vacuum system (37 gm.) clearly shows that decomposition was negligible.

TABLE 10/

TABLE 10

Overall Weight Balance for C-Distillations.

Material	Wt. (Gm.)	Percentage
Fractions obtained	44,753	93.5
Residues	2,720	5.7
Traps	37	0.1
Loss	363	0.7
Total bases charged (B1-19)	47,873	100.0

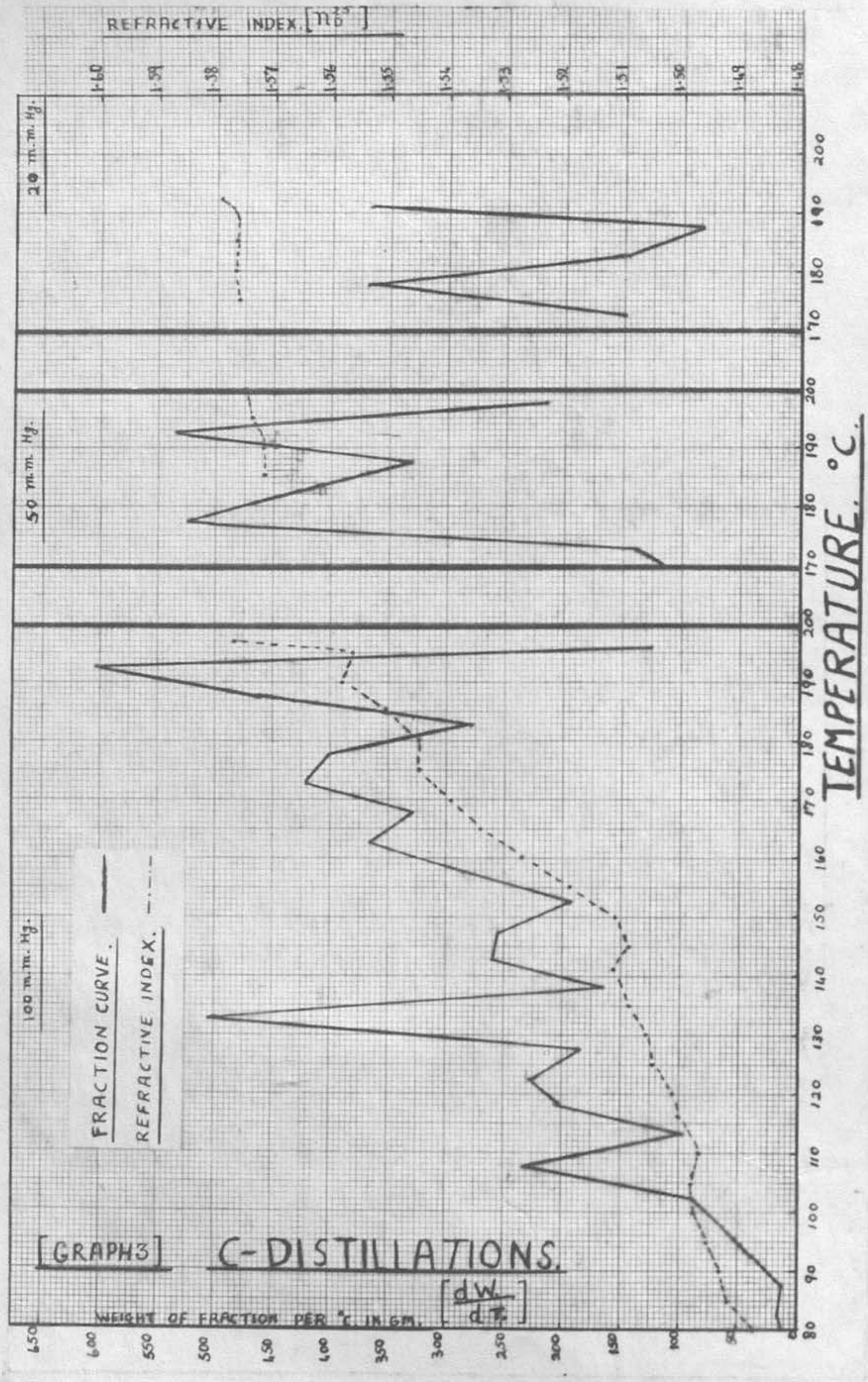
The following (Table 11) is a complete list of the bulked fractions obtained, with their weights and refractive indices (mean). The small base plus water fractions, removed at the beginning of each batch, have been omitted from this list, so that the total weight differs by 740 gm. from that given in the above table.

TABLE 11

Combined fractions from C-Distillations.

Range °C	Pressure mm. Hg.	Wt. gm.	$\frac{\Delta W}{\Delta T}$	N_D^{25} (mean)
60-80	100	98	4.9	1.4870
-85	"	82	16.4	1.4918
-90	"	68	13.6	1.4930
-95	"	195	39	1.4952
-100	"	314	62.8	1.4973
-105	"	450	90	1.4977
-110	"	1163	232.6	1.4967
-116	"	590	98.3	1.5000
-120	"	810	202.5	1.5010
-125	"	1133	226.6	1.5046
-130	"	932	186.4	1.5056
-135	"	2511	502.2	1.5086
-141	"	983	164	1.5111
-145	"	1037	259.3	1.5087
-150	"	1284	256.8	1.5110
-155	"	961	192.2	1.5186
-160	"	1431	286.2	1.5270
-165	"	1821	364.2	1.5342
-170	"	1658	331.6	1.5394
-175	"	1098	419.6	1.5443
-180	"	2005	401	1.5448
-185	"	1389	277.8	1.5502
-190	"	2302	460.4	1.5580
-195	"	3038	607.6	1.5561
-197	"	253	126.5	1.5762
166-180	50	85	-	(mixed fraction)
170-175	"	695	139	-
-180	"	2617	523.4	-
-185	"	2138	427.6	1.5715
-190	"	1653	330.6	1.5715
-195	"	2660	532	1.5736
-200	"	1075	215	1.5750
170-175	20	751	150.2	1.5760
-180	"	1842	368.4	1.5765
-185	"	731	146.2	1.5764
-190	"	428	85.6	1.5766
-192	"	732	366	1.5788

Total Bases Recovered 44,013 gm. (water free)

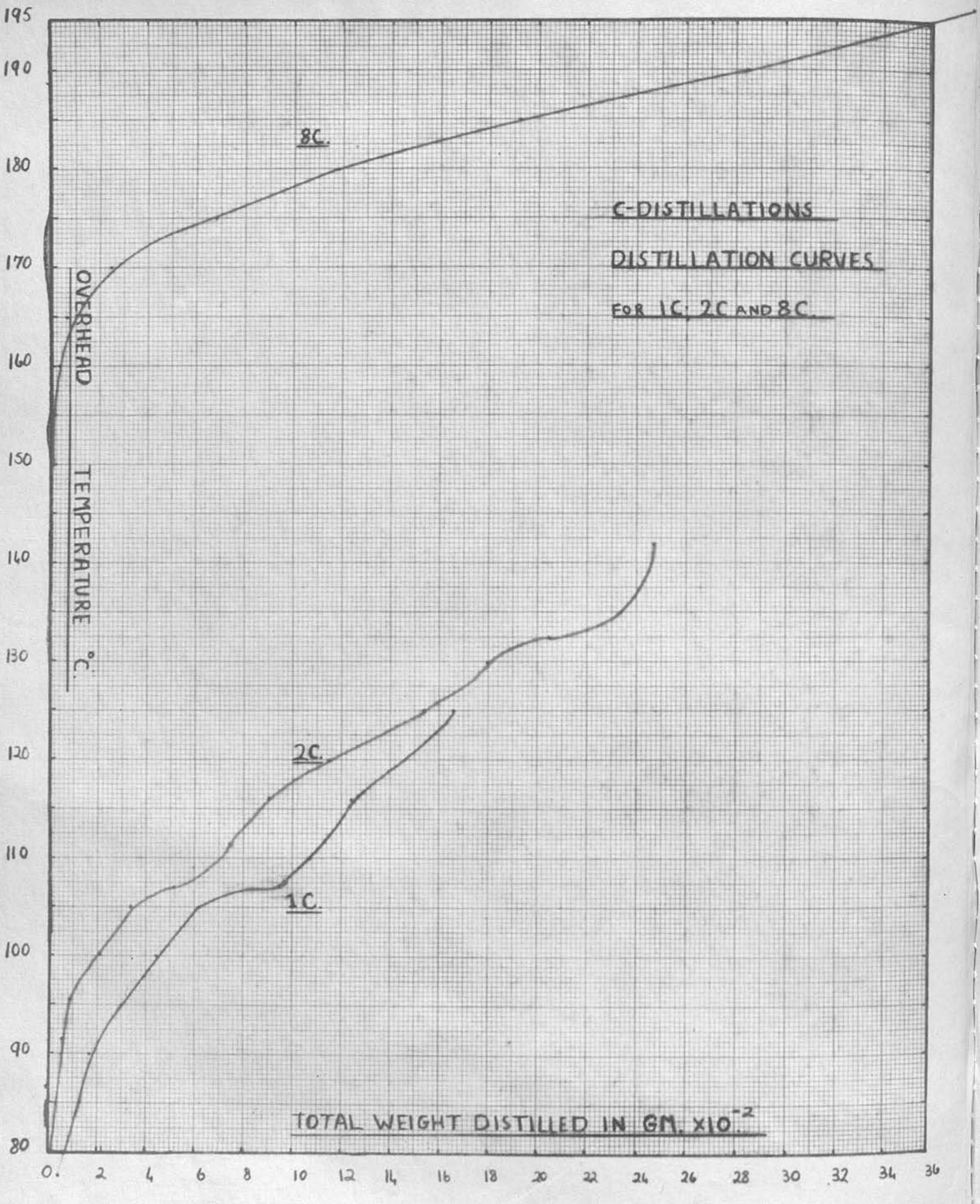

[GRAPH3]
C-DISTILLATIONS.
REFRACTIVE INDEX. [n_D^{25}]
1.60
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.49
1.48
WEIGHT OF FRACTION PER °C IN GM. [$\frac{dW}{dT}$]
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
.50
0
100 m.m. Hg.
50 m.m. Hg.
20 m.m. Hg.
FRACTION CURVE.
REFRACTIVE INDEX.
80
90
100
110
120
130
140
150
160
170
180
190
200
170
180
190
200
170
180
190
200
TEMPERATURE. °C.

GRAPH. 3.

These results are shown graphically in Graph 3, where the weight of each fraction per °C $\left(\frac{\Delta W}{\Delta T}\right)$ has been plotted against the mid-point of the range over which the fraction was collected. This corresponds to differentiating the normal type of distillation curve (temperature plotted against wt. per cent distilled), the flats being thereby translated into peaks. The graph has been divided into three sections corresponding to the 100, 50 and 20 mm. fractions and the refractive index curve is shown on the same graph.

The gradual increase in refractive index, which becomes more marked in the region of 150°/100 mm. Hg. indicates the transition from pyridine homologues (N_D^{25}1.5), to quinoline homologues (N_D^{25}1.6) in the higher ranges, although even well above the boiling point of quinoline (163°C/100 mm. Hg.) there is evidence of the continued presence of pyridine derivatives or other substances of low refractive index.

In Graph 4, normal distillation curves for the first two C-Distillations (0-5 and 5-10 per cent of B-distillate) are contrasted with the corresponding curve for a later batch (50-60 per cent of B-distillate). The slight flats evident in the distillation curves for the lower boiling point bases, are absent in the curve for the higher boiling point materials, indicating the increasing difficulty /


C-DISTILLATIONS
DISTILLATION CURVES
FOR 1C, 2C AND 8C.
8C.
2C.
1C.
OVERHEAD TEMPERATURE °C.
TOTAL WEIGHT DISTILLED IN GM. X10⁻²
195
190
180
170
160
150
140
130
120
110
100
90
80
0.
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36

GRAPH. 4.

difficulty of separation with increasing molecular weight.

Examination of Fractions.

No systematic examination of the C-fractions was carried out, other than determination of refractive index. The combined 5°C cuts were simply used as a feed stock for the 100-plate column. At a later stage in the work, it was observed that the small quantities of non-basic material present in the crude bases, had accumulated in certain of the C-fractions. It became the practice, therefore, before subjecting these bases to further fractionation, to remove these non-basic impurities by steam distillation or solvent extraction in acid solution, followed by regeneration of the dissolved bases. In the lower ranges the impurities seemed to consist mainly of sulphur compounds and highly unsaturated hydrocarbons, but phenols were isolated from some of the higher boiling bases. Further reference will be made to these impurities during the description of the D-Distillations.

The lower boiling C-fractions were colourless mobile liquids. With increasing boiling point the colour changed to pale yellow and ultimately dark brownish-yellow. The higher fractions were also more oily and viscous. A blue fluorescence was observed in the fractions boiling at about 135°C/100 mm.Hg. In the range 160-190°/100 mm.Hg. the /

the fractions were greenish in colour.

On standing all fractions tended to darken in colour, their ultimate colours varying between pale brown and almost black.

D-Distillations.

In this series of distillations the bases, now divided into 5°C temperature cuts, were subjected to their final fractionation under carefully controlled conditions and were thus further separated into narrow boiling-range fractions (usually collected over 1°C ranges) suitable for examination by chemical and other means.

As far as was possible, the charges used for these distillations were already of a fairly narrow boiling range, and ideally each of the 5°C temperature cuts should have been used for a separate D-distillation, thus allowing the final fractionation to be done under the best possible conditions. This, of course was not generally possible, since in the majority of cases it would have meant using a very small charge, and the loss of efficiency resulting from the small charge to hold up ratio would have more than outweighed the advantage gained by working with a narrow cut. In most cases it was necessary to re-combine certain of the 5°C temperature cuts in order to provide a charge of reasonable size, and give a charge to hold-up ratio of the order of 20 to 1

(about /

(about 2000 gm. being required in the case of the 100-plate column).

Initially, the D-distillations were carried out using the 100-plate I.C.I. gauze-packed column at a boil-up-rate of 900-1000 ml. per hour and a reflux ratio of at least 100 to 1. Under these conditions it may be stated with confidence that the column efficiency was of the order of 80-100 theoretical plates and possibly better. Difficulty was at first experienced in maintaining steady operating conditions, but it is not considered that this had any serious effect on the column efficiency, since with the I.C.I. gauze packing a drop in the boil-up-rate (and hence reflux ratio) is compensated within certain limits by a corresponding increase in the efficiency of the packing and vice-versa. In the later distillations, these fluctuations were almost entirely eliminated by fitting the constant voltage transformer, to which reference has already been made (page 61).

Similarly, trouble experienced in maintaining a steady take-off rate was later eliminated by the use of a tipping bucket still head.

The earlier D-distillations were carried out at atmospheric pressure and this procedure was found to be quite satisfactory until the overhead temperature reached about 185°C. At this point the overhead temperatures began to fluctuate slightly, owing to excessive /

excessive heat losses from the column head and this condition became steadily worse until, at an overhead temperature of about 195°C., conditions became so unstable that use of the 100-plate column was discontinued until it was converted to vacuum operation.

Prior to this, the 14-plate vacuum column had been re-packed with $\frac{1}{4}$" I.C.I. gauze-rings and thereby converted to a 30-plate column which was used to refractionate certain of the 5°C. temperature cuts thus providing better charges for the 100-plate column.

In the case of the 100-plate column, the usual practice was to complete a distillation in one stage by continuous night and day operation. This generally involved continuous operation for periods of a week or more. During this period, the work of the laboratory was organised on a twelve hour shift basis, or if the column had to be left unattended over-night, it was put on total reflux. Sometimes when operating on a flat part of the distillation curve, it was possible to leave the take-off running overnight. Shutting down was avoided as far as possible since this involved heavy expenditure of time in re-flooding and running to equilibrium.

With the 30-plate column the loss of time in shutting down was much less and this column was never allowed to operate over-night without attention.

The 100-plate column when converted to vacuum operation was used for fractionation of the higher boiling bases from the C-distillations, and refractionation of certain fractions prepared in the 30-plate column. Operation of the column was if anything easier under reduced pressure than at atmospheric pressure, since there were no longer any fluctuations in the overhead temperatures, either as a result of excessive heat losses or changes in pressure. The vacuum system operated for long periods with the minimum of attention, pressures were held within 0.1 - 0.2 mm. Hg. of the pre-set value and there was little trouble with leakage at the ground joints or taps.

Operation of the Columns.

100-plate.

After weighing in the charge and roughly setting the pressure, the heaters were switched on and the charge refluxed. The boil-up-rate was then set to the required value and the column flooded by closing the magnetic-valve. After slowly de-flooding, the pressure was carefully set to the required value, the boil-up-rate adjusted and the column heaters brought to the correct temperature as indicated by the zero reading of the differential thermocouple galvanometer. The column was then run to equilibrium for 10-12 hours or until the overhead temperature reached a steady minimum value, and take-off started at the correct /

correct rate to give a reflux ratio of at least 100 to 1. Fractions were collected over 1°C. ranges.

30-Plate.

Operation of this column was essentially the same as in the case of the 100-plate. Flooding was carried out by slight reduction of the pressure which was afterwards allowed to return to the desired value. Running to equilibrium required only 3-4 hours and the column was operated at a boil-up-rate of about 1500 ml. per hour, reflux ratio about 30 to 1.

Operating Pressures.

It has been suggested by R.J. Benzie (68), on the basis of data published by Coulson and Jones (69) that separation of pyridine homologues may be less effective at reduced pressures, and it is well known that owing to the higher vapour velocities fractionating columns are more readily flooded at low pressures and hence require to be run at lower boil-up-rates, although, according to Docksey and May (63), there is no serious loss of column efficiency down to about 20 mm.Hg.

It was decided that in the present work all distillations would be carried out at as high a pressure as possible, with due regard to the avoidance of decomposition and excessive heat losses. The 100-plate column was accordingly operated at 100 mm.Hg. /

100 mm.Hg. throughout the present work and bases boiling up to about 200°C. at atmospheric pressure were fractionated with ease at this pressure, the corresponding boiling point at 100 mm.Hg. being about 135°C.

Owing to lack of time, the bases boiling above 200°C. at atmospheric pressure were not fractionated in this column, but there is no doubt that it is capable of handling material of considerably higher boiling point by operation at lower pressures. The practical lower limit is probably about 20 mm.Hg. at which stage any further reduction of pressure would be outweighed by the pressure drop across the packing.

Purification of Charges for D-distillations.

In the course of examining certain of the C-fractions before carrying out the D-distillations, it was found that in some cases the bases were contaminated with small (less than 5 per cent) amounts of non-basic material. The presence of such impurities had been known previously, but prior to fractionation in the 14-plate column (C-distillations) these were so widely distributed as to make their removal impractical.

Before carrying out the D-distillations it was considered advisable to remove these impurities to avoid the possibility of unwanted azeotrope formation. Since the size of the charges was generally of the order /

order of 2.5 to 3.5 litres, this was conveniently done by dissolving the bases in an excess of hydrochloric acid, steam distilling the non-basic matter, liberating the bases with an excess of sodium hydroxide and again steam distilling. With bases boiling above 175°/100 mm., ether or petroleum extraction was substituted for steam distillation.

The nature of the non-basic matter varied with the boiling points of the bases; in the case of the lower boiling fractions it appeared to consist largely of sulphur compounds and unsaturated hydrocarbons. As the boiling point of the bases increased, the sulphur compounds gave way almost entirely to hydrocarbons, while in the higher boiling fractions, particularly those boiling above 170°/100 mm.Hg., phenols were found. In one case the phenols were worked up for subsequent examination and from 3595 gm. of bases of boiling range 165-175°/100 mm.Hg., some 90 gm. of purified mixed phenols were recovered.

Losses were sometimes fairly heavy during these purifications owing to (a) the prolonged boiling in acid solution and (b) handling losses caused by the low steam volatility and the difficulty of extracting large volumes of liquid using normal laboratory apparatus. Details of these purifications are given with the appropriate D-distillations described below.

The following is a list of the D-distillations completed /

completed and attempted, showing the origin and boiling range of each charge and the boiling range of the fractions obtained.

<u>1D</u>. In this distillation a charge of 1192 gm. consisting of the early C-fractions collected over the range 57.8-105°C/100 mm.Hg. was fractionated at atmospheric pressure using the 100-plate column. Fractions were collected over the range 126.8-172.5°C/760 mm.Hg.

<u>2D</u>. 2683 gm. (Mainly C-fractions,105-120°C/ 100 mm.Hg.) Distilled in 100-plate column at atmospheric pressure. Boiling range of fractions 154.9-186°C/760 mm.Hg.

<u>3D</u>. 2694 gm. (Mainly C-fractions 120-130°C/ 100 mm.Hg.) Distilled in 100-plate column at atmospheric pressure. Boiling range of fractions 170.6-198.6°C/760 mm.Hg.

<u>4D</u>. 3484 gm. (C-fractions, 130-141°C/100 mm.Hg.) Distilled in 30-plate column at 100 mm.Hg. Boiling range of fractions 119.5-140.3°C/100 mm.Hg.

<u>5D</u>. 1442 gm. (Fractions ex. 4D 126.8-135°C/ 100 mm.Hg.) Could not be refractionated successfully using 100-plate column at atmospheric pressure.

<u>6D</u>. /

<u>6D</u>. 4201 gm. (C-fractions. 150-165°C/ 100 mm.Hg.) Distilled in 30-plate column at 50 mm.Hg. Boiling range of fractions 119-147.9°C/ 50 mm.Hg.

<u>7D</u>. 1067 gm. (Fraction ex. 4D 135-135.9°C/ 100 mm.Hg.) Distilled in 100-plate column at 100 mm.Hg., after purification to remove traces of non-basic matter. Boiling range of fractions 131.1-136.3°C/100 mm.Hg.

<u>8D</u>. 2624 gm. (Mixed C-fractions 165-180/50 mm.Hg. and 182-197°C/100 mm.Hg.) Distilled in 30-plate column at 100 mm.Hg. after purification to remove traces of non-basic matter. Boiling range of fractions (distillation not completed).

<u>9D</u>. 2320 gm. (End fractions ex. 4D. 135.9-140.3°C/100 mm.Hg. plus residues ex. 4D. and 5D). Distilled in 100-plate column at 100 mm.Hg. after purification to remove traces of non-basic matter. Boiling range of fractions 126-133.9°C/100 mm.Hg.

The scheme followed in these distillations is shown more clearly in the Flow Sheet (Fig. 6).

Those D-distillations from which fractions were taken for detailed examination are described more fully below.

(To /

(To illustrate the separation obtainable with the 100-plate column, a distillation curve is given for distillation 1-D (Graph 5). A combined curve for distillation 1 2 and 3D is also shown (Graph 6) since this provides an interesting comparison with the work of Eguchi. (15). The results of subsequent distillations are shown simply in the form of tables).

Distillation 1-D.

In this distillation the 100-plate column was used for the first time and a rather small charge (1192 gm.) consisting of some early C-fractions was used. The column was operated at atmospheric pressure, with a simple stop-cock type of still-head (Plate 5), and since the constant voltage transformer was not fitted at this stage, conditions were rather variable. The mean boil-up-rate was about 1000 ml. per hour and the reflux ratio rarely less than 100 to 1, so that the column efficiency should have been of the order of 100-110 theoretical-plates. (Allowing for the variable conditions which persisted until the constant voltage transformer was fitted, the column efficiency during these early D-distillations was generally taken as being somewhere between 80 and 100-theoretical plates, which is probably a rather conservative estimate).

Charge: 1192 gm. early C-fractions, boiling range from 57.8 up to 105°C/100 mm. (N^{25}_{D} 1.4870-1.4977).

Fractions:/

Fractions: Total recovery 1102.5 gm. (92.5%)
Residue: 77 gm. (6.46%)
Loss: 12.5 gm. (1.04%) including static hold-up

The following is a complete list of the fractions obtained (Table 12).

TABLE 12

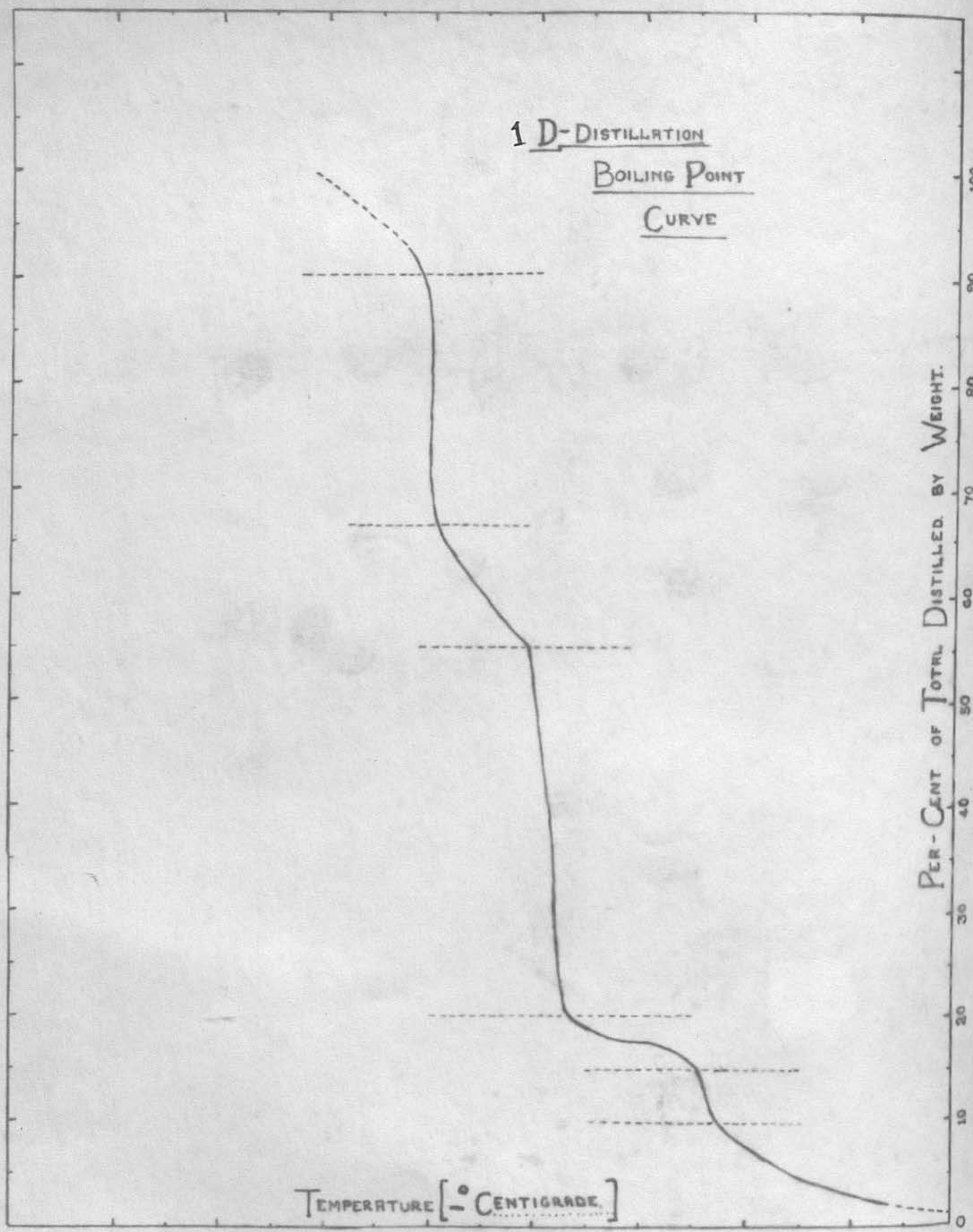
Fractions from Distillation 1-D

Fraction No.	Range (°C/760 mm.Hg.) (a)	Wt. (gm.)	N_D^{25}
W+O (b)	-	7	-
1D1	-126.8	16.5	1.4714
1D2	-135.3	32	1.4887
1D3	-140.3	35	1.4918
1D4	-141.3	9	1.4917
1D5	-142.3	9.5	1.4922
1D6	-143.3	18	1.4941
1D7	-144.3	47	1.4958
1D8	-145.3	11	1.4956
1D9	-146.3	11	1.4945
1D10	-147.3	5	1.4922
1D11	-150.3	7	1.4900
1D12	-153.3	9	1.4872
1D13	-156.3	15	1.4877
1D14	-157.3	14	1.4912
1D15	-158.3	96	1.4958
1D16	158.3	45	1.4974
1D17	-159.1	117	1.4978
1D18	-160.1	89	1.4992
1D19	-160.6	60	1.5013
1D20	-162	10	1.4989
1D21	-163	21	1.4991
1D22	-164	15	1.4984
1D23	-165	18	1.4974
1D24	-166	15	1.4974
1D25	-167	11	1.4971
1D26	-168	16.5	1.4972
1D27	-169	18	1.4972
1D28	-170	48.5	1.4970
1D29	170	12.5	1.4970
1D30	-170.1	33	1.4970
1D31	-171	183.5	1.4969
1D32	-171.2	14	1.4982
1D33	-172.5	33.5	1.4996
Total		1102.5	

(a) Temperatures corrected to 760 mm. by using the factor 2.5 mm.Hg. =t.0.1°C. at or near 760 mm.Hg.

(b) W+O signifies water plus oil fraction i.e. small quantity of water and entrained bases removed at beginning of each distillation.

The /


1 D-Distillation
Boiling Point
Curve
Per-Cent of Total Distilled by Weight.
Temperature [-° Centigrade]
0
10
20
30
40
50
60
70
80
90
100.
200
190
180
170
160
150
140
130
120

GRAPH. 5.

The results have also been shown in the form of a graph (Graph 5) in which boiling point is plotted against the weight per cent of the total charge distilled. The sharpness of separation is clearly brought out in this graph and it will be observed that there are three major flats corresponding to the fractions. 1D7; 1D15-19 and 1D28-33.

The refractive index curve has not been shown since it yields little information other than the fact that the compounds present are mainly lower pyridine homologues (N_D^{25} ca 1.5). As might be expected there is a wider spread in the refractive indices of the fractions than in those of the charge. The low refractive indices of fractions 1D1 and 1D2 possibly indicate the presence of small amounts of hydrocarbons.

Distillation 2-D.

This distillation was carried out at atmospheric pressure using the 100-plate column, the charge consisting of C-fractions boiling within the range 105-120°C/100 mm.Hg. plus the residues and end fractions from 1D. Operating conditions were substantially the same as in the case of Distillation 1-D.

Charge: 2683 gm. consisting of C fractions of boiling range 105-120°C/100 mm.(2558 gm) residues from 1D (77 gm.) and fractions 1D32 and 33 (48 gm.)

Fractions: Total recovery 2166.5 gm. (80.8%)

Residue: /

Residue: 503 gm. (18.75%)

Loss: 13.5 gm. (0.45%)

The following is a complete list of the fractions which were obtained (Table 13).

TABLE 13 /

Fractions from Distillation 2-D

Fraction No.	Range (°C/760 mm.Hg.)	Wt. (gm.)	N^{25}_{D}
W+O	-	5	-
2D1	154.9-157.4	2.5	1.4910
2D2	-161.8	8.5	1.4960
2D3	-164.9	9	1.4969
2D4	-166.5	9	1.4972
2D5	-168.4	25.5	1.4968
2D6	-169.6	20	1.4969
2D7	-170.0	41	1.4969
2D8	-170.6	178.5	1.4964
2D9	169.4-169.9 (a)	9	1.4964
2D10	-170.9	266.5	1.4968
2D11	-171.0	39	1.4976
2D12	-171.4	41.5	1.4979
2D13	-171.8	64	1.4986
2D14	-172.3	27.5	1.4995
2D15	-172.3	31	1.4995
2D16	-172.8	31	1.5000
2D17	-173.1	33.5	1.5002
2D18	-173.8	46	1.5007
2D19	-174.6	45.5	1.5002
2D20	-175.8	101	1.4998
2D21	-176.7	42	1.5004
2D22	176.7	33	1.5010
2D23	-177.3	36	1.5020
2D24	-177.8	33	1.5030
2D25	-178.3	104	1.5042
2D26	-178.8	86.5	1.5042
2D27	178.8	47	1.5050
2D28	-179.0	74.5	1.5050
2D29	-179.4	39	1.5048
2D30	-180.2	117	1.5042
2D31	-180.7	31	1.5032
2D32	178.5-179.0 (a)	13	1.5022
2D33	-181	29	-
2D34	-182.6	16.5	1.5036
2D35	-183.7	20	1.5041
2D36	-184.5	40	1.5032
2D37	-185	53	1.5015
2D38	-185.2	111.5	1.4990
2D39	-186	206	1.4979
Total		2166.5	

(a) After running overnight on total reflux.

Distillation 3-D

Distillation 3D

This distillation was again carried out at atmospheric pressure using the 100-plate column, the charge consisting mainly of C-fractions boiling within the range 120-130°C/100 mm.Hg. with the addition of residues from 2D and a fraction of boiling range 119.5 - 133.5°C/100 mm. from distillation 4D which was meanwhile being carried out in the 30-plate column. In this and subsequent D-distillations in the 100-plate column, the boil up rate was dropped to about 900 ml. per hour, the reflux ratio being maintained at 100 to 1 (or more), which probably increased the efficiency of the column slightly (see Graph 1). The constant voltage transformer was not yet fitted sothat conditions were still subject to minor fluctuations.

Charge:	2694 gm. consisting of C-fractions of boiling range 120-130°C/100 mm.Hg. (2054 gm.), residues from 2D (503 gm.) and fraction 4D1 (119.5 - 133.5/100 mm.Hg.) (137 gm.)
Fractions:	Total recovery 2133 gm. (79.2%)
Residue:	536 gm. (19.9%)
Loss:	25 gm. (0.9%)

The following is a complete list of the fractions obtained (Table 14).

TABLE 14 /

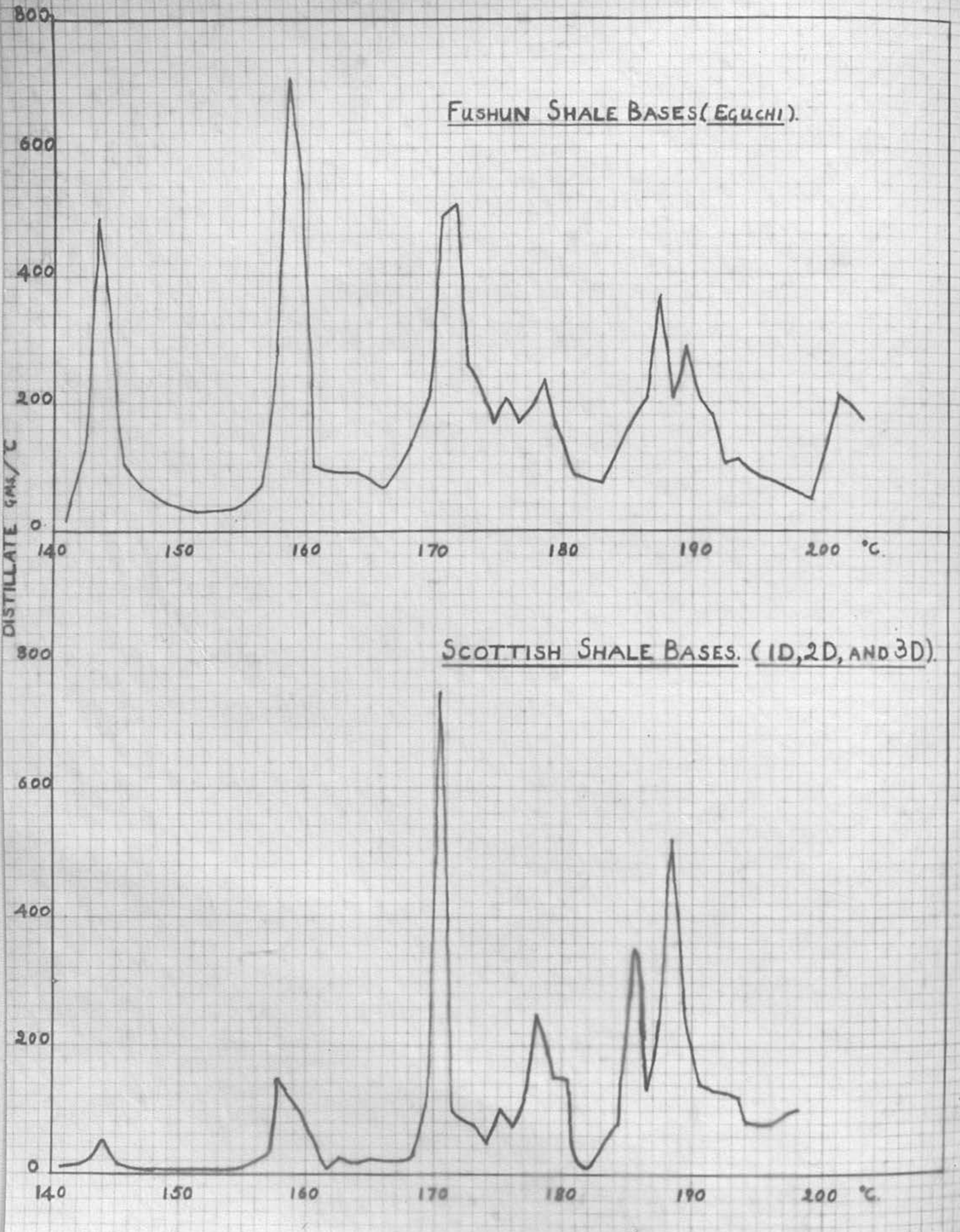
TABLE 14

FRACTIONS FROM DISTILLATION 3D

Fraction No.	Range (°C/760 mm.Hg.)	Wt. (gm.)	N_D^{25}
W + O	-	20	-
3D1	170.6 - 180.3	8.5	-
3D2	-183.4	29.5	1.5183
3D3	-185.1	22.5	1.5111
3D4	-186.1	34	1.5028
3D5	-187.0	137.5	1.5040
3D6	-188.0	233	1.5040
3D7	-188.7	248.5	1.5036
3D8	-188.9	263.5	1.5030
3D9	-190.0	265.5	1.5018
3D10	-191.6	201.5	1.5022
3D11	-193.8	259.5	1.5044
3D12	-197.2	257.5	1.5048
3D13	-198.6	152	1.5046
Total		2133	

The combined results of distillations 1, 2 and 3D have been set out in the form of a graph (Graph 6) in which the ratio of weight and temperature range $\left(\frac{\Delta W}{\Delta T}\right)$ is plotted against temperature, the heights of the peaks indicating the size of the corresponding flats on the distillation curve.

As a matter of interest, a corresponding curve for Fushun Shale bases boiling within the same temperature range is also shown in Graph 6. This latter curve was constructed from the data of Eguchi (15), the values given by this author for the ratio $\left(\frac{\Delta W}{\Delta T}\right)$ have been multiplied by a factor of 7, which /


FUSHUN SHALE BASES (EGUCHI).
SCOTTISH SHALE BASES. (1D, 2D, AND 3D).
DISTILLATE GMS./°C
800
600
400
200
0
140
150
160
170
180
190
200
°C.
800
600
400
200
0
140
150
160
170
180
190
200
°C.

GRAPH. 6.

which brings the largest peaks on the two curves to approximately the same height. Eguchi's figures refer to a total charge of 13,755 gm. of bases, while those for distillations 1, 2 and 3D combined refer to a total charge of 6569 gm.

It will be noticed that there is a remarkable coincidence of the positions of the peaks on the two curves, indicating the similarity between the Scottish and Fushun Shale bases.

Distillation 4D

This distillation was carried out in the 30-plate $\frac{1}{4}$" gauze-packed column at a pressure of 100 mm. Hg., the charge consisting of C-fractions boiling within the range 130-141°C/mm.Hg. All fractions from this distillation were re-distributed among the charges for subsequent D-distillations (3, 5, 7 and 9D).

Charge: 3484 gm. consisting of C-fractions of boiling range 130-141°C/100 mm.Hg.

Fractions: Total recovery 2918.5 gm. (83.8%)

Residue: 548 gm. (15.7%)

Loss: 18 gm. (0.5%)

The following table (Table 15) indicates the use to which the fractions were put.

TABLE 15 /

TABLE 15

FRACTIONS FROM DISTILLATION 4D

Fraction No.	Range °C (100 mm.Hg.)	Wt. (gm.)	Refractionated in -
W+0	-	45.5	
4D1	119.5-133.5	137.5	3D
4D2-4	-135	903	5D
4D5-7	-135.9	1107	7D
4D8-10	-140.3	725.5	9D
Total		2918.5	

Distillation 7D

This distillation was carried out in the 100-plate column, the charge consisting of a very narrow cut (boiling range 135-135.9°C/100 mm.Hg.) from distillation 4D, (after purification to remove non-basic material).

The 100-plate column had by this time been fitted with a constant voltage supply so that operating conditions were more stable than had been the case in earlier distillations. The column was also operated under reduced pressure for the first time and the distillation was carried out at 100- mm. Hg.

Purification of Bases.

The charge, consisting of fractions 4D, 5, 6 and 7 (1107 gm.) boiling range 135-135.9°C/100 mm.Hg. was /

was dissolved in 1000 ml. (ca. 10 mols) of concentrated hydrochloric acid, and steam distilled until no further steam volatile matter was removed. In this way about 30 ml. of a foul smelling oil, which seemed to consist largely of unsaturated hydrocarbons, was removed. The bases were regenerated by the addition of a concentrated solution of 550 gm. (ca. 13.8 mols) of sodium hydroxide, and after steam distillation were separated from the aqueous layer, dried over solid sodium hydroxide and re-distilled under reduced pressure. In this way 1067 gm. of purified bases with a faint bluish fluorescence was obtained, representing a recovery of 96.4%.

Charge: 1067 gm.

Fractions: Total recovery 976.5 gm. (91.9%)

Residue: Not weighed

The following is a complete list of the fractions obtained (Table 16).

TABLE 16 /

TABLE 16

Fractions from Distillation 7D

Fraction No.	Range (°C/100 mm.Hg.)	Wt. (gm.)	N_D^{25}
7D1(W+O)	-	7.5	-
7D2	131.5-133 (a)	8.0	1.5027
7D3	131.1-132.5	8.5	Solid at room temp.
7D4	-133.2	11	Semi-solid at room temp.
7D5	-134	38	1.5018
7D6	-134.1	57.5	1.5030
7D7	-134.4	87	1.5046
7D8	-134.5	103.5	1.5059
7D9	-134.6	217	1.5076
7D10	-135	111.5	1.5076
7D11	135	167	-
7D12	-136.3	160	-
Total		976.5	

(a) fraction removed before flooding column and stabilizing conditions.

This distillation was unique in that a solid base was obtained for the first time (Fractions 7D3-4). A further quantity of this base was obtained in distillation 9D, the charge in this case consisting of fractions 4D8-10 (boiling range 135.9-140.3) plus residues from 4 and 5D.

Unfortunately, time has not permitted a complete examination of this solid pyridine homologue but R.J. Benzie (68) has produced evidence which strongly suggests that it is 2:3:5:6-tetramethyl pyridine.

This /

This base is not listed in Beilstein and there is little reference to it in the literature. Komatsu and Mohri (70) claim to have isolated the three possible tetramethylpyridines from low-temperature coal tar, but give little evidence to substantiate this claim and no physical data of any value.

A solid base having properties very similar to those of the solid base obtained in distillations 7D and 9D is described by Oparina (71) who also suggests that the base is 2:3:5:6-tetramethylpyridine.

Further reference will be made to this compound in part d. of this section, but since most of the work on it was carried out by R.J.Benzie, distillation 9D will not be described in detail.

d. Examination of Narrow Boiling Fractions (D-Fractions)

The four series of distillations which have now been described in detail gave rise to a large number of narrow boiling fractions which could not be resolved by further distillation using the apparatus available, but which were suitable for examination by other methods.

The distillations, together with the construction and testing of the apparatus and certain necessary preliminary studies took up much of the time available and curtailed the time which could be spent /

spent on the separation and identification of pure components. For this reason only three series of fractions were examined and the boiling ranges of these, together with the compounds isolated are listed below. (Tables 17 and 18). Melting points of some of the derivatives prepared are also given.

TABLE 17

Boiling Ranges of Fractions examined.

Range	Boiling Range of Fractions	Origin of Fractions
1	169.9 - 171°C/760 mm.	1D31.2D8, 9, 10
2	186.1 - 188°C/760 mm.	3D5 - 6
3	134.5 - 134.6°C/100 mm.	7D9

TABLE 18 /

TABLE 18

Fractions Examined and Compounds Identified

Range	Compound	B.Pt. °C.	Picrate M.P. °C.	Picrolonate M.P. °C.	Methiodide M.P. °C.
1	2:4:6-Collidine	169.2 - 169.9/ 750 mm.	156.5	229 - 30	212 - 13
	3:5-Lutidine		244	-	-
2	2:3:5-Collidine	-	182.5 - 183	-	-
	2:4:5-Collidine	189/745 mm.	160.5 - 161	218	-
	Not identified	-	188 - 9	-	-
	" "	-	174.5 - 175.5	-	-
	" "	-	oil	183 - 4	225 - 226.5
3	2:3:4:6-Parvoline	202.5 - 203	122.5 - 123.5	225.5	-

In addition it has been shown that the solid base obtained in distillations 7D and 9D is probably identical with a base synthesised by Oparina (71) and is therefore in all probability 2:3:5:6-parvoline.

When possible the identity of compounds isolated has been established by preparation and analysis of one or more derivatives and comparison of the melting points of derivatives with those of reference compounds of known constitution, or with values given in the literature.

It is unfortunately the case that there are serious discrepancies in the literature regarding the physical constants of the pyridine homologues and their derivatives and this is particularly true of the collidines ($C_8H_{11}N$) and higher homologues, for many of which there is no data of any kind. The identification of such compounds therefore depends, as a rule, on oxidation in one or more stages and identification of the oxidation products. Unfortunately, such a procedure requires a reasonable quantity of the compound and if this is not available, the identity cannot be readily established. This state of affairs has arisen on more than one occasion during the present investigation and in such cases the identity of the compound isolated must remain in doubt until further quantities are obtained by the working up of neighbouring fractions.

In addition to the isolation and identification of pure compounds, the opportunity has been taken of having infra-red absorbtion spectra prepared (through the courtesy of Dr. E.A.Coulson) and of determining the dissociation constants of certain bases. Owing to the lack of time these topics could only be studied superficially and the dissociation constants could only be determined approximately. Nevertheless, the results obtained show that this field of work is one which would repay further study, and it is hoped that the work will be continued as a later part of the research programme, of which this thesis embodies the preliminaries.

Method of Examining Fractions.

The general method adopted during this part of the work was as follows.

Preliminary examination of the crude bases (A-distillate) had established the fact that primary and secondary bases were present in only insignificant quantities, (no reaction with nitrous acid) although traces of pyrroles were present (Ehrlich reaction). It would have been interesting if the pyrrole compounds could have been isolated and identified but bearing in mind the fact that the Basic Tar is obtained by treatment of the crude oil with concentrated sulphuric acid, it is fairly certain that only small quantities of pyrroles can be present and /

and the possibility of recovering them is therefore remote. The present investigation was confined to the tertiary bases.

The fractions to be examined were freed from traces of non-basic material (when necessary) by the procedure which has been described (page 114-5). The theoretical amount of picric acid was then added as a saturated solution in 95% alcohol. This process was usually carried out in three stages, the picrate being filtered off after each addition of picric acid. The total quantity of picric acid used was based on the mean molecular weight of the fraction, as determined either by titration or by assuming the type of pyridine homologues likely to be present in a fraction of the appropriate boiling point.

The picrates obtained by this method were purified by repeated crystallisation, usually from more than one solvent, and fractions of similar melting points were combined and again recrystallised. Picrates which showed no change in melting point when recrystallised repeatedly from at least two different solvents were regarded as pure and were submitted to analysis.

When a sufficient quantity of pure picrate was obtained, the base was regenerated by steam distillation from sodium hydroxide solution and the pure base isolated by the usual methods. Further derivatives /

derivatives were then made from the pure base.

In one case (Range 2), the bases were examined before and after fractional acid extraction and a comparison of the results showed beyond question the value of this method. It is interesting to note in this connection that in the examination of Range 1, a partial separation was achieved by fractional steam distillation. This method was not followed up, but may be worthy of further consideration.

Details of the examination of each of the three Ranges are given below.

Range 1

169.9 - 171°C/760 mm.Hg.

This narrow boiling range was the first to be examined and was chosen since it represents the largest 1°C fraction obtained during the early D-distillations and corresponds to the largest peak on the combined curve for distillations 1, 2 and 3D (Graph 6). It was anticipated that this fraction would contain 2:4:6-trimethylpyridine (b.p. 170.3/760 mm. (15)) and this base was, in fact, found to be the main constituent of the fraction. A small quantity of 3:5-dimethylpyridine, not previously isolated from Scottish Shale bases was also isolated, as the picrate, and it is reasonable to assume that more of this compound is present in fractions adjacent /

adjacent to the range examined. This compound was isolated from Fushun Shale Oil by Eguchi (15) who reports the boiling point as 171.6°C/760 mm. Garrett and Smythe (12) examining the Scottish Shale Bases boiling over the range 164-180°C, in the year 1903, were able to isolate only 2:4:6-trimethyl pyridine and 2:3-dimethylpyridine from this wide range and reported the boiling points of these compounds as 171°C (768 mm.) and 163-164° (768 mm.) respectively. These authors experienced difficulty in obtaining crystalline derivatives (mercurichlorides and picrates), from the mixed bases, an observation which emphasises the need for efficient fractionation in work of this nature.

The fractions initially examined were 1D31 and 2D10, the combined weight of the two being 450 gm. The characteristics of the two fractions were as follows:

<u>1D31</u> 183.5 gm. boiling range 170.1 -171/760 mm.
N_D^{25} 1.4969

<u>2D10</u> 266.5 gm. boiling range 169.9 - 170.9/760 mm.
N_D^{25} 1.4968

The combined fraction was pale yellow in colour and had a not unpleasant odour. A 10 gm. sample of the mixed bases was almost completely dissolved by the addition of 18 ml. of ca 5N HCl leaving only a few droplets of undissolved oil. The acid solution had an unpleasant hydrocarbon odour. The quantity of acid required to effect complete solution was /

was in fair agreement with the calculated volume (17 ml.) assuming the fraction to consist mainly of trimethylpyridines. ($C_8H_{11}N = 121$).

To remove traces of hydrocarbons, the bases (Ca.400 gm) were dissolved in a mixture of 400 ml. concentrated hydrochloric acid and 1800 ml. water and steam distilled until nothing further could be removed. In this way a few gm. of an evil smelling mixture of unsaturated hydrocarbons was recovered, while a small amount of tarry matter separated in the distillation flask.

The bases were liberated in stages by the addition of sodium hydroxide solution as follows. A solution of sodium hydroxide (ca. 5N) was prepared containing slightly more than the requisite amount of sodium hydroxide to neutralise the acid used. Samples of the acid solution of bases and the sodium hydroxide were then diluted 100 times and the acid solution of bases titrated with the alkali using a magic-eye conductometric titration apparatus. The alkali was added in stages and the conductivity of the solution plotted against ml. of alkali added after each addition. The resulting curve showed clearly, the neutralisation of the free excess acid, the buffering effect of the base hydrochlorides and the final end point, indicating complete decomposition of the hydrochlorides. In addition there /

there were several small inflections in the curve which may have been due to instability in the instrument, but which at the time were thought to indicate the successive liberation of bases of increasing strengths. The positions of these inflections on the curve corresponded to approximately 41, 67, 77 and 92 per cent neutralisation of the base hydrochlorides.

The 5N sodium hydroxide solution was therefore added to the solution of base hydrochlorides in stages corresponding to these figures and the liberated bases steam distilled out after each addition of sodium hydroxide, a slight excess of alkali being added during the final stage of neutralisation.

The steam distilled bases were separated from the aqueous layer which was then extracted with ether, the ether extract being added to the bases. After drying the ether solutions over sodium hydroxide followed by magnesium sulphate, the solvent was removed and the bases distilled at atmospheric pressure.

The following table (Table 19) summarizes the results of this operation.

TABLE 19 /

TABLE 19

Fractional Steam Distillation of Bases (Range 1)

Fraction	%Neutralisation of Hydrochlorides	Wt. of Fraction (gm.)	% of Total Bases Recovered	N_D^{25}
X1	41	70.5	22.0	1.4977
X2	67	119.5	59.3	1.4973
X3	77	40.0	71.8	1.4971
X4	92	68.0	93.0	1.4966
X5	100	22.5	100	1.4962

The total recovery of purified bases was 320.5 gm. representing an overall recovery of 80 per cent.

It was obvious from the steady fall in refractive index that some slight separation had been achieved by this operation, and the fractions were accordingly worked up separately. The results of picration, however, showed that the separation achieved had been unsufficient to be of any material benefit.

The distribution of refractive indices indicated that the stronger bases (fraction X5) probably consisted of substantially pure 2:4:6-trimethylpyridine (N_D^{25} 1.4959 (15)), while the weaker base fractions contained increasing amounts of a compound, or compounds, of higher refractive index. It was ultimately established that this base was 3:5-dimethylpyridine (N_D^{25} 1.5032 (15)), which is in agreement with the general observation that dimethylpyridines are weaker bases than trimethylpyridines (See Section F.)

A sample of each of the fractions X1 to X5 was treated with picric acid in three stages as follows. Half the requisite amount of picric acid was added as a saturated solution in alcohol, the precipitated picrate was dissolved by heating to the boiling point and the mixture cooled rapidly to ensure the /

the formation of small crystals which were filtered off and washed with alcohol.

The remainder of the picric acid was added to the mother liquor in two equal portions, the total amount used being approximately one molecular equivalent, based on the assumption that the bases present had a molecular weight of approximately 121 (trimethylpyridines).

The results in each case were very similar and the following types of picrate were separated, a total of 148 gm. of bases being used in all.

Type 1. 273 gm. of fine needles which appeared to homogeneous under the microscope and melted sharply within the range 153-157°C.

Type 2. 48 gm. of fine needles contaminated with small amounts of a powdery picrate. The melting points were more diffuse than those of type 1 but fell within the range 126-140°C.

Type 3. 40 gm. similar in appearance to type 2 but melting indefinitely within the range 90-110°C. and presumably contaminated with excess picric acid.

2:4:6-Trimethylpyridine.

Part of the picrate of type 1 which melted within the range 155-157°C (193.5 gm.) was recrystallised from 95 per cent alcohol which raised the m.p. to 156.5-157°C. A second recrystallisation from /

from the same solvent caused no change in the m.p. and a sample recrystallised from acetone melted at the same temperature. The pure picrate was deposited from alcohol as fine hair-like yellow needles. The yield was 123.5 gm.

The remaining 79.5 gm. of the type 1 picrates (m.p. 153-156°C) was recrystallised from the mother liquors of the first part and by removing part of the solvent a further 121.5 gm. of pure picrate was obtained. m.p. 155.5-156.5°C. The identity of the two batches of picrate was checked by a mixed melting point determination.

The combined pure picrates (245 gm.) suspended in 2 l. of water were treated with a 25 per cent excess of 10N sodium hydroxide and the base separated in the usual manner. 66 gm. of a colourless liquid with a not unpleasant odour was obtained. The pure base remained colourless for several months when stored in the dark and only darkened slightly on exposure to light for a period of several weeks.

The picrate, picrolonate and methiodide were prepared from the pure base by the usual methods.

Physical Constants.

B.P.	169.2-169.9/750 mm.	Lit.	171-172/760 mm. (49) 170.3/760 mm. (15)
N_D^{25}	1.4958	Lit.	1.4959 (15)

Equivalent Weight /

Equivalent Weight.

As found by electrometric titration with $\frac{N}{20}$ hydrochloric acid 123.1

$C_8H_{11}N$ requires 121

The high value found was probably due to absorption of water in weighing as the free bases are rather hygroscopic.

Picrate.

M.P. 156-157°C Lit. 156°C (49)
157°C (15)

Found. N, 15.72

$C_8H_{11}N.C_6H_3O_7N_3$ requires N, 16.00

A sample of picrate made from synthetic 2:4:6-collidine which was prepared by Hantzsch's synthesis had m.p. 156.5°C and gave no depression in a mixed melting point determination.

Picrolonate.

Straw coloured needles from acetone.

M.P. 229-230°C. (decompn.) Lit. 230°C (49)

Found N,18.50

$C_8H_{11}N.C_{10}H_8N_4O_5$ requires N, 18.18

Methiodide

Colourless needles from alcohol. M.P. 212-213°C. A sample prepared from synthetic 2:4:6-collidine had m.p. 213.5°C and gave no depression in a mixed melting point determination.

Found /

Found C, 40.8; H, 5.35; $C_8H_{11}N{\cdot}CH_3{\cdot}I$ requires

N, 5.42 C,41.08; H,5.36;N,5.32

Identification

The compound was considered to be 2:4:6-collidine onthe basis of the observed physical data and the melting points mixed melting points and analyses of the derivatives prepared.

Confirmatory evidence was provided by the infra-red absorption spectrum which was identical with that of 2:4:6-collidine (See section G)

3:5-Lutidine.

It was apparent that the 2:4:6-trimethylpyridine fraction was contaminated with small amounts of at least one other base and it was considered that the most likely impurity was 3:5-lutidine, the boiling point of which (171.6°C/760 mm.) differs by little more than 1°C from that of 2:4:6-trimethyl pyridine.

The amount present being very small there was little possibility of effecting a satisfactory separation by fractional crystallisation of the picrates. Use was therefore made of the fact that methyl groups substituted in the 2- and 4- positions in the pyridine nucleus are sufficiently reactive to form styryl compounds with aldehydes while those in the 3- and 5- positions are not.

Normally /

Normally the styryl compounds are prepared by heating the alkyl pyridine and the aldehyde in a sealed tube at a temperature of about 220°C in the presence of a dehydrating agent such as zinc chloride. Symmetrical collidine, however, having three reactive methyl groups reacts readily at lower temperatures to give a mixture of products depending on the conditions used. It was found by a trial experiment that when a mixture of 2:4:6-collidine and a slight excess of benzaldehyde was heated under reflux for about 8 hours in the presence of zinc chloride by means of an oil bath maintained at 180-200°C, very little of the free base could be recovered from the reaction mixture by steam distillation in the presence of excess alkali. This method was therefore used to enrich a fraction of bases in the hope of being able to separate 3:5-lutidine from the unreacted bases.

Unfortunately the fractions boiling within the range 171-172°C (2D13-2D16) had been used for another purpose, the bases used were therefore fractions 2D8 and 9 (B.p. 170.6-170.9°C/760 mm. N_D^{25} 1.4964).

60 gms. of the combined bases (ca. 0.5 mols) which had not been treated to remove the small amount of non-basic material present, was mixed with 185 gm. (1.75 mols) of benzaldehyde and 70 gm. (0.5 mols.) of powdered anhydrous zinc chloride in a flask with a long /

reflux air condenser. The mixture was heated in an oil bath at 160° when a vigorous reaction soon set in. Heating was stopped until the reaction had subsided and the mixture was then heated for 12 hours, the temperature of the oil bath being gradually increased to 200°C. The reaction mixture became dark red and ultimately black and very viscous.

The viscous product was poured into water, 50 ml. of concentrated hydrochloric acid added and the excess benzaldehyde steam distilled out. A solution of 40 gm. of sodium hydroxide was then added to the residue and the unreacted bases separated by steam distillation. Extraction of the steam distillate with petroleum ether followed by removal of the solvent yielded 2 gm. of bases having an odour resembling that of 2:4:6-collidine. Addition of picric acid yielded a powdery mixture of picrates from which a small quantity of a picrate melting diffusely between 223-235°C was isolated by fractional crystallisation; the amount, however, was too small for convenient working up. 3:5-lutidine picrate has m.p. 244° (15).

It was clear from this experiment that the amount of 3:5-lutidine present was too small to permit a satisfactory separation of this compound directly from the mixture of bases. Attention was therefore directed to the low melting picrates remaining from the 2:4:6-collidine separation, which were presumably richer /

richer in 3:5-lutidine. Two fractions of mixed picrates were available:-

Type 2 48 gm. m.p. 126-140°C.
Type 3 40 gm. m.p. 90-110°C.

These were worked up separately as follows.

The mixed picrates were treated with an excess of 4N sodium hydroxide solution and heated almost to boiling point. The sodium picrate which separated on cooling, was filtered off and washed with petroleum ether. The filtrate was also extracted with petroleum ether and the combined petroleum ether extracts dried over solid sodium hydroxide. Removal of the solvent followed by distillation of the residual bases gave from

Fraction 2, 6.5 gm. of bases N_D^{25} 1.5020
and from Fraction 3, 2.5 gm. of bases N_D^{25} 1.5010

This showed that the two batches of picrate were substantially identical, the lower melting batch being contaminated with a large excess of picric acid.

The refractive indices also indicated a considerable enrichment of the 3:5-lutidine content.

2:4:6- collidine has N_D^{25} 1.4959 (15)
3:5- lutidine has N_D^{25} 1.5032 (15)
Mean 1.4995

The combined bases 8.5 gm. (ca. 0.07 mols). benzaldehyde 15 gm. (0.14 mols) and zinc chloride 9.5 gm. /

9.5 gm. (0.07 mols) were heated under reflux for 10 hours at 160-180° and then for 2 hours at 180°. The product worked up in the same way as previously yielded 1 gm. of bases. This was treated with 2 gm. of picric acid and by recrystallisation from acetone-alcohol there was finally separated a small amount of picrate which had a m.p. of 244°C. The amount of this (less than 1 gm.) was too small to justify reconversion to the base.

Picrate M.P. 244°C. Lit. 244-5 (15, 49)

Found N 16.66% $C_7H_9N.C_6H_3O_7N_3$ requires N. 16.86.

Identification.

Unfortunately, no pure specimen of 3:5-lutidine picrate was available for mixed melting point determination, however, the analysis of the picrate and the characteristic high melting point exclude the possibility of any other compound likely to be present in a fraction of this boiling range.

Range 2.

186.1-188°C/760 mm.Hg.

This fraction was of a more complex nature than the one previously examined. It appeared to consist of a mixture of collidines, of which the 2:3:5- and 2:4:5-isomers were identified, the former as the picrate and the latter as the free base and small amounts of several other compounds, two of which were isolated as crystalline picrates. The identities /

identities of these have not yet been established.

At least one compound was present from which no crystalline picrate could be obtained, although a crystalline methiodide and picrolonate were isolated from the mixture of bases regenerated from the non-crystalline picrate.

Analysis of the unidentified compounds obtained did not help to clarify the situation, as the analytical results in each case agreed fairly closely with those which would be expected from the corresponding derivatives of monomethylpyridines. The melting points of the compounds however, excluded this possibility.

The results of an infra-red absorption analysis of the base regenerated from the non-crystalline picrate were similarly inconclusive.

The bases used in the examination of this range were made up of fractions 3D5 and 6 combined (370.5 gm.) The fractions had the following characteristics.

3D5 b.r. 186.1-187/760 mm.Hg. N_D^{25} 1.5040 137.5 gm.

3D6 b.r. 187-188/760 mm. Hg. N_D^{25} 1.5040 233.0 gm.

The mixed fraction was first of all examined by direct picration, this, however, yielded a complex mixture from which only a small quantity of 2:3:5-collidine picrate was isolated. The /

The bases were therefore submitted to fractional acid extraction using the procedure of Jantzen (51). This provided a series of fractions of gradually increasing basic strength, of which the first and last (i.e. the weakest and strongest bases respectively) were examined. From the weakest bases several compounds were isolated, none of which were identified, while the strongest bases were found to consist mainly of 2:4:5-collidine. The 2:3:5-collidine was presumably concentrated in one of the intermediate fractions which were not examined.

Examination of Bases before Fractional Extraction.

12 gm. (ca. 0.1 mols.) of fraction 3D5 was dissolved in a mixture of 20 ml. of concentrated hydrochloric acid and 80 ml. of water. The solution was extracted with petroleum ether to remove traces of non-basic material and added to a hot solution of 81 gm. (0.3mols.) of mercuric chloride in 1500 ml. of water. White crystals of the mercurichloride were deposited on cooling. m.p. 156-162°C.

On attempting to purify the compound by recrystallisation from dilute hydrochloric acid, the melting point was reduced and ultimately a mixture of crystalline and oily mercurichlorides was obtained from which no pure compound could be isolated. Attention was therefore directed to the picrates.

2:3:5-collidine./

2:3:5-Collidine.

A mixture of 30 gm. of each of fractions 3D5 and 6 (ca. 0.5 mols.), which had not been treated to remove traces of non-basic material, was added to a solution of 114 gm. (0.5 mols.) of picric acid in 1425 ml. of alcohol. After standing for a few minutes a brownish-yellow mixture of picrates separated. The picrate was re-dissolved by boiling and allowed to crystallise slowly. The crude yellow picrate so obtained had a melting point of 133-137°C (Picrate A). On washing with warm ether, a substantial part was dissolved while the colour was reduced to a muddy yellow. The undissolved picrate was recrystallised from acetone which raised the m.p. to 162-168°C. and changed the colour to pale yellow. A further recrystallisation from alcohol gave a small crop of pale yellow microcrystals which melted sharply at 182-182.5°C. A final recrystallisation from acetone gave pale greenish yellow felted needles melting sharply at 182.5-183°C. The yield of pure picrate was approximately 3.5 gm.

Identification.

Owing to lack of time and the small amount of material available the free base was not regenerated. Nitrogen analysis of the picrate, however, indicated that it was probably that of a trimethylpyridine or a methyl ethyl pyridine.

Found. N, 16.38

$C_8H_{11}N.C_6H_3O_7N_3$ requires N, 16.00

The possibility of the picrate being that of a dimethyl or ethyl pyridine ($C_7H_9N.C_6H_3O_7N_3$ requires N, 16.66) is rendered unlikely by the fact that the highest boiling of the lutidines (3:4-dimethyl pyridine) has a boiling point of only 178.9°C/760 mm. Hg. (15), while the fractions used for the examination had a boiling range of 186-188°/760 mm Hg.

It therefore seems probable that the picrate obtained was that of 2:3:5-collidine, the melting point of which is 183-184°C (15, 72).

Unfortunately, no sample of the pure base was available for a mixed melting point examination.

2:3:5-collidine was previously isolated from Fushun Shale Oil by Eguchi (15).

Further Picrates obtained.

The mother liquors from the original picration and recrystallisations of Picrate A were concentrated in stages and the small amounts of picrates so obtained systematically recrystallised. A number of low melting point mixtures of picrates were separated, but it was found impossible to separate any pure compounds.

Complete removal of the solvent left the major /

major fraction of the picrate in the form of a viscous dark reddish brown oil which crystallised only partially after standing for several months and from which no pure compound could be isolated.

Fractional Acid Extraction.

It was obvious from the results of this picration, that the fraction consisted of a complex mixture and contained at least one component which either did not react normally with picric acid, or did so to form a picrate which did not crystallise readily. An attempt was therefore made to simplify the fraction by fractional acid extraction as follows.

The remainder of fractions 3D5 and 6 were combined (294 gm.), taken up in 300 ml. of concentrated hydrochloric acid and steam distilled to remove traces of hydrocarbons. The bases were liberated in the usual way by addition of sodium hydroxide solution and steam distilled over. This operation was carried out in two stages and it was observed that the last fraction of bases to be liberated (i.e. the stronger bases) had an unusually penetrating and unpleasant odour. Since, however, it was expected that fractional acid extraction would achieve better separation than fractional steam distillation, the two fractions were combined.

The recovered bases amounted to 264 gm. (89.8 per cent recovery) and had a slight carbylamine odour, /

odour, presumably due to the action of minute traces of primary amines on the chloroform used for extraction of the bases from the steam distillate.

The recovered bases were dissolved in an exactly equivalent amount of ca. 2.5N hydrochloric acid, the amount of acid required being determined by titration. A solution of sodium hydroxide (ca. 10N) was then added in ten equal portions and the liberated bases extracted after each addition of alkali with 150 ml. of benzene, the total amount of alkali used being exactly equivalent to the acid used to dissolve the bases. In this way, ten benzene fractions were obtained (S_1- S_{10}) containing bases of increasing strength, the strength increasing in the direction $S_1 \longrightarrow S_{10}$.

S_1 was shaken with an exact equivalent of ca. 1.5N hydrochloric acid (i.e. 1/10th of the amount of acid originally used), the acid extract was then separated and shaken with S_2, S_3, S_4.....S_{10}, in turn so that an interchange of bases between the acid layer and the solvent layer took place at each stage, the stronger bases tending to accumulate in the acid layer.

Meanwhile, S_1 (stripped solvent) was shaken with a second portion of acid to remove final traces of bases and the whole process was repeated. A third portion of acid was then added to S_2 and the process repeated /

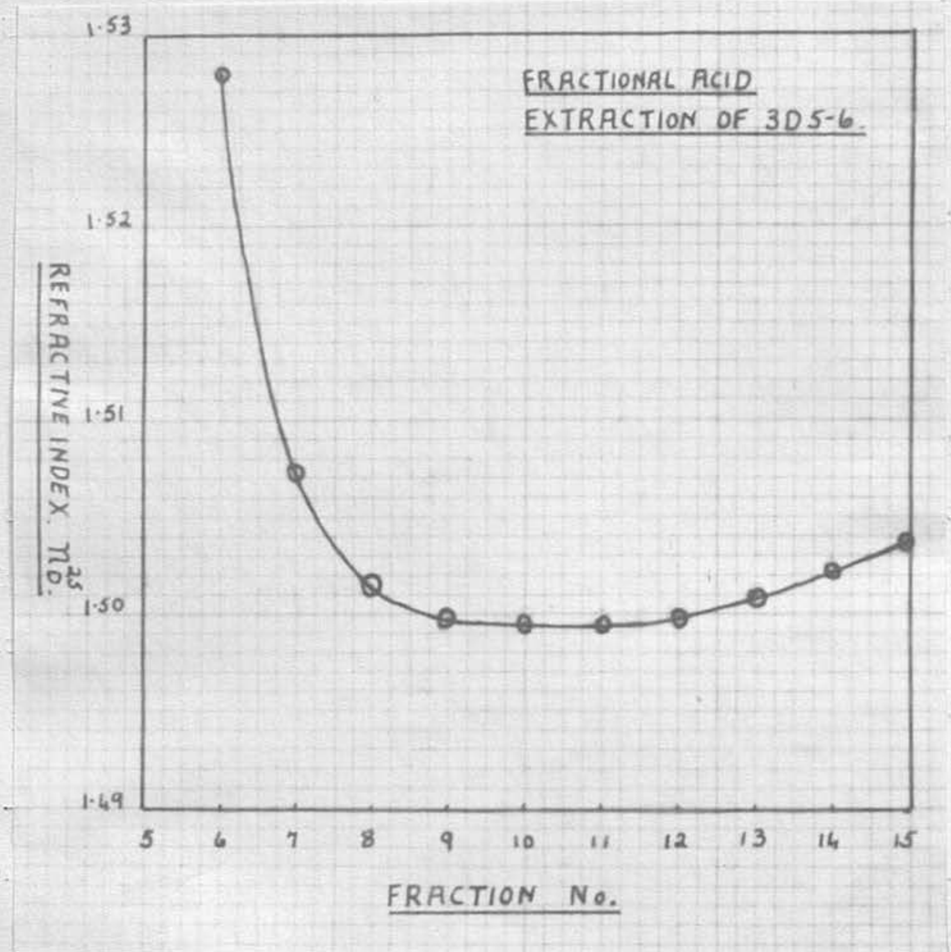
repeated again and so on until five portions of acid had been added.

By this time, the first acid extract had been shaken with all the fractions $S_1 - S_{10}$, and was neutralised by adding an exact equivalent of ca. 10N sodium hydroxide, the liberated bases being taken up in fresh solvent and carried through the remaining stages of the extraction. The complete scheme, which is described more fully in the literature appendix, is that of Jantzen (51).

Ultimately, ten fractions of solvent ($S_6 - S_{15}$) were obtained, containing bases of strength increasing in the direction $S_6 - S_{15}$. The bases were recovered from each fraction in the usual manner by removal of the solvent and distillation of the residue at atmospheric pressure.

The results of the fractional acid extraction are shown in Table 20, in which the weights and refractive indices of the fractions are given and in Graph 7, in which the refractive index curve is shown.

TABLE 20 /


FRACTIONAL ACID
EXTRACTION OF 3D5-6.
REFRACTIVE INDEX. n_D^{25}
1·53
1·52
1·51
1·50
1·49
5
6
7
8
9
10
11
12
13
14
15
FRACTION No.

GRAPH 7

TABLE 20

Refractive Indices of Bases after Fractional Distallation

Fraction	Weight gms.	N^{25}_D
6	15.5	1.5279
7	26.0	1.5073
8	24.0	1.5015
9	24.5	1.4998
10	23.5	1.4996
11	24.0	1.4996
12	23.5	1.4999
13	25.5	1.5008
14	24.5	1.5022
15	24.5	1.5036
Total	235.5	-

The total weight of the fractions recovered was 235.5 gm. representing a recovery of 89.2 per cent of the bases used. The low yield of fraction 6 was probably due to the cumulative effects of solubility and slight discrepancies in the volumes of acid and alkali.

The high refractive index of this fraction, which is outside the range of the simpler pyridine homologues (N^{25}_D ca 1.50) suggests the presence of compounds such as pyrindane (N^{25}_D 1.541) isolated by Eguchi (15) from Fushun Shale Oil. The boiling point of pyrindane, however, is given by Eguchi as 199.8/760 mm.Hg. while that of the fraction used for the extraction was 186.1-188/760 mm.Hg.

Several compounds of unknown composition were in fact isolated from this fraction and a non-crystalline /

crystalline picrate was obtained, the bases regenerated from which had N_D^{25} 1.5123 and boiled over a wide range.

Time permitted the examination of only two of the fractions from the fractional acid extraction; these were the two end fractions, numbers 15 and 6, containing the strongest and weakest bases respectively.

Fraction 15.

The fraction (24.5 gm.) was treated with picric acid in three stages as follows.

A saturated alcoholic solution of 16 gm. of picric acid was added which caused an immediate precipitation of picrate. After standing overnight this was filtered off and washed with alcohol.

The mother liquors were treated with a further 16 gm. of picric acid, which again caused an immediate precipitation of picrate. This was filtered off after standing for several hours and washed with alcohol.

The mother liquors were then treated with 8 gm. of picric acid and yielded a further small crop of picrate.

The three crops of picrate obtained had the following characteristics:

P_1 Yellow micro-prisms m.p. 148-150°C. Sample recrystallised from acetone had m.p. 161°C. preceded by sintering.

P_2 Yellow micro-prisms m.p. 146-147 preceded by sintering.

P_3 Pale greenish-yellow, not homogeneous, m.p. 135°C preceded by sintering.

P_1 Recrystallised from acetone gave lemon yellow micro-prisms. m.p. 161°preceded by sintering.

P_2 recrystallised from the acetone mother liquors from P_1 gave lemon yellow micro-prisms m.p. 159-160°C preceded by sintering.

P_3 was not examined further as the amount was very small.

The recrystallised picrates P_1 and P_2 were combined and recrystallised from alcohol to give short needles m.p. 160°C. preceded by sintering. Under the microscope the crystals were seen to be contaminated with traces of a fine powdery picrate.

A final recrystallisation from acetone gave small square prisms sintering at 159-160°C. m.p.160.5-161°C which appeared to be homogeneous under the microscope. The yield of pure picrate was ca. 20 gm.

2:4:5-collidine.

The picrate (20 gm.) was treated with an excess of ca. 10N sodium hydroxide, steam distilled and the base recovered in the usual manner. Redistillation of the pure base gave 6.5 gm. (94 per cent recovery) /

recovery) of a colourless liquid with a not unpleasant odour reminiscent of that of 2:4:6-collidine. The picrolonate was prepared from the pure base in the usual manner.

Physical Characteristics.

B.P. 189°C/745 mm.Hg. Lit. 189.8/760 mm.Hg.(15)

N_D^{25} 1.5057 Lit. 1.5054 (15)

Picrate.

Short needles from alcohol

M.P. 160.5 - 161°C. Lit. 161°C (15)

Found N, 16.22

$C_8H_{11}N.C_6H_3O_7N_3$ requires N, 16.00

Picrolonate.

Fine needles from acetone.

M.P. 218°C.

Found N, 18.33

$C_8H_{11}N.C_{10}H_8O_5N_4$ requires N. 18.18.

Identification.

The compound was considered to be 2:4:5-trimethylpyridine on the basis of the close agreement between the physical properties of the base and melting point of the picrate and the values given in the literature. Analysis of the picrate and picrolonate supported this view, but unfortunately reference compounds were not available for direct comparison. Further confirmation was provided by the infra red absorption spectrum, although no reference spectrum was available for direct comparison. (Section G.)

Fraction 6.

The fraction (15 gm.) was treated with picric acid (saturated alcoholic solution) in three stages.

A solution of 8 gm. of picric acid was added to the bases, the solution became orange in colour and on standing a small crop of the picrate separated, m.p. 172-3°C. A sample recrystallised from acetone had m.p. 179-180°C (Picrate 1). **NOTE**. This m.p. was not obtained when the remainder was recrystallised (see p.161).

The mother liquors from the above were treated with 8 gm. of picric acid, but as very little picrate separated on standing in the ice chest, a further 8 gm. of picric acid was added. After 24 hours in the ice chest a small crop of crystals was obtained. These had m.p. 183-4°C. Recrystallisation from alcohol raised the m.p. to 187-188°C. (Picrate 2) The mother liquors from this operation were used to recrystallise picrate 1.

The original solution of bases plus picric acid was concentrated to about 100 ml. and after standing several days in the ice chest a fraction of a gm. of granular orange picrate was obtained, m.p. 147-150°C. (Picrate 3).

Further concentration of the original solution gave no solid picrate and complete removal of the solvent left a viscous orange coloured oil, which became pasty on stirring with petroleum ether. The petroleum /

Petroleum ether washings left no residue on evaporation, indicating the absence of free bases.

The oily picrate was taken up in acetone and the solvent allowed to evaporate slowly. In this way a semi-solid mixture of solid and oily picrates was obtained and by dilution with a few mls. of methanol it was possible to filter off much of the solid (Picrate 4).

Removal of the solvent from the filtrate yielded about 30 gm. of a dark red viscous oil which constituted the major part of the total picrate (Picrate 5). The oil resisted all attempts to induce crystallisation.

The picrates were examined separately as follows.

Picrate 1 (m.p. 172-3°C).

Recrystallised from alcohol mother liquors from recrystallisation of picrate 2. M.P. substantially unchanged (173-174°C). Recrystallisation from methanol and acetone caused little change in the m.p. (174.5-175.5°C). The picrate was therefore taken as pure. The yield was less than 1 gm. and the base was not regenerated.

Analysis of the picrate was inconclusive and suggested a monomethylpyridine or a partially reduced monomethylpyridine picrate. The former possibility was ruled out by the melting point and boiling /

boiling range of the original bases. Identification of the compound has been left until a further quantity of the picrate can be isolated. The empirical formula of the picrate calculated from the analysis was $C_{12}H_{11-12}N_4O_7$.

Found C, 45.13; H, 3.55; N, 17.28

Picoline picrate $C_6H_7N.C_6H_3O_7N_3$ requires

C, 44.71; H, 3.13; N, 17.39

Dihydropicoline picrate $C_6H_9N.C_6H_3O_7N_3$ requires

C, ~~44~~ 44.44; H, 3.73; N, 17.28

The compound has not been identified with any compound described in the literature.

Picrate 2 (m.p. 188-9°C)

The picrate was again recrystallised from alcohol, the melting point, however, remained almost unchanged at 188-9°C. A sample recrystallised from acetone showed no appreciable change in melting point and the picrate was therefore taken as pure. The yield was 1 gm. (needles sparingly soluble in alcohol) and the free base was not regenerated.

Analysis of the picrate gave similar results to those obtained in the case of Picrate 1 and similar remarks apply.

Found. C, 45.11; H, 3.45; N, 17.75

The compound has not been identified with any compound described in the literature.

Picrates 3 and 4

Picrates 3 and 4

Both picrates were obviously mixtures and the melting points were not improved by crystallisation. As the combined weight of the two was less than 1 gm. they were not examined further.

Picrate 5.

The dark red viscous oily picrate resisted all efforts to induce crystallisation and was therefore converted back to the free base in the usual manner. Traces of carbylamines were observed during the steam distillation of the bases and these were destroyed by boiling in dilute acid solution for a short time before the final distillation of the liberated bases.

The bases obtained had a strong rather unpleasant odour and distilled over a wider boiling range than the fraction originally used for the fractional acid extraction. A small amount of high boiling material (b.p. over 200°C/760 mm.) remained in the distillation flask indicating that slight decomposition had taken place during the acid extraction or subsequent treatment. On redistillation, the bases came over mainly within 1.5°C.

Physical characteristics.

b.r. 185.5 - 187°C/749 mm.Hg. N_D^{25} 1.5123

Picrate.

An attempt to prepare the picrate of the regenerated bases led once again to the formation of

an /

an oil which did not crystallise.

Picrolonate.

The picrolonate prepared in the usual manner came out as an oil which partially crystallised on standing. The crystalline picrolonate separated from the oil and twice recrystallised from alcohol had m.p. 183-4°C.

Analysis was again inconclusive and the compound was not identified. This picrolonate may have corresponded to one of the picrates previously isolated. The high hydrogen value suggests a partially reduced pyridine homologue. The picolines and dimethylpyridine picrolonates are excluded by the low melting point and by the high boiling range of the free bases. The ethyl pyridines are similarly excluded by boiling point considerations.

Found. C, 54.02; H, 4.54; N, 19.72

Picoline picrolonate ($C_6H_7N.C_{10}H_8O_5N_4$) requires

C, 53.76; H, 4.23; N, 19.60

Lutidine picrolonate ($C_7H_9N.C_{10}H_8O_5N_4$) requires

C, 54.96; H, 4.62; N, 18.86

Methiodide.

The methiodide prepared in the usual manner separated as an oil which partially crystallised on standing. The solid methiodide, separated from the oil and recrystallised from methanol, had m.p. 225-226.5°C.

Analysis /

Analysis was again inconclusive and the compound was not identified. It may have corresponded to one of the other derivatives previously obtained.

Found. C, 35.59; H, 4.57; N, 6.12

Picoline methiodide ($C_6H_7N.CH_3I$) requires

C, 35.75; H, 4.26; N, 5.96.

The possibility of a picoline methiodide was excluded by the melting point and by the low boiling points of the free picolines. The high hydrogen value however suggests once again the possibility of a partially reduced compound.

Identification of Compounds obtained.

Unfortunately, all of the solid derivatives from this range were obtained in such small amounts as to render their identification difficult. The high hydrogen analyses in all cases suggest the presence of reduced or partially reduced pyridine homologues, but the differences between the calculated analyses of such compounds and those of the unreduced compounds are close to the limits of experimental error for the analysis of compounds of this type. It is therefore impossible to make any suggestions regarding the identity of the compounds obtained, until further quantities are available for examination by chemical methods.

The oily picrate could not be purified by the usual methods and therefore the base regenerated from it /

it was not pure. It was apparent that at least one compound was present which did not react in the normal manner towards picrolonic acid and methyl iodide and this is in agreement with the findings of earlier workers in this field (12, 18, 20).

The presence of traces of primary bases, as evidenced by the formation of carbylamines during a chloroform extraction of the original bases from alkaline solution was surprising. Examination of the original A-distillate had indicated the absence of primary amines. It is certain, however, that the amount of primary bases present was very small. Presumably it had been concentrated in this range during the exhaustive distillations to which the bases were previously subjected, (aniline for example (b.p. 184.4/760 mm.Hg.) would be expected to accumulate in this range if present).

Infra red absorption analysis of the base regenerated from the oily picrate gave inconclusive results. The absorption spectrogram (Section G) was such as might have been expected from a mixture of highly alkylated pyridines, a result which suggests the possible presence of compounds quite different from the simple methyl and polymethyl pyridines present in the lower boiling fractions. The unusually high refractive index of the base from the oily picrate (N_D^{25} 1.5123) supports this view. Nothing has been found in the literature which gives any indication of the identities of the picrates and other/

other derivatives isolated.

Range 3

134.5-134.6°C/100 mm.Hg. (199-200°C/745 mm.Hg.)

This range was chosen for examination since it represented a pronounced flat on the 7D distillation curve and since it occurred close to the interesting solid base (2:3:5:6-parvoline) obtained during distillations 7 and 9D. The only compound isolated in a pure state was 2:3:4:6-parvoline previously found in Fushun Shale Oil by Eguchi (15). As in the case of Range 2, a non-crystalline picrate was also obtained; this has not yet been examined.

It is interesting to note that the only other tetramethylpyridine (the 2:3:4:5-isomer) has already been isolated from Scottish Shale Oil (20).

The fraction used in this examination was

7D9 b.r. 134.5-134.6°C/100 mm.Hg. 217 gm. N_D^{25} 1.5076

The charge used for distillation 7D was freed from non-basic matter before distillation and the fraction was therefore ready for reaction with picric acid without any treatment other than a preliminary distillation at atmospheric pressure (b.r.199-200°C/745 mm.Hg.) The redistilled base was a colourless oily liquid with a strong characteristic odour. The equivalent, as determined by titration, was 140.6 (tetramethylpyridines require 135).

140 gm./

140 gm. of bases (1 gm. equivalent) was treated with 229 gm. (1 mol.) of picric acid in three equal portions, the picric acid being added as a saturated alcoholic solution. In this way, three batches of picrate were obtained.

Picrate 1.

Fine needles m.p. 106-107°C raised to 121-123°C by recrystallisation from alcohol.

Picrate 2.

Fine needles m.p. 121-123°C, unchanged by recrystallisation from alcohol.

Picrate 3.

Needles m.p. 117°C, unchanged by recrystallisation from alcohol.

Picrates 1 and 2 were combined and recrystallised from methanol (m.p. 122-123°C) and acetone (m.p. 123.5°C). The latter recrystallisation caused heavy losses, as the compound was rather soluble, but gave a very pure product.

Picrate 3 recrystallised from methanol had m.p. 118-119°C; an attempt to recrystallise from hot water, in which it was appreciably soluble, lowered the m.p. slightly. Recrystallisation from the acetone mother liquors from picrates 1 and 2 raised the m.p. to 121.5-123°C.

A mixed sample of the purified picrates 1, 2 and /

and 3 recrystallised from alcohol appeared quite homogeneous under the microscope and had m.p. 122-123°C.

2:3:4:6-Tetramethylpyridine.

The combined purified picrates (P_1, P_2 and P_3) amounted to only about 32 gms., although there is no doubt that considerably more could have been obtained by systematically working up the mother liquors.

32 gm.s of the pure picrate was decomposed with sodium hydroxide and the base regenerated in the usual manner. 10 gm. (84.3 per cent recovery) of a colourless liquid with a rather unpleasant odour was obtained. The picrolonate and mercurichloride were made in the usual way from the pure base.

Physical Characteristics.

b.p. 202.5-203/746 mm.Hg.	Lit. 203.3/760 mm.(15)
N_D^{25} 1.5087	Lit. 1.5084 (15)
d_4^{25} 0.9345 (a)	Lit. 0.9229 (15)
M_D 43.18 calc. 44.10 (b)	Lit. 43.34 (15)

(a) The density could not be determined with great precision as no accurate thermostat was available at the time.

(b) From atomic refractions of Roth and Eisenlohr (73).

Picrate.

Fine needles from alcohol.

M.P. 122.5-123.5°C. Lit. 107°C (15)

Found C, 48.97; H, 4.43; N, 15.41

$C_9H_{13}N.C_6H_3O_7N_3$ requires

C, 49.45; H, 4.43; N, 15.38

Picrolonate

Prisms from methanol.

M.P. 225.5° (decomp.)

Found N, 17.46

$C_9H_{13}N.C_{10}H_8O_5N_4$ requires

N, 17.53

Mercurichloride

Needles from dilute hydrochloric acid

M.P. 154°C (not completely purified)

Found C, 26.27; H, 3.08; N, 3.48

$C_9H_{13}N.HCl.HgCl_2$ requires

C, 24.39; H, 3.18; N, 3.16

Identification.

The compound was considered to be a parvoline on the basis of the analyses of the picrate and picrolonate. The mercurichloride was not isolated in a pure state.

The close agreement between the physical data of the base and these given by Eguchi (15) suggest that the compound is the 2:3:4:6-tetramethyl isomer and /

and the boiling point of this compound, as calculated by Eguchi from an empirical relationship is 203.3°C/760 mm.Hg., which is in fair agreement with the boiling point found during the present work and in exact agreement with the value observed by this author. The molecular refraction, as calculated from the density and refractive index of the base, was in reasonable agreement with the value obtained by summation of the atomic refractions, assuming a parvoline structure.

The observed melting point of the picrate does not agree with the value found by Eguchi, but it was noticed that when the picrate was heated, a well defined shrinking of the crystals occurred at 107°C, which is the melting point given by Eguchi. The temperature at which this phenomenon occurred was quite sharp and reproducible and it is quite possible that it may have been mistaken for fusion of the solid.

Evidence in favour of the tetramethyl structure was provided by the infra red absorption spectrogram in which the band due to $- C - CH_3$ deformation was particularly strong while the $- CH_2 - CH_3$ frequency was absent (Section G.)

Of the three possible tetramethylpyridines, the 2:3:4:5-isomer is described in the literature (74) as having b.p. 232-234°C, picrate m.p. 170-172°C. The /

The 2:3:5:6-isomer, to which reference has previously been made is believed to have been isolated during the present work as a solid, m.p. 71-72°C, picrate m.p. 173-174°C. The only remaining possibility therefore is 2:3:4:6-tetramethylpyridine.

An attempt to oxidise to base with potassium permanganate in acetone, was unfortunately not successful and has not yet been repeated.

Further Picrates isolated from Range 3

The original alcohol mother liquors and certain of the recrystallisation mother liquors were systematically reduced in bulk and a series of mixed picrate fractions were obtained. The main constituent of the solid picrates obtained appeared to be 2:3:4:6-parvoline picrate and no doubt more of this compound could have been isolated in a pure state by systematic recrystallisations. No other compound was isolated in a pure state.

Complete removal of the remaining alcohol from the original mother liquors yielded about 50 gms. of a viscous red-brown oily picrate similar to that obtained from Range 2. This has not been examined.

Solid Base from Distillations 7D and 9D

2:3:5:6-Tetramethylpyridine.

Reference has been made to the solid base isolated during distillations 7D and 9D. This base was /

was examined by R.J. Benzie (68) during the course of the present work and it was established fairly conclusively, from the analyses of derivatives and consideration of the physical and chemical properties of the free base that the compound was 2:3:5:6-parvoline.

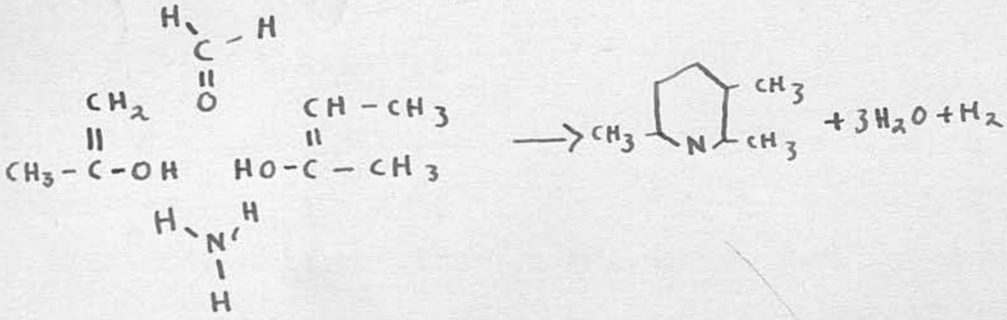
There are few references to this compound in the literature and of these, one (70) is of no value as the compound is not definitely characterised. In another case (71) the compound is not indicated in the indices of Chemical Abstracts, while in a further case (75) it is described as the 2:3:4:6-isomer, although the 2:3:5:6-structure is given in the original paper (and in Chemisches Zentralblatt).

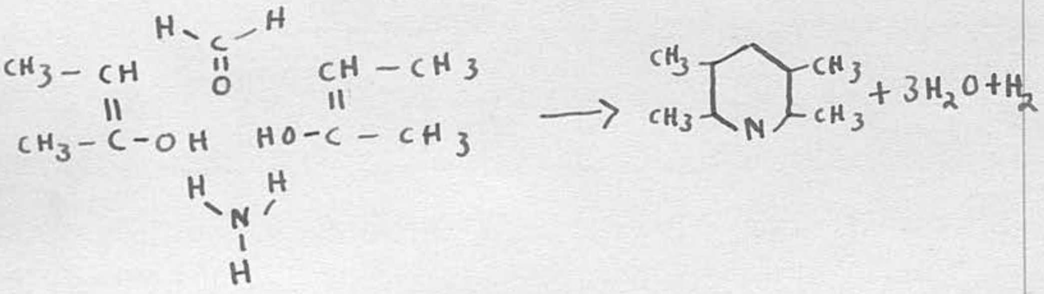
In the course of examining the literature on 2:3:5-trimethylpyridine, it was found that this collidine had been synthesised by Oparina (71) and that a compound believed to be 2:3:5:6-parvoline was also found among the reaction products. The compounds were prepared by the action of methyl iodide on 3;5-lutidine at 300°C in a sealed tube and on working up the product two picrates were isolated with m.p.s. of 183 and 173-4°C respectively. The former was shown to be the picrate of 2:3:5-collidine while the latter gave a base $C_9H_{13}N$, which by analogy with the formation of the 2:3:5-trimethyl isomer was presumably the 2:3:5:6-tetramethyl compound although this fact was not definitely established.

The /

The same compound was subsequently obtained by this author in another way (75).

By condensation of a mixture of acetone, methyl-ethyl ketone and formaldhyde in the presence of an alumina catalyst the main product was 2:3:6-trimethylpyridine but a small amount of a base $C_9H_{13}N$, identical with the base obtained by condensation of methyl iodide and 3:5-lutidine, was also obtained. By condensation of 2 mols. of methyl-ethyl ketone with 1 mol. of formaldehyde this compound was the main product obtained. The reactions may be represented as follows where the acetone and methyl-ethyl ketone are shown as the enol forms.





The formation of the base $C_9H_{13}N$ by the two different reactions mentioned, with, in the one case, simultaneous formation of 2:3:5-trimethyl pyridine /

pyridine and in the other case simultaneous formation of the 2:3:6-isomer would seem to be very strong evidence in favour of the 2:3:5:6-tetramethyl structure for this compound.

It has now been shown (by preparation and analysis of the gold chloride double salt) that the compound isolated during distillations 7D and 9D is almost certainly identical with the compound described by Oparina, which further supports the view that this compound is 2:3:5:6-tetramethylpyridine.

Solid Base from 7D and 9D	Solid Base Synthesised by Oparina
M.P. 76°C	71 - 72°C
Picrate M.P. 176°C	173 - 174°C
Aurichloride M.P. 181-182°C	178°C

Analysis of Aurichloride

Found C, 22.56; H, 2.93; Au, 41.17

$C_9H_{13}N.HCl.AuCl_3$ requires C, 22.74; H, 2.97; Au, 41.49.

SECTION F

Dissociation Constants of Pyridine Bases.

The dissociation constants of pyridine homologues are of obvious interest as providing a convenient measurement of the relative strengths of the bases. In view of the value of fractional acid extraction as a method of separating such compounds, a knowledge of these values is of considerable importance since, although the separation achieved is dependent to some extent on the distribution coefficients, the main factor involved is the relative strengths of the bases. It is possible also, that the use of ion-exchange resins may be of value in achieving separation of these compounds, and in this connection too a knowledge of the strengths of the bases (even of a qualitative nature) is of obvious value.

A survey of the literature reveals that little work has been done on the dissociation constants of pyridine homologues and the few values recorded were in some cases obtained by unreliable methods.

The opportunity has been taken, during the course of the present work, of determining the dissociation constants of all the compounds isolated in sufficient quantity and in addition those of several analogous compounds obtained from other sources. The work which has been done on this topic however can /

can only be regarded as a preliminary study.

As no reliable potentiometer was available, a direct reading pH meter constructed by Dr. K.R.Buck of the Chemistry Department, Heriot-Watt College, was used in conjunction with a glass electrode and a calomel half cell. The probable accuracy of the instrument was ± 0.05 pH units and all measurements were carried out at laboratory temperature (ca.18°C) without any temperature control. The temperature correction in all cases was almost certainly less than the probable error of the instrument.

Method.

A sample of the base (0.1 - 0.2 gm.) which was not accurately weighed, was dissolved in about 50 ml. of distilled water, and the pH of the solution determined, after standardising the instrument against buffers of known pH. Hydrochloric acid (ca.$\frac{N}{20}$) was added in stages and the pH determined after each addition of acid, until further additions produced no significant change. The pH values were plotted against the total volume of acid added and the end-point of the titration estimated from the smooth pH curve.

The pH value at half-titration, as estimated from the curve, gave the value of (pKa) the "acidic constant." The dissociation constant (Kb) was then determined by subtracting this value from the ionic product /

product of water (taken as 14) and eliminating the logarithm.

The results obtained are shown in Table 21, which includes a number of lower pyridine homologues isolated from Scottish Shale Oil by R.J.Benzie (68) and several compounds from other sources. Quinoline, 2-methylquinoline (quinaldine) and 4-methylquinoline (lepidine) have been included for purposes of comparison.

It must be emphasised that these values are not claimed to be of first order accuracy. In one or two cases where a recent value has appeared in the literature, this has been included in the table for comparison.

TABLE 21 /

TABLE 21

Dissociation Constants of Pyridine and Quinoline Homologues

Base	pKa	Kb x 10^9 (at ca. 18°C.)	Literature Value (Kb x 10^9)
Pyridine (a)	5.04	1.1	1.07 at 18°C (76)
2-Picoline (b)	5.82	6.6	1.4 at 18°C (77)
3-Picoline (b)	5.62	4.2	
4-Picoline (b)	5.88	7.6	
4-Et Pyridine(b,f)	5.80	6.3	
2:3-Lutidine (b)	6.42	26	
2:4-Ludidine (b)	6.68	48	
2:6-Lutidine (b)	6.66	46	
3:4-Lutidine(b,c)	6.55	36	
2:4:5-Collidine(d)	7.35	224	
2:4:6-Collidine	7.18	152	
2:3:4:6-Parvoline	7.75	562	
2:3:5:6-Parvoline(b)	7.50	316	
Quinoline	4.70	0.501	0.63 at 25°C (78)
Lepidine (c)	5.50	3.16	1.59 " " "
Quinaldine (c)	5.70	5.01	2.64 " " "
Bases from oily picrate (e)	7.06	115	

See
Brown &
Barbaras
JACS (1947)
69 1137

(a) Kahlbaum's.
(b) Determination by R.J.Benzie
(c) D.S.I.R. samples.
(d) Isolated from strongest bases after fractional extraction on 3D5-6. Range 2.
(e) Isolated from weakest bases after fractional extraction on 3D5-6. Range 2.
(f) Synthetic.

In the case of very weak bases such as the quinoline homologues, it is difficult to estimate the end point on the pH titration curve, and this is reflected in the poor agreement with the literature values in the cases of lepidine and quinaldine, the dissociation constants of which were measured by Felsing and Biggs (78) by measurement of the hydrogen ion concentration of solutions of the perchlorates. These authors carried out similar measurements on a series of compounds which included all the mono- and several di- and trimethylquinolines, all of which are very weak bases of approximately the same strength.

It is anticipated that in the continuation of this research programme, the dissociation constants of the above and other pyridine homologues will be re-determined with greater accuracy, but in the meantime it is possible to make one or two general remarks.

1. The introduction of a methyl group into the pyridine nucleus causes an appreciable increase in the strength of the base and this is enhanced by the introduction of a second methyl group and so on.
2. The strengths of the monomethyl pyridines and 4-ethyl pyridine are of the same order and similarly in the case of the dimethylpyridines, the trimethylpyridines and the tetramethylpyridines.

3. The effect of a methyl group may be regarded as being due to the overall electrical moment of the methyl group as a whole and in cases where the substituents are in the 2- or 4- positions a second effect makes its appearance. This is the well known inductive or tautomeric effect which may be correlated with the known chemical reactivity of methyl groups in these positions.

It is this latter effect which is presumably responsible for the fact that the 2- and 4-picolines are rather stronger bases than 3- picoline, and similarly in the case of the lutidines. It would appear also that substitution in the 4- position has a slightly larger effect than substitution in the 2-position in the pyridine nucleus, although the difference is small. The reverse is so in the case of the methyl quinolines (78)

4. At first sight it is unexpected that 2:4:6-collidine, which is substituted in the three favourable positions should be a weaker base than 2:4:5-collidine in which one of the substituents is unfavourably situated. It seems, however, that in this case a third effect is being brought into play, and this may be related to the fact that in the case of 2:4:6-collidine, the molecule /

molecule is more nearly symmetrical than in the case of 2:4:5-collidine. In the former case it might be expected therefore, that the vector sum of the overall field moments of the methyl groups will be less than in the case of the 2:4:5-isomer. This is borne out to some extent in the cases of 2:3:4:6- and 2:3:5:6-parvolines.

Here, the relative strengths of the two bases are in the order which would be ecpected from the fact that, in the former case, three of the methyl groups are in the appropriate positions to increase the strength, while in the latter case only two are so placed. The difference in strengths, however, is rather greater than might be expected on these grounds alone and may again be connected with the fact that the molecule of the latter compound is more nearly symmetrical than that of the former, the symmetry again tending to reduce thestrength of the base.

These remarks are, however, merely tentative and more reliable determinations of the dissociation constants are required before it would be profitable to pursue the matter further.

5. It is apparent that fractional acid extraction should effect a good separation of pyridine and quinoline homologues and between pyridine homologues containing different numbers of substituent groups.
6. The bases regenerated from the oily picrate ex fractions 3D5 and 6 are of the same order of strength as the trimethyl pyridines.

The mean dissociation constant of Fraction 7D9 (Range 3), from which 2:3:4:6-parvoline was isolated, was also measured. The fraction had (pKa) 7.88, Kb x 10 = 759. It will be recalled that an oily picrate was also isolated from this fraction, although not examined, and presumably the base to which this corresponds is of a differant type to those previously isolated, and to those regenerated from the oily picrates obtained from fractions 3D5 and 6. (Range 2).

SECTION G.

Infra-red Absorption Spectra.

The infra-red absorption spectrum of a given compound is a unique property which cannot be duplicated by any other compound. This characteristic is invaluable in identifying unknown compounds, providing that reference spectra are available and has the advantage that the samples required are small and may be recovered unchanged.

Comparisons of spectra of large numbers of pure compounds have shown that absorption bands occurring at certain frequencies can be correlated with certain bonds or atomic groups within the molecule and thus, even in the absence of reference compounds, valuable evidence may be obtained in support of conclusions reached by other means. For example, the position of the absorption band of a carbonyl group, in general, indicates whether it forms part of an anhydride, ester, ketone or acid.

Although all the structural units of a given compound may not be determined in this manner, at least a considerable number of the more common ones may be identified.

In the course of the present work, the opportunity was taken of having infra-red absorption spectrograms prepared from several of the compounds isolated. /

isolated. This was done 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,using the Hilger double-beam instrument at the Chemical Research Laboratory, Teddington.

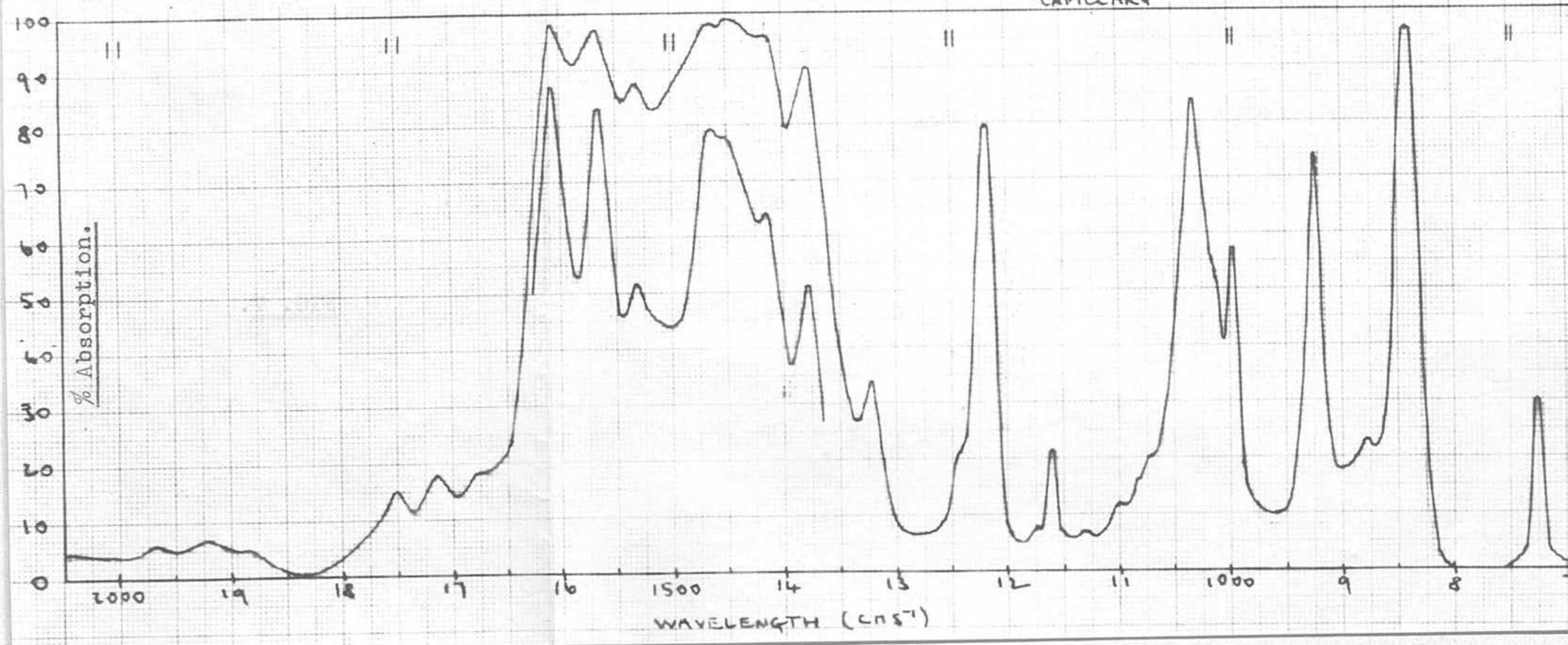
The compounds examined were, 2:4:6-collidine, 2:4:5-collidine, 2:3:4:6-parvoline and the mixed bases regenerated from the oily picrate obtained from Range 2. In the case of the first three compounds the absorption spectrograms were in support of the structuresallocated to the compounds. The results obtained with the bases regenerated from the oily picrate were inconclusive.

Unfortunately, few infra-red absorption spectrograms of pyridine homologues have been published and in the cases of 2:4:5-collidine and 2:3:4:6-parvoline it has not been possible to make any direct comparison.

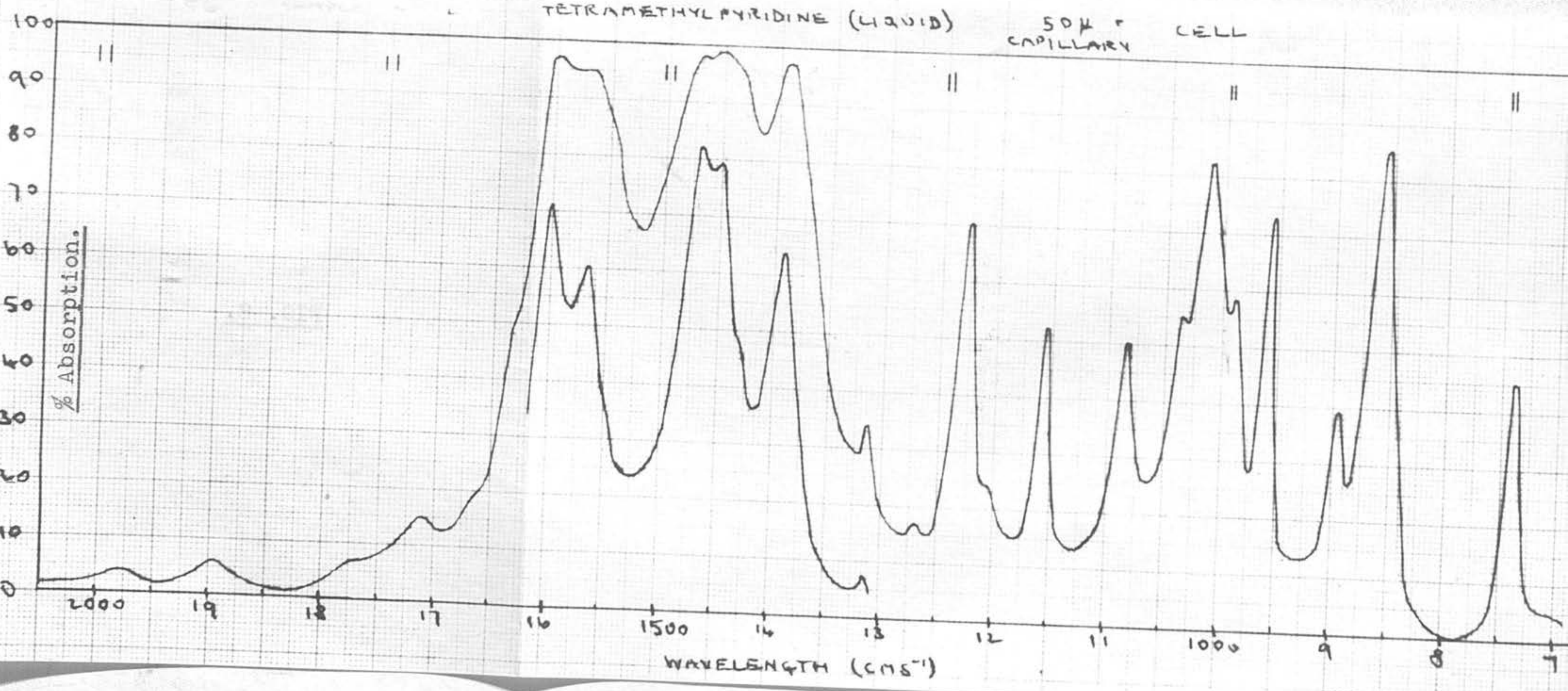
Barnes et al (79) have published data for some 363 compounds including a number of pyridine homologues and in the case of 2:4:6-collidine excellent agreement was obtained between the spectrogram of the base isolated during the present work and that given by Barnes.

The spectrograms of the four compounds examined are reproduced for reference, with a short note on each.

2:4:6 — COLLIDENE (LIQUID) 50 μ CELL
*CAPILLARY



TETRAMETHYLPYRIDINE (LIQUID) 50 μ * CELL
CAPILLARY



2:4:6-Trimethylpyridine (Fig. 7)

The excellent agreement with the spectrogram published by Barnes (loc cit) confirms that this compound is 2:4:6-trimethylpyridine. All the pyridine homologues have an intense rather broad band at 750-855 cms^{-1} and this is quite probably due to ring deformation. In the case of 2:4:6-collidine this band occurs at 840 cms^{-1}. The band due to -C -CH$_3$ deformation which normally occurs at 1375-1390 cms^{-1} is also well marked, while the band due to the -CH$_2$ -CH$_3$ frequency (760-780 cms^{-1}) is absent.

2:4:5-Trimethylpyridine (Fig. 9)

The clean spectrum of this compound indicates that it is fairly pure, while the strong general resemblance to 2:4:6-collidine is in keeping with the suggestion that the compound has the structure assigned to it. Unfortunately no reference spectrum was available for direct comparison, but the above notes on the spectrum of 2:4:6-collidine apply very similarly in this case and support the view that this compound is 2:4:5-collidine, although not definitely establishing the fact.

2:3:4:6-Tetramethylpyridine (Fig. 8)

As in the previous cases the band due to ring deformation (855 cms^{-1}) is well marked, while the band due to -C -CH$_3$ deformation (1375-1390 cms^{-1}) is particularly strong in this case, which supports the /

the view that the compound is 2:3:4:6-tetramethyl pyridine, although not definitely establishing this fact. Further evidence in favour of the tetramethyl structure is provided by a comparison of the ring deformation frequencies of the pyridine substituents and those of the corresponding bezene substituents (Table 22)

TABLE 22

Ring Deformation Frequencies of Benzene and Pyridine Substituents

Benzene Substituents	Ring Deformation Frequency	Pyridine Substituents	Ring Deformation Frequency
Mono-	704-750	Picolines	750-800
Di-	740-830	Lutidines	780-820
Tri-	760-860	2:4:6-collidine	840
Tetra-	840-880	?-tetramethyl pyridine	855

Bases Regenerated from Oily Picrate (Range 2)(Fig.10)

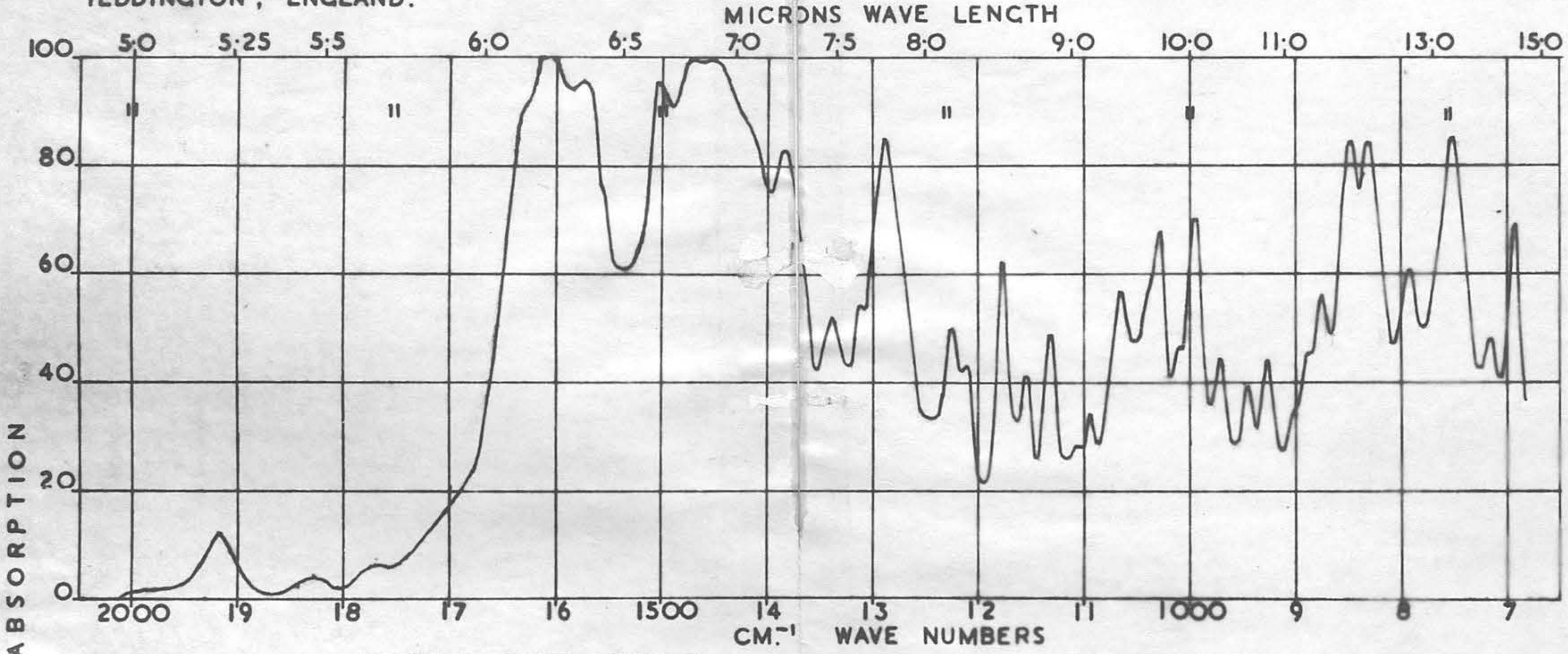
The spectrum of this compound is not very informative. The large number of absorption bands indicates that it is a mixture and the general band structure at 6.3 μ and 6.8 μ is typical of the substituted pyridines, the band at 995 cm^{-1} also appears to be characteristic of the series.

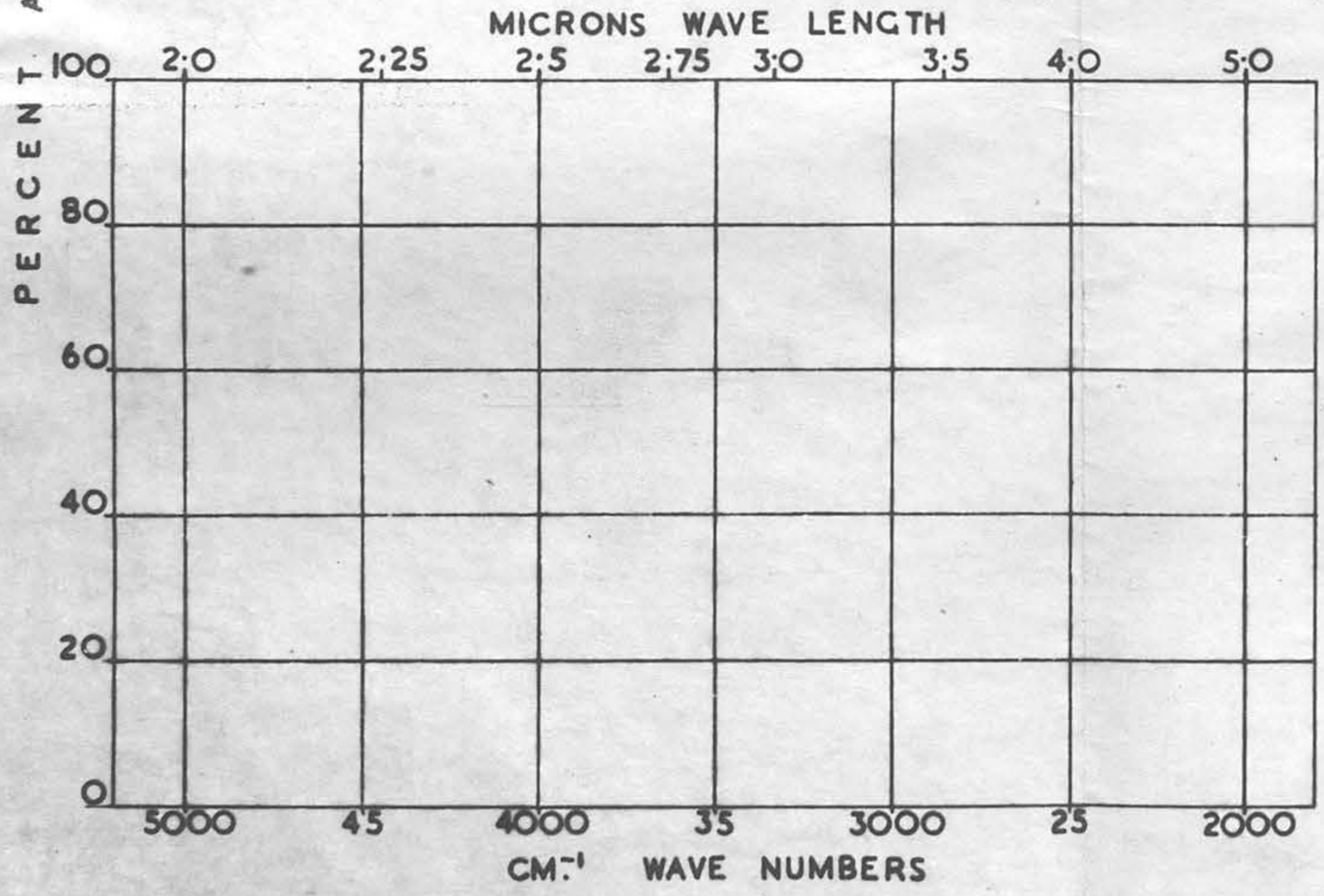
Comparison with the spectra of other compounds is not very illuminating, but there is some resemblance to 2:4:6-collidine. This combined with /

INFRARED ABSORPTION SPECTROGRAM

CHEMICAL RESEARCH
LABORATORY, D. S. I. R.,
TEDDINGTON, ENGLAND.

No.





COMPOUND BASES FROM OILY PICRATE (Range 2.)

SOURCE

PURITY

STATE LIQUID

CELL LENGTH 50 μ

SPECTROMETRIC MEASUREMENT HILGER DOUBLE-BEAM

CHEMICAL RESEARCH LAB. TEDDINGTON.

with the very high value of what seem to be the ring frequencies (850-830 cms^{-1}) point to the presence of one or more highly substituted pyridines.

These facts considered along with the chemical behaviour of this fraction indicate that the bases present are of rather a different nature to those found in the lower boiling ranges, but until larger quantities of the compounds present can be isolated in a pure state, it will be impossible to ascertain their structure.

DISCUSSION.

The crude oil obtained in the distillation of Scottish Shale contains about 0.6 - 1 per cent of nitrogen. This is recovered from the oil as a complex mixture of organic bases during the refining processes. The manner in which this nitrogen is combined in the raw shale is not known and attempts to extract the organic matter or "kerogen" from shale by solvent or acid extraction have met with little success.

During the refining of the oil the nitrogen compounds are extracted with acid and subsequently precipitated in the form of a viscous black "Basic Tar" which also contains sulphur compounds. By vacuum distillation, up to 40 per cent of volatile bases may be recovered from the "Basic Tar", while the more complex compounds, polymerisation products and entrained carbon, remain in the form of an undistillable pitch. Much of the sulphur is eliminated in the form of gaseous and low boiling decomposition products during this distillation.

Examination of the volatile bases shows them to consist substantially of a complex mixture of tertiary heterocyclic bases, although primary bases, at first thought to be absent, were subsequently detected in minute amounts in the bases boiling between 180-190°C and may also be present in the higher ranges. Traces of pyrroles are apparently distributed /

distributed throughout the lower ranges and may be present in the higher ranges.

Examination of the lower boiling point bases has shown them to consist of a mixture of pyridine homologues with methyl side chains. It seems probable that all the methyl, dimethyl, trimethyl and tetramethylpyridines are present, although a number of these have not yet been isolated. Compounds with ethyl side chains have also been isolated (68) and compounds with longer alkyl side chains may be present, but have not as yet been detected.

There is a general resemblance between the bases present in Scottish Shale Oil and those present in similar materials found in other countries. The resemblance is particularly striking in the case of the bases from Shale Oil of the Fushun district of Manchuria. This is not really surprising, since there is a similarity between the two shales and the oils obtained from them. There also seems to be a resemblance between the Scottish Shale bases and those isolated from cracked Californian Petroleum distillates.

In the case of the petroleum distillates two types of compounds are found. These are the aromatic and non-aromatic bases.

The aromatic bases are of the alkyl pyridine and quinoline types; the non-aromatic bases, while apparently /

apparently containing the pyridine or quinoline nucleus have lost their aromatic character through the accumulation of bulky side chains, or additional rings, or by hydrogenation of the ring system. Most of the aromatic bases isolated from the petroleum distillates are simple methyl homologues of quinoline and it is to be expected that compounds of this type will occur in the higher boiling Scottish Shale bases.

Earlier workers on shale bases have experienced difficulty in obtaining crystalline derivatives, and this has been found to a lesser extent during the present work. Although in the case of earlier investigations this may have been largely due to inefficient fractionation of the bases, it probably indicates also the presence of compounds analagous to the non-aromatic petroleum bases.

The low refractive indices of the higher boiling shale bases suggest the presence of compounds which are not of the simple alkyl quinoline type, while in the course of the present work, a small quantity of mixed bases was obtained which had an unusually high refractive index and from which no crystalline derivatives were obtained. (Range 2)

The possibility of using the "Basic Tar" as a source of valuable intermediates has been kept in mind throughout the present work. The quantity available is of the order of 1500 gallons per day and its only application at present is as a fuel in the refinery. The method of formation is such that most of the water /

water soluble bases are preferentially removed and are at present not recovered. Some of these find their way into the "Cracker Exhaust Oil" but the yield of this is small.

The complexity of the mixture is such that no one compound is present in sufficient amount to make its extraction commercially feasible. It appears that, in the lower boiling ranges at any rate, pyridines substituted in the 2- and 4- positions are more abundant than those substituted in the 3- and 5- positions. It has not been possible to make a reliable estimate of the percentage composition, but 2:4:6-collidine, which is one of the most abundant compounds present probably constitutes about 0.25 per cent of the "Basic Tar".

Any commercial outlets found for the bases will almost certainly be for mixed fractions. The mixed bases appear to have some value as acid inhibitors in acid pickling baths and other uses which suggest themselves include the preparation of high boiling solvents, acid absorbing reaction media, insecticidal sprays and detergents of the quaternary alkyl halide type.

Separation of the bases can be achieved by fractional distillation, although it is unlikely that pure compounds can be separated this way. Fractional acid extraction appears to be a valuable method of achieving separation of the stronger and weaker bases and might be combined with the use of ion-exchange resins /

resins and fractional steam distillation.

The mixed bases available from this source provide a valuable starting point for a comprehensive study of the chemistry and physical chemistry of the heterocyclic nitrogenous bases of the pyridine, quinoline and associated types.

SUMMARY

1. Efficient columns have been constructed for the fractional distillation of bases at atmospheric pressure and under precisely controlled vacuum. These include the following -

   a. 14-Plate vacuum column (Eyelet Packing)
   b. 40-Plate column (Fenske Helices)
   c. 100-Plate vacuum column (I.C.I. gauze rings)
   d. 14-mm. column (I.C.I. gauze rings)

   Column a. was subsequently converted to 30-Plates by re-packing with I.C.I. gauze rings.

   Plate efficiency tests were carried out on columns a. and b. and estimates made of the efficiency of column c.

   A simple type of rotary fractional extraction apparatus has also been constructed.

2. A typical sample of "Basic Tar" from Pumpherston Oil Refinery was examined and found to contain some 40 per cent of volatile bases boiling up to 310°C at atmospheric pressure.

   210 litres of "Basic Tar" were distilled under vacuum in a 16-litre pot-still and 25 per cent (53 litres) of bases boiling up to 190°C at 20 mm. Hg. recovered The bases were found to consist substantially of tertiary heterocyclic nitrogen compounds, the lower boiling ranges were mainly simple homologues of pyridine with methyl side chains. Quinolines are believed to be present in the higher ranges and /

and more complex compounds are also thought to be present.

3. The bases were subjected to a series of systematic fractional distillations and ultimately bases boiling up to 210°C at atmospheric pressure were fractionated in a column of 100-theoretical plates.

4. Three ranges have been examined by chemical methods. These are Range 1, 169.9-171°C/760 mm.Hg. Range 2, 186.1-188°C/760 mm.Hg. and Range 3, 134.5-134.6°C/100 mm.Hg.

   The following compounds were identified, 3:5-lutidine; 2:3:5-collidine; 2:4:5-collidine; 2:4:6-collidine and 2:3:4:6-parvoline. Several compounds were isolated as crystalline derivatives, the identities of which have not been established. Two oily picrates were obtained, the bases regenerated from one of which had an unusually high refractive index and gave no crystalline derivatives.

5. Infra red absorption spectrograms have been obtained from several of the compounds isolated and these favour the proposed structures.

6. The dissociation constants of a series of pyridine and quinoline bases have been determined and discussed.

7. A survey has been made of the literature dealing with separation methods and this has been included as an appendix.

ACKNOWLEDGMENTS

The author's thanks are due in the first instance to Professor H.B. Nisbet of the Heriot-Watt College, who has directed this research, for his sustained interest, encouragement and advice throughout the course of the work, and to the Department of Scientific and Industrial Research for a Maintenance Allowance.

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The construction of apparatus and distillation work was carried out in collaboration with Mr. R.J. Benzie.

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APPENDIX.

SURVEY OF LITERATURE ON SEPARATION METHODS.

It would be impossible within a limited space to effectively summarise the very extensive literature on the methods which may be used to separate mixtures of two or more components having similar chemical and physical properties. The following is intended to be a brief survey of the more recent literature on some of the methods used or considered in the course of the present investigation.

The following topics have been included, in the order given below.

a. Fractional Distillation
b. Azeotropic Distillation
c. Fractional Extraction
d. Fractional Crystallisation
e. Chromatographic Adsorption

In discussing these topics, emphasis has been placed, as far as possible, on their application to the separation of pyridine and quinoline homologues.

a. FRACTIONAL DISTILLATION.

Within recent years and particularly within the last two decades great advances have been made in the study of fractional distillation as a means of separating simple and multi-component mixtures of compounds of similar boiling points. This is reflected in the ever increasing volume of literature dealing with this subject both from the theoretical

/and

and practical stand points. Much of the impetus for this intensive study has been provided by the increasing demands of the petroleum industry for the large scale separation of narrow boiling cuts and pure components from complex mixtures of hydrocarbons. Consequently emphasis has been placed on the study of continuous distillation on the large scale. The fundamental principles, however, apply similarly to the small scale batch distillation which is more commonly used in the laboratory.

A number of excellent reviews of the literature dealing with distillation have been published from time to time, of which those by Ward (1) and Fay (2) are particularly useful. The bibliography of Stage and Schultze (3) covers the years 1920 - 1944 (although the war years are incomplete) while that of Rose and Rose (4) 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 (5). The extensive literature on the design and testing of fractionating columns has been summarised by Underwood (6) who has applied the various graphical and analytical methods to the solution of a standard type of problem.

1. Determination of the Efficiency of Laboratory Fractionating Columns.

The efficiency of a fractionating column is usually determined by distilling a binary mixture through the column and determining the resulting change in composition of the mixture. In the case of laboratory batch columns the efficiency is usually determined under conditions of total reflux; the feed composition, which in this case is the composition of the liquid in the boiler then remains constant, and similarly, the product composition does not change once thermal equilibrium has been established. The reflux ratio under such conditions is of course infinite, where reflux ratio is defined as the ratio of the quantity of reflux to the quantity of product withdrawn from the column. Continuous columns are usually tested under similar conditions of constant feed and product compositions, the reflux ratio, however, being finite.

From the change in composition of feed and product, the efficiency of the column may be expressed in a number of ways, the simplest of which is the Enrichment Ratio introduced by Hill and Ferris (7). This may be expressed in the following form:

$$E = \frac{Xn}{1 - Xn} \Big/ \frac{Xo}{1 - Xo}$$

where E = Enrichment Ratio

Xn = mol. fraction of the more volatile component at the top of the column

Xo = mol. fraction of the more volatile component at the bottom of the column.

A more useful concept is that of the theoretical plate introduced by Sorel (8) who made the following assumptions when dealing with distillation in bubble-plate columns.

a. The thermal properties of the components and particularly the Molal Latent Heats are similar. There is thus a constant Molal Overflow from plate to plate.

b. The heat supplied to any section of the column is derived solely from the vapour entering the section.

c. Heat losses from the column are negligible.

d. On a theoretically perfect plate the vapour leaving the plate is in equilibrium with the liquid leaving the plate.

Making these assumptions Sorel was able to proceed stepwise, making material and heat balances on each plate throughout the column thus calculating the separation obtainable for a given number of theoretical plates. In practice, of course, the plates are never theoretically perfect.

Although the concept of a theoretical

plate is strictly applicable only to bubble plate columns, it is readily extended to packed columns by determining the number of theoretical plates to which the column is equivalent. The efficiency of the column may then be expressed in terms of the Height Equivalent to a Theoretical Plate, a concept introduced by Peters (9).

By making assumptions similar to those of Sorel, McCabe and Thiele (10) have evolved a graphical method for determining the number of theoretical plates required to achieve a given separation in a continuous column. By making the appropriate assumptions this method may be applied to a batch column, operating under conditions of total reflux. The method has the advantage that it may be applied equally well to ideal and non-ideal mixtures providing the vapour-liquid equilibrium data ~~is~~ are known. Randall and Longtin (11) have modified the McCabe and Thiele method to facilitate its application in cases where large numbers of theoretical plates are involved.

To avoid the often tedious graphical methods a number of analytical methods have been devised which employ the concept of relative volatility (12).

Of these, probably the best known is that of Fenske (13) who has related the enrichment ratio (E) to the number of theoretical plates and the relative volatility by the equation

$$E = \alpha^{n+1} = \frac{Xn}{1 - Xn} \bigg/ \frac{Xo}{1 - Xo}$$

where α = relative volatility (average)

and n = number of theoretical plates.

This may be written in the form

$$n + 1 = \frac{\log \left(\frac{Xn}{1 - Xn} \Big/ \frac{Xo}{1 - Xo} \right)}{\log \alpha}$$

where n + 1 is the number of theoretical plates in the fractionating column including the still pot and still head. One theoretical plate is allowed for the fractionation taking place in these zones.

Fenske's equation can only be applied in cases where the binary test mixture is ideal, that is to say where Raoult's Law is obeyed, and under conditions of total reflux.

Smoker (14) and Dodge and Huffman (15) have evolved equations which are applicable for conditions of finite reflux. Under conditions of total reflux, Smoker's equation reduces to the same form as that of Fenske. The equation of Dodge and Huffman although strictly accurate for transfer units (vide infra) is only correct for large numbers of theoretical plates. As in the Fenske equation, these equations are strictly applicable only to ideal mixtures.

/Since

Since the value of α (relative volatility) varies with composition, the arithmetic mean value for the top and bottom compositions is generally used. Robinson and Gilliland (16) have pointed out that for appreciable variations it is better to use the geometric mean.

Height of a Transfer Unit.

The use of the term H.E.T.P. to express the efficiency of a packed column has the disadvantage that it gives no indication of the continuous change of composition through the column. For this reason Chilton and Colburn (17) prefer to use the height of a Transfer Unit (H.T.U.)

Thus $\text{H.T.U.} = \frac{H}{n_T}$

where H = height of column

and n_T = number of transfer units.

n_T is defined by the integral

$$\int_{p_1}^{p_2} \frac{dp}{\Delta p}$$

where p = partial pressure of the diffusing component of the liquid

$\Delta p = p_o - p$

p_o = equilibrium partial pressure of the diffusing component of the liquid

p_1 and p_2 = partial pressures of the component at the top and bottom of the column respectively.

n_T can also be expressed in terms of the vapour composition

$$n_T = \int_{y_1}^{y_2} \frac{dy}{\Delta y}$$

where y_1 and y_2 = vapour composition at the top and bottom of the column respectively.

Under conditions of total reflux and where α is substantially constant for the top and bottom compositions, this equation can be integrated to give

$$n_T = \frac{2.3}{\alpha - 1} \log \frac{y_2(1 - y_1)}{y_1(1 - y_2)} + 2.3 \log \frac{(1 - y_1)}{(1 - y_2)}$$

For most cases the values of H.T.U. and H.E.T.P. are almost identical and the latter is more frequently used.

2. Test Mixtures and Determination of Column Efficiency.

The usual procedure in determining the efficiency of a laboratory fractionating column is as follows. The still-pot is charged with a suitable test mixture which is boiled under total reflux for a sufficient length of time to establish thermal equilibrium throughout the column. Samples are then withdrawn simultaneously from the still-head and still-pot and analysed by measurement of the refractive index or density. The number of theoretical plates is then calculated by either the graphical method of McCabe and Thiele or by the use of the equations of Fenske, Smoker or Dodge and Huffman.

The composition of the charge should be chosen so that a high concentration of one component does not occur at either end of the column. In this way the working is confined to the centre portion of the vapour liquid equilibrium curve where small errors in the composition have less effect on the result.

Test Mixtures.

The requirements which must be met by a test mixture for determining the efficiency of columns are:-

a. The compounds must be miscible in all proportions, readily obtained in a pure state, and must not react with each other or with the column packing.

b. The components should not form a constant boiling mixture.

c. Analysis of the mixture should be accurate and easy.

d. The molal latent heats of the components should be as close as possible and the difference in boiling points should be small.

e. The vapour liquid equilibrium data and relative volatility must be known and if the mixture deviates from Raoult's Law a graphical solution must be employed.

f. The components should, when possible, possess physical properties closely resembling those of the materials for which the column is intended.

The mixtures in most common use are benzene-ethylene dichloride, benzene-carbon tetrachloride and n-heptane-methylcyclohexane. The advantages and disadvantages of each of these mixtures are discussed at some length by Ward (1) who also summarises the vapour liquid equilibrium data.

Tables or graphs which simplify calculation of the results have been published for the three mixtures (18, 19, 20).

The use of a dilute solution of thiopene in benzene as a test mixture has recently been recommended by Coulson, Hales and Herington (21); these authors also discuss the errors introduced into theoretical plate determinations by the use of inaccurate values of the relative volatility of a non-ideal mixture (22) and conclude by thermodynamic reasoning and experimental evidence that better results should be obtained by using low concentrations of one component in the still charge, which is contrary to the normally adopted practice.

Test mixtures suitable for use at reduced pressures have been described by Bragg and Richards (23), Williams (24) and Perry and Fuguitt (25)

Summarising, it may be said that for comparable results to be obtained, columns should be tested under strictly similar conditions, which should, when possible, closely simulate the conditions under which the column is to be operated.

3. Additional Factors in the Evaluation of Columns.

It has become increasingly evident that the complete evaluation of fractionating columns involves many factors other than the number of theoretical plates to which the column is equivalent, and among these may be cited time to reach equilibrium, throughput rate, hold-up, pressure drop etc.

Ward (1) elaborates the factors to be observed in the design of fractionating equipment and similar points in design are discussed by Podbielniak (26) who concludes that separation into sharp fractions depends on the following factors, among others.

a. Time of Distillation.

There is always an optimum time of distillation. If this is exceeded, the slightly improved separation does not justify the extra expenditure of time, and conversely any reduction entails a corresponding sacrifice in accuracy.

b. Reflux-Ratio.

This is defined as the ratio of the number of mols. of vapour returned as reflux, to the number of mols. of product, both per unit time. This should be varied according to the difficulty of separation. A high efficiency of separation requires a high reflux-ratio.

c. Hold-up of Column.

The hold-up should be reduced to a minimum compatible with scrubbing effectiveness, and an

/adequate

adequate column capacity.

d. Thermal Insulation.

Almost perfect thermal insulation is required to avoid disturbing column equilibrium, and to separate components boiling only a few degrees apart.

Various attempts have been made to introduce overall factors by which the merits of a fractionating column may be assessed and one of the most useful of these is the "hold-up-factor" of Docksey and Hyde. According to Fay (2) this factor is expressed as the number of mls. of hold-up per theoretical plate divided by the operating boil-up rate in ml. per second, and gives a direct measure of the time required to carry out a given distillation. Similar factors have been introduced by Bragg (27) and Podbielniak (28).

The loss of fractionating efficiency due to column hold-up has been investigated theoretically by Rose, Welshans and Long (29) and a simple illustration of the effect is given by Fay (2).

The rate of approach to equilibrium in distillation columns has recently been studied by Coulson (30) and by Berg and James (31).

A valuable contribution to the literature on the evaluation of fractionating columns is provided by The American Petroleum Institute Symposium on High Temperature Analytical Distillation (32).

4. Types of Fractionating Columns.

It would be impossible within a short space to discuss fully all the types of fractionating columns which are described in the literature and the most that can be done is to draw attention to the main types.

Bubble-cap Columns.

Bubble-cap columns are not frequently used in the laboratory owing to the difficulty of construction, large hold-up and high pressure drop.

Bruun and Faulconer (33) describe a jacketed, heat insulated column, about 2 metres long containing 100 bubble-cap plates. The column has a separating power equivalent to about 70 theoretical plates. Oldershaw (34) describes an efficient all glass bubble-plate column with low hold-up and high capacity. Collins and Lantz (35) have constructed an improved type of Oldershaw column with automatic solenoid operated take off and other accessories. The same authors have made a study of the effect of reflux-ratio on efficiency.

A perforated-plate column having removable plates is described by Langdon and Tobin (19). At low operating rates, plate efficiencies up to 90 percent were obtained.

Packed Columns.

Fenske et al (36, 37, 38) have made a careful study of packed columns, and have investigated a large number of packings. The most efficient packings, which had a large surface area and a high percentage of free space, were one and two turn helices of wire or glass, and 1/8" carding-teeth. It was concluded that single turn helices were the most efficient packing yet described in the literature. Fenske and his co-workers have described numerous columns using this packing. Columns of 11.9 and 13.1 metres have been constructed each having approximately one hundred theoretical plates (39); one of these is so arranged that it may be used with a reversed feed, the highest boiling point component being obtained first(from the bottom of the column).

Bailey (40) has used single turn glass Fenske helices to construct a column with a hold-up of less than 0.1 ml. per theoretical plate, and an H.E.T.P. of 5 cm. A still-head for reduced pressure is also described. A continuous apparatus described by Hufferd and Kranzt uses nickel helices and has over 50 theoretical plates and a throughput of 0.75 gallons per hour (41).

Other packings in common use in laboratory and industrial columns include Raschig rings, Lessing rings, jack-chains, Berl saddles, etc.

It has been observed by Fenske (38) that the efficiency of packed columns is often considerably enhanced by thorough wetting of the packing. This is usually carried out in the case of laboratory columns by increasing the operating rate at the beginning of a distillation, to the point at which the column

/floods

floods, i.e. vapour velocity becomes so great that reflux is unable to pass down the column. The resultant building up of liquid in the column wets the packing thoroughly and increases vapour-liquid contact. Similar observations have been made by Bragg (42) and Podbielniak (28).

A recent development in the design of packed columns has been the introduction of "dumped" gauze packing, one form of which is described in a recent paper by McMahon (43). The packing described by McMahon is stamped out from fine (100 x 100 mesh) wire cloth in the form of $\frac{1}{4}$" x $\frac{1}{4}$" Berl-saddles. The packing is characterised by its low weight, one cubic foot weighing only 25 lbs. and containing about 450,000 pieces of packing, free space being estimated at about 95 percent. The material used was brass gauze having a wire diameter of 0.0045 inches. In an 18 inch column, 2$\frac{7}{8}$ inches inside diameter, the H.E.T.P. was estimated to be only 1.5 inches, which for a column of this diameter represents a high standard of efficiency. This figure was calculated from the results of liquid air rectification, and is probably not very reliable as an absolute figure. Accurate test data for a six inch diameter column, using $\frac{1}{4}$" McMahon packing, fabricated from brass and Monel wire cloth, are given by Forsythe and co-workers (44). Using benzene-ethylene dichloride these authors found H.E.T.P. values of 2 and 4 inches with heights of 5 and 9 feet respectively. These are comparable with

/Bragg's

Bragg's published figures (42) for 6" Stedman packing. The pressure drop was found to be lower than with Stedman packing, maximum capacity and hold-up being substantially the same.

Another type of "dumped" gauze packing has been developed by Messrs. I.C.I. Ltd., (Brit. Patent 578,309). This is in the form of small Lessing rings of fine mesh gauze.

Dostrovsky and Hughes (45) describe a 20 mm. column packed for a length of 12 feet with 1/16" I.C.I. rings made from 100 x 100 mesh phosphor-bronze gauze. These authors use their column in a continuous still for the concentration of the O^{18} isotope, and estimate that the efficiency is about 450 theoretical plates at a boil-up-rate of 500 ml. of water per hour. A larger column using the same packing and having similar characteristics is also described by the same authors (46).

The use of I.C.I. packing in the columns used in the present research has already been described (Thesis, Section D).

Uniformly Packed Columns.

The need for fractionating columns offering a minimum resistance to the passage of vapours, with low operating hold-up and high fractionating power has resulted in the introduction of a number of uniform packings in which every effort has been made to combine all of these characteristics. Such columns are particularly useful in analytical work and for use under reduced pressure; throughput, however, is generally lower than with a bubble-cap column or one containing a "dumped" packing. Columns of this type depend for their efficiency on a long vapour path, equilibrium being established between the vapours and the liquid film on the surface of the packing.

Dufton (47) makes use of a wire spiral wrapped about an inner core, the whole being ground so as to fit the column closely. Smith and co-workers (48) have described a fully automatic column with metal vacuum jacket, in which the packing is a modified Dufton spiral about 10 feet in length. The column has a 50 ml. hold-up, 1,200 ml. per hour throughput and an efficiency of about 120 theoretical plates. Arrangements are provided for automatic collection of the distillate in separate containers, and recording of the volume of distillate and distillation temperatures.

A column having similar properties to the Dufton is the concentric tube column in which the packing consists of two or more concentric tubes. Columns of this type are described by Craig (49) and Selker, Burk and Lankelma (50). The very low H.E.T.P. obtainable with this type of column has been strikingly demonstrated by Naragon, Burk and Lankelma (51). The main disadvantage of this type of column is the very low throughput. The theory of concentric tube columns is discussed by Westhaver (52)

/Lecky

Lecky and Ewell (20) describe an extremely efficient packing consisting of a cupped stainless-steel gauze spiral fabricated around a central grooved metal rod, the whole being fitted closely into a glass tube. Efficiency is as high as 18 theoretical plates per foot, with hold-up and pressure drop of only 0.4 ml. per plate and 0.1 mm. Hg. per foot respectively. The heligrid packing of Podbielniak (28) is rather similar in construction and characteristics.

In the spinning band column described by Lesesne and Lochte (53) the packing is replaced by a rapidly rotating blade occupying the full length of the column. High efficiency and low hold-up and pressure drop are claimed for this type of column, which has been further developed by Baker, Barkenbus and Roswell (54). A spinning band column designed for operation in the pressure range 0.01 - 2.5 mm. Hg. and incorporating a novel type of manostat and take-off system is described by Birch, Gripp and Nathan (55).

The theory of the concentric tube type of column as developed by Westhaver (52) shows that separating efficiency should be improved by increasing the diffusion co-efficient in the gas phase. This has been accomplished in the rotary concentric tube column of Rossini and co-workers (56) in which the rectifying section is the empty annular space about 1 mm. in width formed by the inside surface of a

/stationary

stationary outer cylinder and the outside surface of a closed rotating inner cylinder. This type of column should prove to be of value in effecting fractionation at low pressures. The efficiency factor (throughput divided by hold-up per equivalent theoretical plate) is stated to be about 10 times the best values reported for other rectifying columns.

A new approach to the technique of vacuum fractionation is provided by the Bowman rotary vacuum still which makes use of a cooled rotating central core and heated outer walls (57).

5. Ancillary Equipment.

Developments in column design have been closely followed by improvements in column heads and associated equipment and automatic devices for the control of reflux ratio, automatic fraction collection and automatic pressure control. A number of recent references to such devices are given by Lloyd and Hornbacher (58) and by Rose (5).

b. AZEOTROPIC DISTILLATION.

In cases where fractional distillation of a mixture is ineffective in achieving a satisfactory separation owing to the similarity between the boiling points of the components, it is often possible to improve the separation by the addition of an azeotrope former which forms a maximum or minimum boiling point mixture with one or more of the compounds

/present

present, the differences in boiling points of the azeotropes being frequently greater than those of the components of the original mixture. If the desired compounds can then be separated from their azeotropes by chemical or physical methods, the advantages of such a method are obvious.

The selection of suitable azeotrope formers is frequently a matter of some difficulty although attempts have been made to evolve a system of classification of liquids and to predict the behaviour of mixtures. Ewell et al (59) evolved a system of classification based on the non-ideality of solutions due to hydrogen bonding and recognised five classes of liquids whereby it was possible to predict the qualitative behaviour of the mixture and the type of azeotrope likely to be formed. Work on similar lines has been done by Colburn (60) and by Benedict, Manson and Rubin (61).

Early literature on azeotropism is summarized in the classic works of Young (62) and Lecat (63). Horsley (64) has presented a condensed and systematic summary of azeotropes and non-azeotropes based largely on the work of Lecat (63). The same author (65) describes a graphical method for predicting the effect of pressure on azeotropic systems.

Examination of the literature summarized by Lecat (63) revealed that little work had been done which had any bearing on the present problem.

In a recent paper, however, Coulson and Jones (66) investigated the separation of 2- and 3- picolines and 2:6-lutidine by azeotropic distillation, using acetic and propionic acids and were able to separate the three bases in purities of 95 - 98 percent with little loss.

It is reasonable to assume that this method could be extended to include the higher homologues of pyridine and the quinoline homologues and it should prove to be a useful method of increasing the separation of the more complex fractions.

An important extension of azeotropic distillation is extractive distillation in which compounds of the same or similar boiling points but differing in chemical type are separated by the use of a third component which is fed to the column as reflux. The theory and advantages of this type of distillation are discussed by Benedict et al (61).

c. FRACTIONAL EXTRACTION.

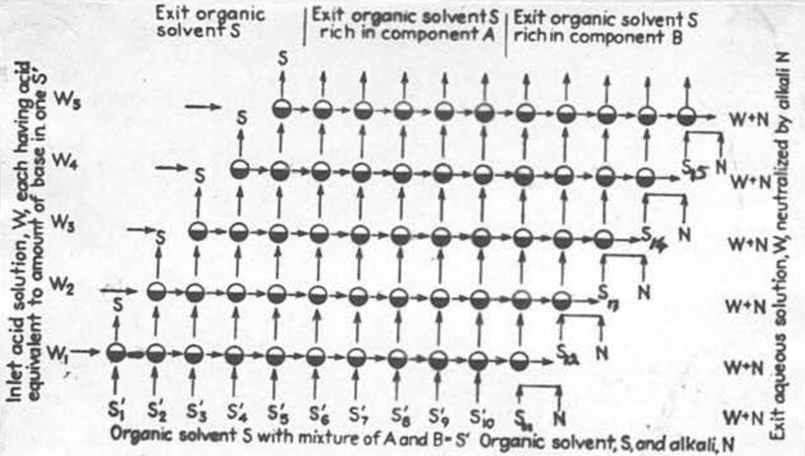
The use of liquid-liquid extraction on the industrial scale is a subject of continually increasing importance and its application in a diversity of ways to the recovery of valuable materials from effluents and in the refining of industrial products, particularly petroleum products, is too well known to require comment.

Processes in which a single solvent is used are usually extractive in character, their object being to separate a valuable material from a large bulk of liquid or alternatively to remove small quantities of a soluble impurity. Processes which employ two immiscible or partially miscible solvents are generally used to achieve separation of a mixture into its components and may be conveniently referred to as "fractional distribution" processes to distinguish them from those where a single solvent is used.

Such processes are in many respects similar to distillation processes and may be treated similarly from a theoretical standpoint. Fenske and Varteressian (67) for example, have studied the use of packed columns in distribution processes and have applied the concept of a theoretical plate and deduced exact mathematical relationships, while the use of the McCabe and Thiele method in the investigation of the system chloroform-water-acetic acid is described by Othmer (68).

Bailey and Axe (69) have used a continuous liquid-liquid extraction apparatus for the separation of petroleum bases by fractional distribution and a similar apparatus is described by Lochte and co-workers (70).

Jantzen (71) has made an exhaustive study of fractional distribution as a method of separating bases and describes apparatus and methods. He finds that the results obtained in practice agree closely with those expected from theoretical considerations.



Multiple-fractional-extraction method for separation of two bases.

FIG. 1

Of particular value is the simple scheme devised by Jantzen for separation of bases by distribution of the free bases and their hydrochlorides between an aqueous phase and an organic solvent phase. The process may be conveniently carried out in separating funnels and has been used in the course of the present work (Thesis, Section E). The operation is carried out as follows (see Fig. 1.).

The mixed bases are dissolved in an exactly equivalent amount of acid and are then liberated in ten equal stages by the addition of sodium hydroxide solution in portions, each of which is equivalent to one-tenth of the acid originally used. After each addition of alkali the bases are extracted with a solvent. In this way ten solvent fractions $S_1 - S_{10}$ are obtained containing bases of increasing strength.

S_1 is stripped with an exact equivalent of acid (one-tenth of the amount originally used for neutralisation of the bases) and the acid layer is then shaken with S_2 to S_{10} in turn. An interchange of bases takes place at each stage, the stronger bases accumulating in the acid layer while the weaker bases pass into the solvent layer. Meanwhile S_1 is shaken with a second portion of acid to remove final traces of bases and this is contacted with $S_2 - S_{10}$ in turn as previously. S_1 (stripped solvent) is then rejected and a third portion of acid is added to S_2 and the process repeated and so until five portions of acid have been added and five stripped solvents

/$S_1 - S_5$

S_1 - S_5 have been rejected. The remaining stages of the process are carried out as shown in Fig. 1 where each emerging acid layer is neutralised by adding an equivalent amount of sodium hydroxide solution and extracted with fresh solvent before proceeding through the remaining stages. Finally ten equal fractions S_6 - S_{15} containing bases of successively increasing strength are obtained. In the scheme shown the solvent layers move continuously in a vertical direction while the aqueous layers move horizontally.

Hunter and Nash (72) and Morton (73) have described Jantzen's method, but state that the original bases are simply divided into ten equal portions. The method given by Jantzen whereby the bases are roughly divided into fractions of increasing strength before starting the extraction scheme, seems to be much more logical and should increase the efficiency of the process.

There is no doubt that this method should be of great value in the study of the higher boiling shale bases and should effect an easy separation of pyridine and quinoline homologues.

d. FRACTIONAL CRYSTALLISATION.

Fractional crystallisation of picrates has been used throughout the present investigation as a method of separating pure components and the methods are too well known to require comment.

It is important to note, however, that mixed melting points are not always reliable as

/tests

tests of the identity of two picrates, as in some cases mixed picrates show no depression in the melting point. This behaviour is exhibited by the isomeric trimethylnaphthalene picrates (74) and by thiophene picrate with the picrates of thionaphthene and naphthalene (75).

e. CHROMATOGRAPHIC ADSORPTION.

The literature on chromatographic adsorption has been exhaustively reviewed by Zechmeister and Cholnoky (76) but the method does not appear to have been much used for the separation of pyridine homologues. Kondo (77) was able to separate pyridine and 2-picoline by adsorption on an alumina column and it is possible that the method could be extended to the higher homologues.

Chromatographic separation of picrates is rendered difficult by the ease with which these compounds are decomposed to the free base and picric acid, but presumably this difficulty could be overcome by the use of suitable adsorbents.

A review of recent developments in chromatography which includes paper and partition chromatography and the use of ion exchange resins has been given by Strain (78).

Although unsuited to the larger scale separation of bases, chromatographic methods may be of value in removing trace impurities and in determining the number and nature of the components of mixed fractions.

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PLATE 1.

General view of 14-Plate and 100-Plate columns, showing vacuum system and control panels.

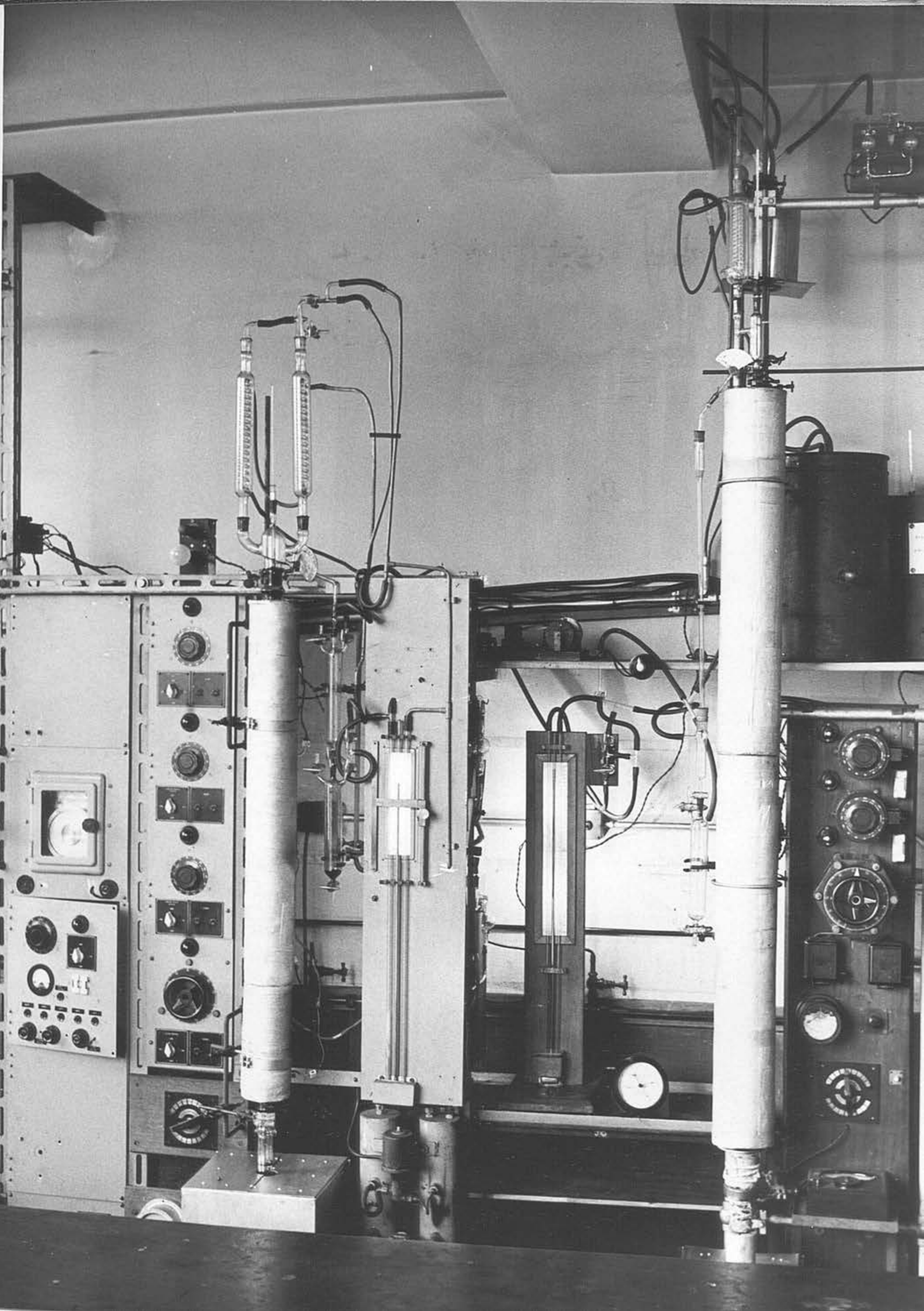


PLATE 2.

General view of 14-Plate column, showing vacuum receivers, control panel and manometers.

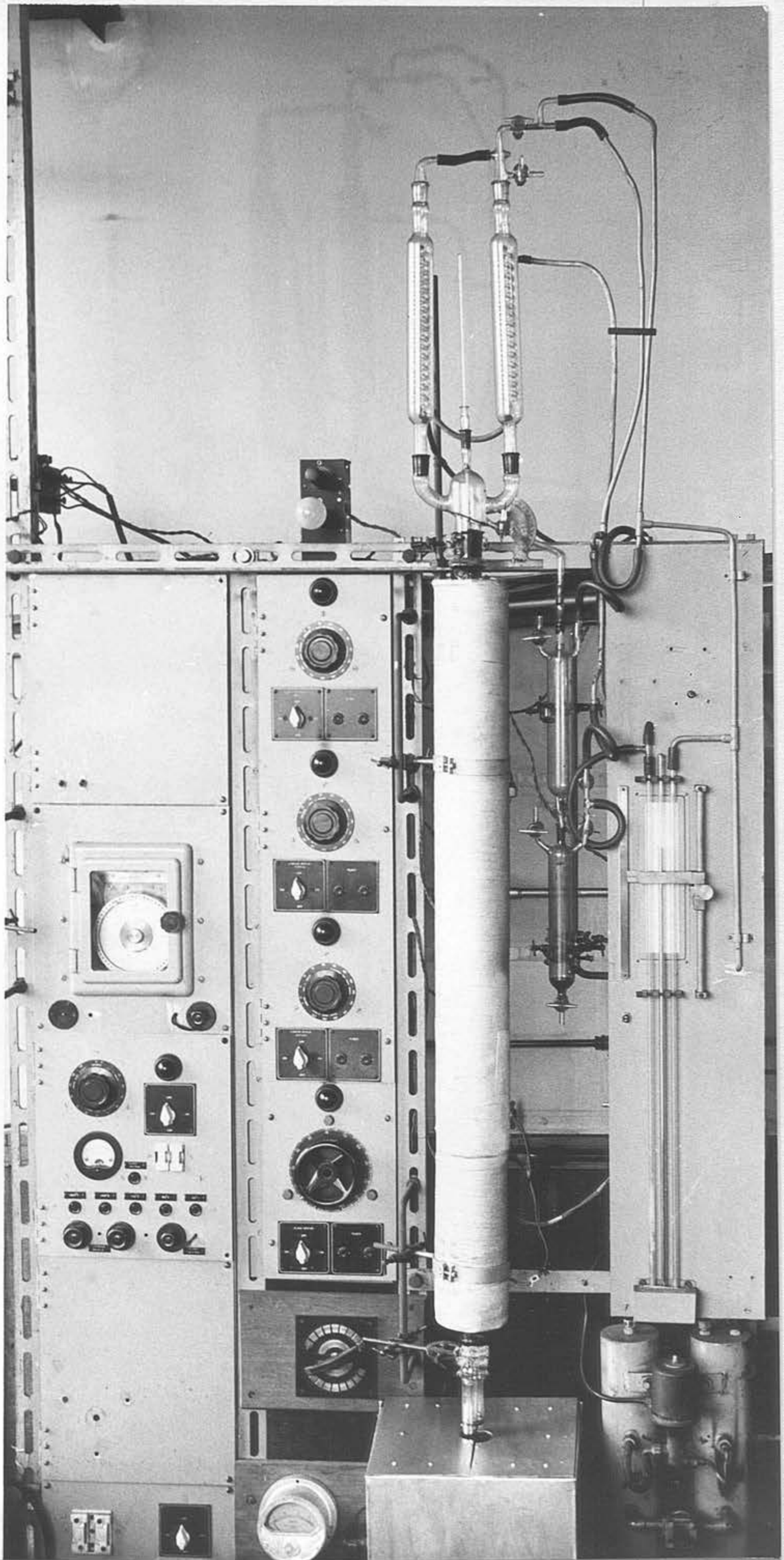


PLATE 3.

Base of 14-Plate column, showing heating arrangement, vacuum cylinders and solenoid valve.

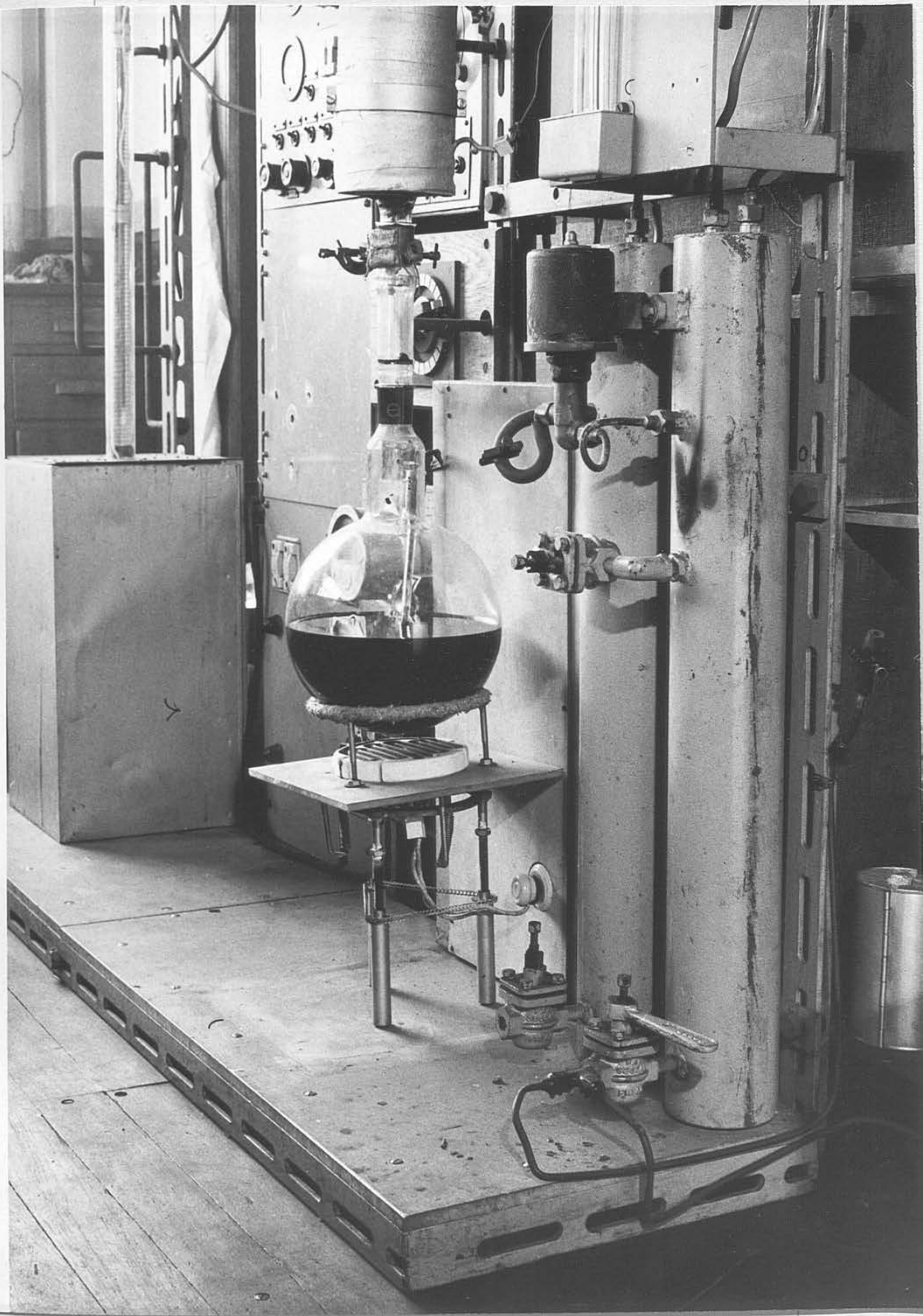


PLATE 4.

Electronic valve relay set for 14- and 100-Plate vacuum systems.

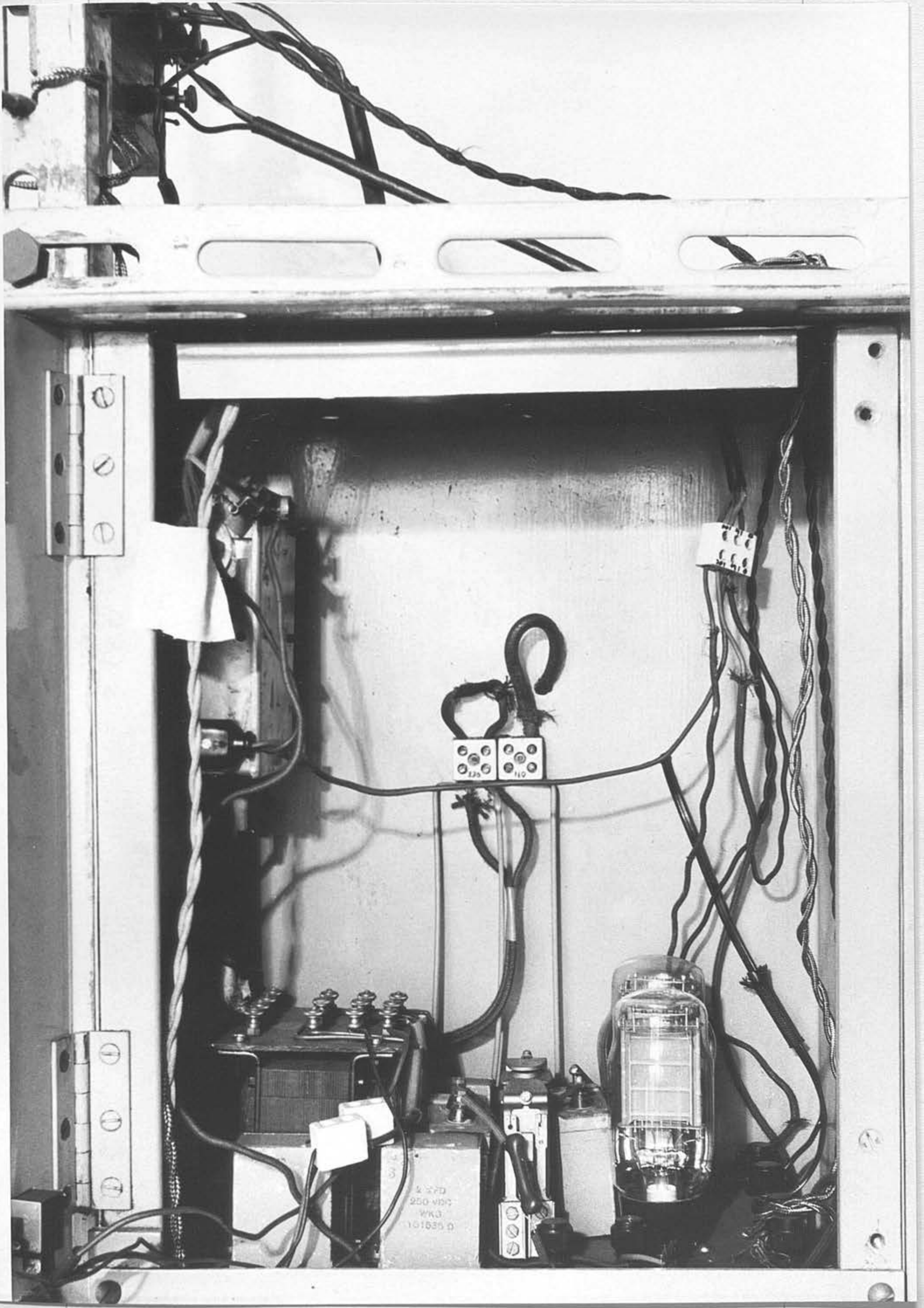

220
110
2 MFD
250 VDC
WKG
101535 D

PLATE 5.

General view of 100-Plate column. The protective casing around the buffer vessel and the thermostat box for the sulphuric acid manostat are to be seen mounted on the shelf behind the column.

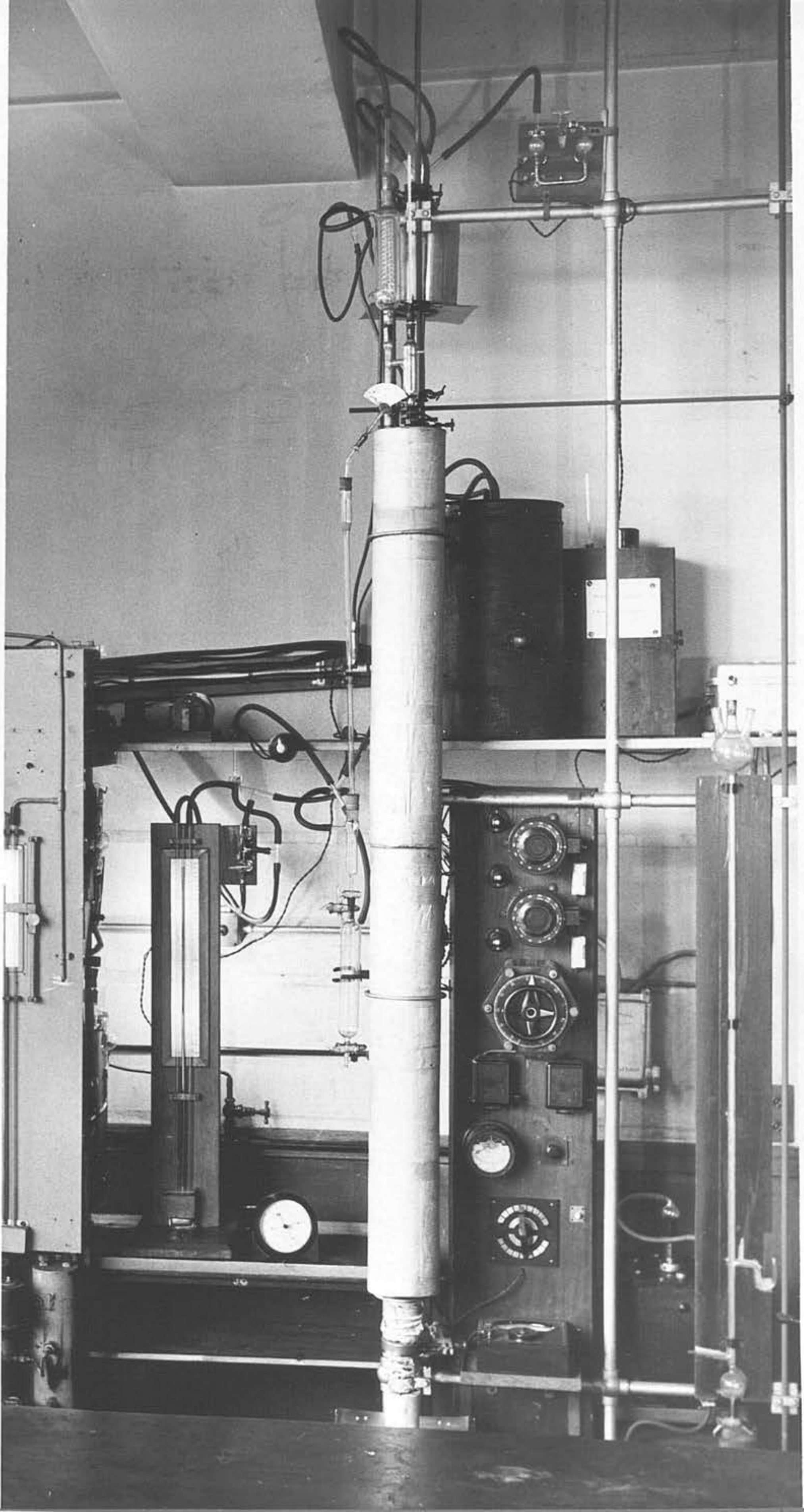


PLATE 6.

Base of 100-Plate column, showing heating arrangement (for vacuum operation), reflux meter and magnetic valve.

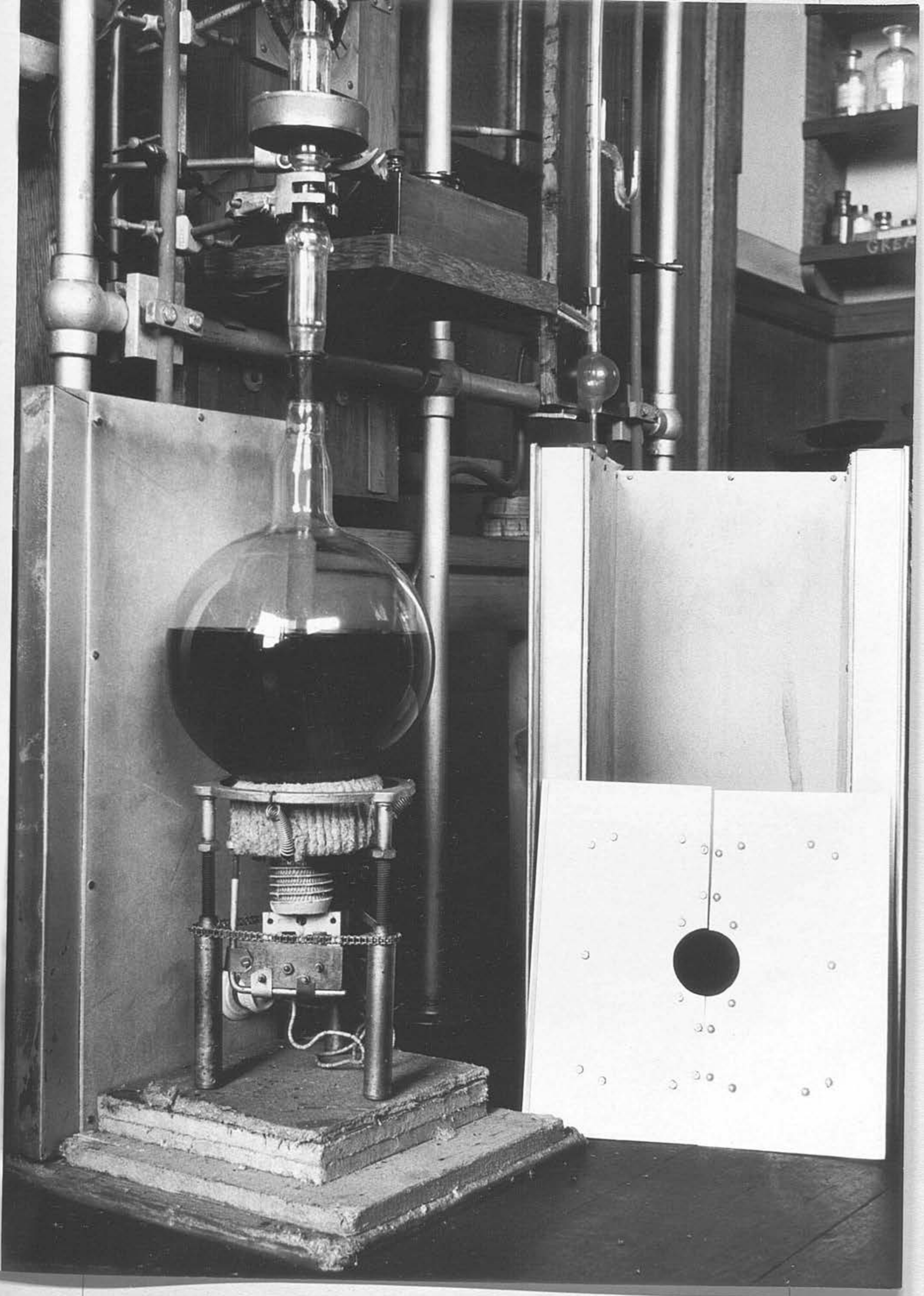

GREA

PLATE 7.

Top of 100-Plate column, showing tipping bucket still-head, catch-pot and safety-manostat.

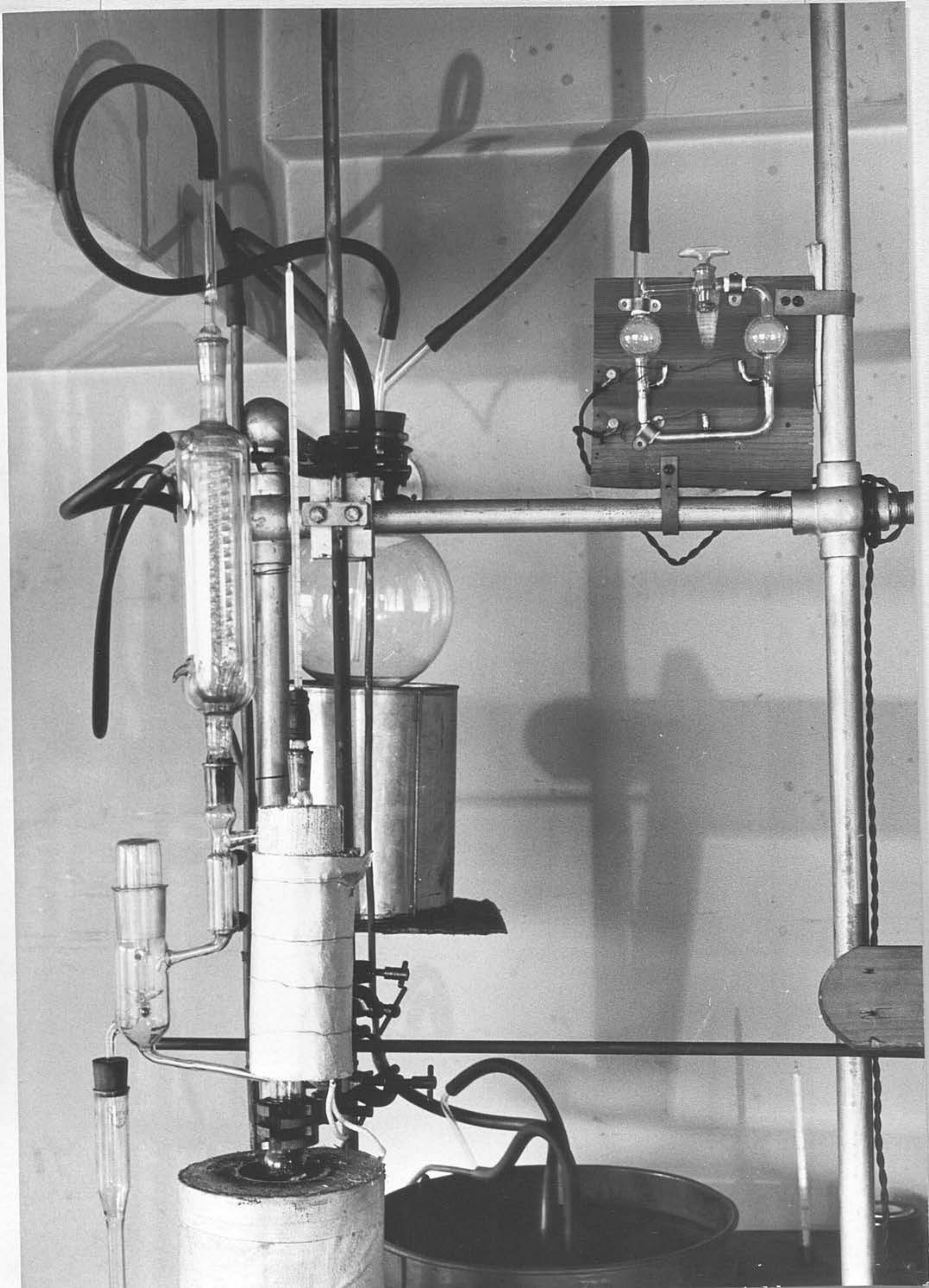
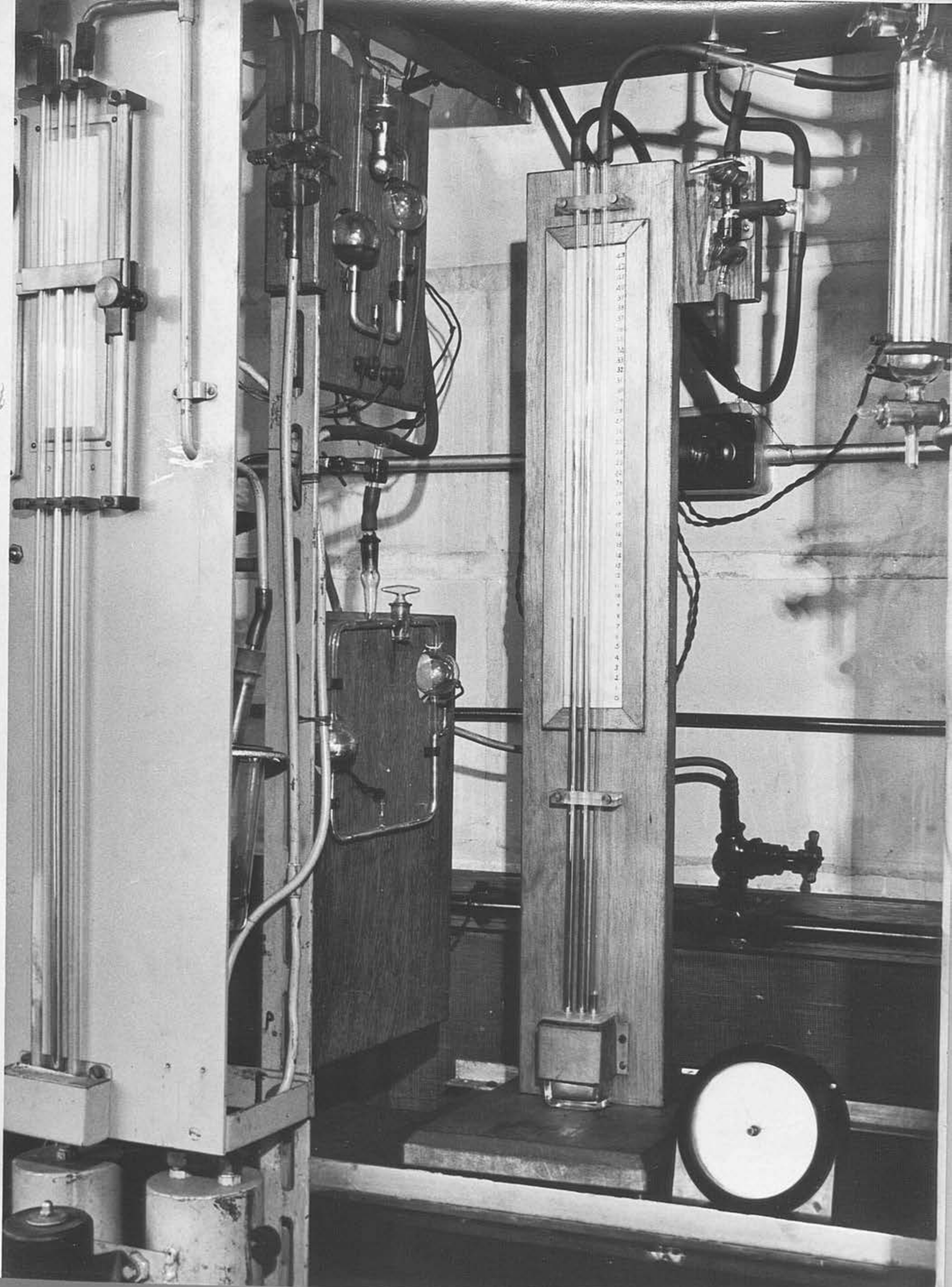


PLATE 8.

Left - 14-Plate column, manometers and manostats.

Right - 100-Plate column, manometers.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