THE BASIC COMPONENTS OF LIGNITE TAR

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

OBJECT OF RESEARCH

The object of this research was to identify and estimate the abundance of the basic (nitrogenous) components in Saskatchewan lignite tar as obtained by the Parry process of low temperature carbonization.

A fraction of the tar bases was separated from the crude tar by steam distillation followed by acid extraction. Vapour phase chromatography and infrared spectroscopy were utilized as the prime methods of compound separation and identification.

INTRODUCTION

I. Nature of the Lignite Tar Fraction Under Investigation

A representative sample of lignite coal (5.5 tons) that had been obtained from the Bridge Mine near Estevan, Saskatchewan, was shipped in sealed 45 gallon drums to the United States Bureau of Mines, Denver, Colorado. There, after crushing and drying, the lignite was carbonized by the Parry process (1) at a temperature of 499°*. The resulting tar and char were collected and sealed in separate containers and shipped to the Saskatchewan Research Council.

The Parry process is a method for the low temperature (ca. 420-540°) carbonization of lignite. It is a continuous process using a fluidized carbonizer. For a more complete discussion of this process reference should be made to the report by Parry (1). Tables giving the analysis of the Saskatchewan lignite before carbonization by the Parry process as well as yields of carbonization products and properties of the dry tar are given (2).

*All temperatures are given in Centigrade degrees.

II. Previous Investigations of Saskatchewan Lignite Tar

There have been several recent investigations into the composition and properties of Saskatchewan lignite tar.

i. Investigations Conducted on Tars Produced by Carbonization Methods Other than the Parry Process

Hudson and Cavers (3) carried out standard American Wood Preservers' Association distillations on Saskatchewan lignite creosote*. The tar acid (phenolic compounds) content in the fraction boiling below 355° at atmospheric pressure was found to be 33.5 per cent and the basic material comprised about 5 per cent of the whole creosote. The specific gravity was determined to be 0.980 as compared to 0.967 for North Dakota lignite creosote. No naphthalene and only a small amount of paraffin wax was indicated. The bromine test showed no unsaturated compounds were present. Catechol was isolated and the presence of polyhydric phenols was indicated.

Using lignite creosote obtained from Dominion Briquettes and Chemicals Ltd., Bienfait, Saskatchewan, Coxworth (4) identified several constituents of the phenolic fraction. The results of this work are summarized in Table I.

McKay (5) used a York-Scheibel counter-current extraction column to effect a partial separation of lignite creosote obtained from Dominion Briquettes and Chemicals Ltd. into its component fractions. Using a continuous phase of "Skelly F" and a dispersed phase of 10 per cent methanol - 30 per cent water, McKay was able to remove 97 per cent of the acidic material, which constituted about 38 per cent of the whole creosote.

*Creosote is the low boiling fraction of the tar.

Table I

Acidic Components of Lignite Creosote According to Coxworth (4)

Compound	Weight per cent of whole creosote
Catechol	0.9
4-methylcatechol	2.0
n-heneicosane	4.4
phenol	1.4
cresols	3.0
3-methoxy-4-methyl-phenol	2.4
C_8H_9OH phenols	1.7
$C_9H_{11}OH$ phenols	1.7
β -naphthol	0.3 (minimum)

Heidt, Rutherford and Pepper (6), in a continuation of the work done by McKay, found that ethanolamine was just as effective as methanol - water for the dispersed phase but less convenient. They found that shaking with a separatory funnel gave comparable results to the York-Scheibel extractor. Using a sample of Dakota Star Tar, Heidt, Rutherford and Pepper found that 17.1 per cent of the whole tar was steam volatile, of which 51 per cent was acidic. An atmospheric distillation on Garrison Dam tar to a vapour temperature of 306° indicated 30.5 per cent water, 39 per cent distillate and 27 per cent pitch residue.

ii. Investigations Conducted on Tar Produced by the Parry Process

Cram (7) studied the composition of a sample of Saskatchewan

lignite tar obtained by the Parry low temperature carbonization process (1). The carbonization was done at the United States Bureau of Mines in Denver, Colorado. Steam distillation was used for the preliminary separation of the tar. Three separate steam distillations were done. Run 1. was done by steam distilling the tar first from a basic medium and then from an acidic medium. The distillate from the basic medium contained the steam volatile tar bases and part of the steam volatile neutrals from which the tar bases were separated by extracting with dilute mineral acid. Alkali extraction of the distillate from the acidic medium was done to separate the tar acids from the neutrals. Runs 2. and 3. were done by steam distilling from the original neutral tar. This distillate was first acid washed then alkali washed to effect separation of the tar acids, tar bases and neutral oils. The results are given in Table II.

Table II

Quantitative Analysis of Lignite Tar

According to Cram (7)

Nature of Component	Weight Per Cent of Lignite Tar		
	Run 1.	Run 2.	Run 3.
Steam volatile tar acids	4.75	4.46	4.52
Steam volatile tar bases	0.34	1.62	1.29
Steam volatile neutrals	15.80	19.86	21.00
Non steam volatile tar	47.40	44.20	40.50
Water*	28.70	28.70	28.70
Losses, by difference	3.01	1.16	3.89

* Found by distilling whole tar to slightly over 100° and weighing the aqueous distillate.

It is apparent that the method of distilling first from a basic medium and then from an acidic medium has the effect of sharply reducing the yield of basic components that may be isolated. This is possibly due to oxidation and/or polymerization of these types of compounds.

The acidic fraction isolated from the second steam distillation (neutral medium) was thermally distilled using a Podbielniak "Mini Cal" series 3400 spinning band fractionation column. Cram reported the separation was not complete and most of the components appeared in several different distillate fractions. Each of the fractions obtained by thermal distillation was analysed by gas chromatography. By comparing the relative retention times of the unknown peaks to those of available authentic compounds, eleven phenolic compounds were identified conditionally.

To confirm his results further Cram collected the eluted tar acids from the chromatographic analysis and examined them by means of infrared spectroscopy. A short glass tube held over the exhaust port of the gas chromatography machine proved to be a good fraction collector. Both the spectra of authentic compounds and data compiled in the literature were used in interpreting the infrared spectra of the collected tar acid fractions.

By measuring the areas under the peaks in the chromatograms Cram estimated the concentrations of most of the phenols identified. A summary of the results of Cram's work is shown in Table III.

Cram also reported the presence of catechol, pyrogallol and a third polyhydric phenol in the lignite tar.

Table III

Identified Components of Lignite Tar as Reported by Cram (7)

Tar Component	Abundance* %
phenol	1.7
o-cresol	0.65
m-cresol, p-cresol	1.38
2,6-xylenol	0.025
2,4-xylenol	0.33
2,3-xylenol	0.04
3,4-xylenol	0.005
o-ethylphenol	0.02
p-ethylphenol	0.46
3-ethyl-5-methylphenol	0.01
indan-4-ol	trace
2,3,5-trimethylphenol	trace
2,3,4-trimethylphenol	trace

*Based on wet tar found to contain 28.7% water.

III. Related Investigations on the Basic (Nitrogenous) Fraction of Coal Tar

i. Investigations Involving Methods of Analysis Other Than Vapour Phase Chromatography and Infrared Spectroscopy

Several reports have appeared on the separation and identification of one, or a small group of coal tar bases. Many of the methods that were

used were based on types of chromatographic analysis other than vapour phase chromatography. Walker (8) was able to identify pyridine, 2-methyl-, 2,6-dimethyl-, and 2,4,6-trimethylpyridine in "crude pyridine oil". Oŝcic (9, 10) gave conditions for the separation of pyridine and its methyl derivatives using activated carbon and a variety of solvents. Column chromatography was used by Amemiya and Koguchi (11) to identify and determine the concentration of pyridine, 2-methyl-, 3-methyl- and 2,6-dimethylpyridine. They used a method originally devised by Vignes (12). Kalechits, Salimgaruva and Tumbusova[13] developed a chromatographic procedure for the separation of mono- and bicyclic phenols and bases from coal tar. Paper chromatography was used by Faderl and Kuffner (14) to identify the oxidation products of some alkyl pyridines. In analysing Colorado shale oil Dinneen, Smith, Van Meter, Albright and Anthoney (15) used Florisil, a synthetic magnesium silicate, to concentrate the nitrogen containing compounds. Florisil shows an affinity for such compounds. After this initial separation a Florex column was used to separate the nonbasic nitrogen compounds from the basic nitrogen compounds. In a later paper Dinneen, Cook and Jensen (16) estimated the abundance of the different types of nitrogen compounds in Colorado shale oil. They reported that over half of the basic nitrogen compounds were pyridines, dihydropyrindines, indoles and quinolines with the pyridines being the most abundant group. The pyrrole fraction was small.

Isolation and identification by chemical means, usually following a preliminary fractionation, has also been an important method for the analysis of coal tar bases. Ochiai (17) reported the isolation of pyridine, 2-methyl-, 2,4-dimethyl-, 2,6-dimethylpyridine and aniline from low boiling

coal tar fractions. By forming the dithiocarbamates with carbon disulphide Shannon and Warren (18) were able to separate primary and secondary amines from coal tar. Ishikawa and Sai (19) separated 2-methyl-, 2,6-dimethyl-, 2,4-dimethyl- and 2,4,6-trimethylpyridine from coal tar by forming the corresponding N-oxides. Using aqueous urea, Milner (20) isolated 2,3-dimethylpyridine from a mixture containing 2,3-, 2,4-, and 2,5-dimethylpyridine. The 2,3-dimethylpyridine formed an insoluble urea addition complex. Using a similar method Arnall (21) was able to isolate 4-ethylpyridine from the 2,4,6- 2,3,6-trimethylpyridine fraction of the coal tar bases. Bartz (22) described a reaction involving the condensation with formaldehyde that was used to separate a mixture of 3-methyl-, 4-methyl- and 2,6-dimethylpyridine. Other processes have been patented for the isolation of carbazole from coal tar (23, 24). 2,3-Cyclopentenopyridine (25) and 2-ethylpyridine (26) have been reported to be present in coal tar.

Matsumoto and Ihara (27), using fractional distillation and chemical analysis, were able to identify sixteen pyridine bases in the fraction of low temperature carbonization tar bases boiling below 190°. Pyridine, all of the monomethyl derivatives and several di- and trimethyl derivatives were found. Using similar methods on three fractions of low temperature carbonization tar bases boiling below 230° Sugiura, Ueno and Yokoyama (28) concluded that derivatives of pyrrole and indole also exist as well as the high boiling pyridine homologues. Rostafinska (29) attempted to separate the tar base fraction containing 3-methyl-, 4-methyl- and 2,6-dimethylpyridine into its constituents by forming the hydrochloride salts and then carrying out a fractional crystallization of these salts. This method met with little success. In a similar project Komatsu (30)

was able to separate quinoline, 2-methylquinoline and isoquinoline by crystallization of the corresponding sulphates.

Countercurrent distribution was studied by Golumbic (31) as a method for the separation and analysis of tar bases. Yamamoto, Arakawa, Higuchi and Yoshimura (32) also used liquid - liquid extraction for the separation of nicotinic and isonicotinic acids.

A review written in 1951 by Franck (33) covers several methods for the elucidation of the composition of coal tar including distillation, azeotropic distillation, selective solvent extraction, low temperature fractionation, partial chlorination and selective sulphonation. Oberkobusch (34) compiled a comprehensive list of 95 basic compounds that have been reported in the literature as having been isolated from coal tar. The list of compounds may be found in Appendix A.

ii. Investigations Involving the Use of Vapour Phase Chromatography and Infrared Spectroscopy

Of great importance are several recent papers dealing with the use of vapour phase chromatography and infrared spectroscopy for the identification of pyridine compounds in mixtures similar to the coal tar basic fraction. Using sixteen pyridine compounds boiling below 195° Brooks and Collins (35) reported retention times for six different stationary phases (Nujol, trixylenyl phosphate, Carbowax 1000, silicone oil M430, triethanolamine and glycerol) on Kieselguhr.

In general it has been found that the chromatographic peaks for the higher boiling pyridines are frequently quite unsymmetrical. This asymmetry appears in the form of tailing. It has been suggested (36) that this undesirable tailing effect was due to non ideal adsorption of the

sample compound on the surface of the solid support and not due to any property of the liquid substrate. Decora and Dinneen (37) reported the use of the solid support, "Tide", (a commercial detergent produced by Procter and Gamble) for the gas - liquid chromatographic separation of synthetic mixtures of pyridines. Tailing with Tide columns was much less than with the corresponding columns using Celite or Chromosorb as the solid support.

It was found that only if highly polar liquid substrates were used would Chromosorb or Celite give symmetrical peaks with pyridine compounds. The new solid support was used to study the selectivity of several nonpolar and slightly polar liquid substrates. The following such substrates were used; squalane, mineral oil, Apiezon-L, silicone hi-vacuum grease, silicone oil (D.C.703), Octoil, Octoil S, tri-*m*-cresylphosphate, diphenyl phthalate and L-699 (monohydroxyethyl-trihydroxypropylethylenediamine). Symmetrical peaks with little tailing were obtained for the pyridine mixtures. A study of the retention times using these columns indicated that the various liquid substrates could be separated into two groups. The first group (silicone oil, silicone grease, Octoil, Octoil S) gave non-selective separation dependent only on the boiling point of the pyridine compound. For these, the logarithm of the relative retention time plotted against the normal boiling point gave straight lines. The second major group, those that gave a selective separation based on differences of the activities of the pyridines in the liquid substrate, were classified into two sub groups:

(1) For squalane, mineral oil and Apiezon-L, in general the more basic pyridines had a greater relative retention time than the

less basic compounds of similar boiling point.

(2) For tri-m-cresyl phosphate, L-699 and diphenyl phthalate, the the pyridines of greater basicity had lower relative retention times.

Decora and Dinneen connected in series two columns having different liquid substrates to obtain a separation of close boiling pyridines; e.g. 2,6-dimethyl-, 3-methyl- and 4-methylpyridine boiling at 144.1°, 144.2° and 145.4° respectively. An L-699 on Tide column was used in series with a diphenyl phthalate on Tide column. The result was a good separation with symmetrical peaks for a synthetic mixture of several pyridine compounds boiling from 115° to 194°.

In the elucidation of the composition of coal tar spectroscopic methods have been used to analyse distillate fractions, or, as in the case of Cram (7), to analyse the eluent from gas - liquid chromatography columns. Kimura and Katsumoto (38) used ultraviolet spectroscopy to analyse quantitatively the coal tar fraction containing 3-methyl-, 4-methyl- and 2,6-dimethylpyridine. The abundance of each component was determined by absorption measurements on the mixture.

Using infrared spectroscopy Tsuda, Ikekawa, Shindo and Sato (39) analysed the fraction of coal tar pyridine bases boiling between 150°-200°. They identified 13 methyl-substituted pyridine homologues as well as 2-methyl-4-ethyl- and 4-methyl-2-ethylpyridine. Cook and Church (40) similarly used infrared spectroscopy for the determination of a synthetic mixture of twenty four pyridines similar in composition to the low boiling basic coal tar fraction. The mixture was fractionated and the infrared spectrum recorded for each fraction. The spectra of

commercial pyridines with little or no purification were used as standards for calibration. A plot of absorption (logarithm $\frac{I_o}{I}$) versus concentration in grams/liter at the wavelength of some characteristic peak was prepared for each of the components. A table of wavelengths of characteristic peaks for the 24 pyridines was given. The procedure is applicable to distillate fractions, each of which contains only a few homologues. Available standards limit the procedure to fractions boiling below about 185°. Shindo and Tamura (41) synthesized all of the monomethylquinolines and recorded their infrared absorption spectra. Karr, Estep and Papa (42) recorded the infrared absorption spectra for ten polymethylquinolines including 2,8-dimethylquinoline, 2,4,6-, 2,4,7-, 2,4,8-, 2,5,7-, 2,5,8-, 2,6,8-, 2,7,8-, 2,3,8-trimethylquinoline and 2,4,7,8-tetramethylquinoline. All but the 2,3,8-trimethylquinoline were synthesized by this group.

In a more fundamental work Podall (43) attempted to correlate absorption spectra and structure of alkyl pyridines. He observed that alkyl pyridines have characteristic infrared absorption maxima in the region from 11 to 15 microns and characteristic band patterns in the region from 5 to 6 microns which depend primarily upon the position of the alkyl group on the pyridine ring. The alkyl groups on the pyridine ring have characteristic bands in the 7 to 9 micron region depending on whether the alkyl group is methyl, isopropyl or tert-butyl. He also showed that the ultraviolet absorption maxima can be similarly correlated with the position of substitution of the alkyl groups and are essentially independent of whether the alkyl group is methyl, ethyl, isopropyl or tert-butyl.

A table of the principal absorption maxima in the region from 11 to 15 microns for 29 alkylpyridines has been reported by Podall. He

also reported the band patterns of several alkyl pyridines in the 5 to 6 micron region. The band patterns are not very distinct but they do depend on the position of substitution and are independent of the nature of the group present. A similar table of absorption maxima characteristic of the alkyl groups present in alkyl pyridines for the range 7 to 9 microns was given.

Podall compared the alkyl benzenes with the analogous pyridines in the 11 to 15 micron region. The principal absorption maxima for these two types of compounds showed the greatest resemblance when the compounds being compared had the same number of aromatic hydrogens and the closest symmetry; e.g. 1,2,3,5-tetramethylbenzene and 2,4,6-trimethylpyridine.

EXPERIMENTAL PROCEDURES

I. Isolation of the Tar Base Fraction from Whole Tar

The Saskatchewan Research Council supplied a sample of Parry low temperature carbonization (1) tar obtained from Saskatchewan lignite coal. The water content was determined by the Dean and Stark method (44).

To reduce the extent of cracking and polymerization a steam distillation rather than a thermal distillation was used as a preliminary separation step. On the basis of Cram's findings (7) distillation was carried out from a neutral solution. Cram had noted that distillation from a basic medium had the effect of reducing the yield of basic components. He stated that this was possibly due to polymerization and/or oxidation.

Steam distillation was carried out on 1014 grams of tar. To be consistent with the work of Cram the tar-water mixture was first thoroughly mixed before the sample was taken for distillation. The steam was superheated 20-25° and heat was also supplied to the distillation flask through a heating mantle. The exit temperature of the gaseous distillate was thus kept between 102 and 105°. The purpose of the heating mantle and superheated steam was to prevent bumping caused by the accumulation of water in the flask.

After 20 l. of distillate had condensed it was apparent that essentially all of the steam volatile material had been removed from the tar. The accumulated distillate was saturated with salt and then continuously extracted with ether using a liquid - liquid extractor. The organic material obtained by evaporating the ether weighed 298.1 g.

(29.4 per cent of the whole tar). This material was extracted first with 10 per cent aqueous sodium hydroxide (6 x 50 ml.) to remove the steam volatile tar acids (phenolic compounds), then with 10 per cent hydrochloric acid (6 x 50 ml.) to remove the steam volatile tar bases. The residue was the neutral (mainly hydrocarbon) fraction. It was noted that a small fraction of the steam volatile tar was both ether and alkali soluble. This fraction (12.9 g.) was isolated and tested for the presence of nitrogen by the sodium fusion method. The test was negative and the fraction was not further examined. A flow diagram of the separation procedure is presented in Figure 1. The results are summarized in Table IV.

Table IV

Analysis of Saskatchewan Lignite Tar*

Fraction	Weight, g.	Percentage of Tar
Steam volatile tar bases	7.1	0.70
Steam volatile neutral oil	221.5	21.84
Steam volatile tar acids	56.6	5.57
Steam volatile alkali and ether soluble material	12.9	1.27
Water, Dean and Stark method	304.4	30.02
Non steam volatile tar (by difference)	411.5	40.60
Total	1014.0	100.00

*Initial weight of tar - 1014 g.

II. Thermal Distillation of Tar Bases

Gas chromatography was to be used as the principal method of

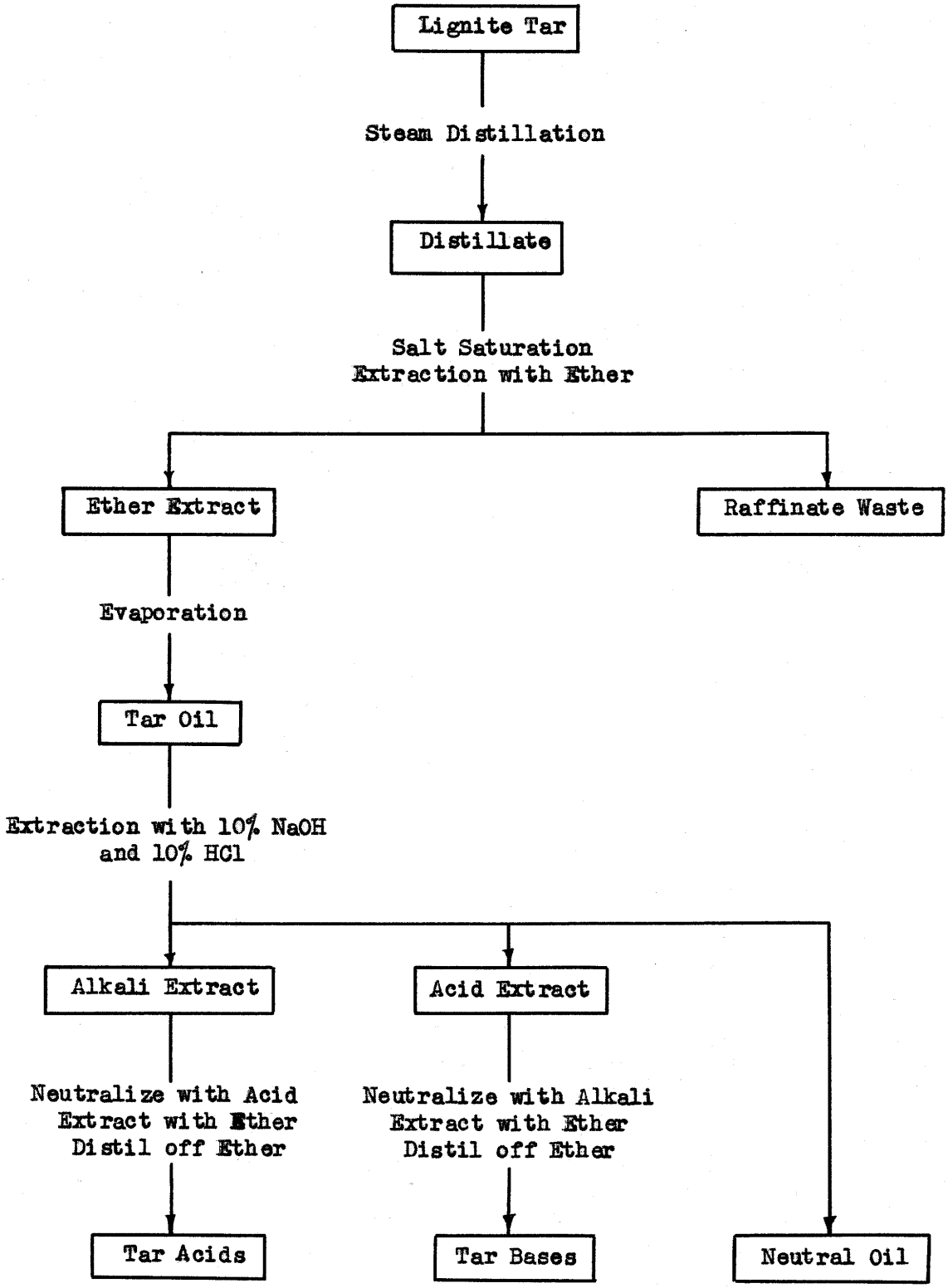

Figure 1

Separation Procedure for Lignite Tar

separation and identification. To simplify the problem and get fractions more suitable for chromatographic analysis the mixture was first distilled under reduced pressure using a semimicro fractionating flask and fraction collector. The vacuum distillation was carried out under a pressure of 27 mm. of nitrogen. Six fractions were collected. The residue was then distilled at atmospheric pressure directly from a small flask into a seventh receiver. The results are shown in Table V.

Table V

Thermal Distillation of Tar Bases

Fraction	Temp. Range, °C (at 27 mm.)	Weight, g.	Description
1	67-80	0.795	Colorless oil
2	80-121	0.956	Colorless oil
3	121-156	1.254	Straw colored oil
4	156-166	1.092	Amber oil
5	166-182	0.827	Dark amber, viscous oil
6	182-190	0.252	Red, very viscous oil
7	Heated to char; atmospheric pressure	0.350	Red, semi-solid

Total recovery - 5.526 g.

Starting material - 6.631 g.

Per cent recovery - 83.3%

III. Methods Used for Analysis

i. Preliminary Identification by Vapour Phase Chromatography

Vapour phase chromatography was to be used in the separation

and characterization of the components of the seven fractions resulting from the thermal distillation. After a suitable chromatographic column was chosen, several runs were made to determine the optimum conditions for the separation of the fraction being studied. Then all the available authentic compounds that could occur in this fraction, as well as the fraction itself, were chromatographed under identical conditions. Since relative retention times are more nearly constant for a compound than are retention times themselves each authentic compound was mixed with an internal standard before injection. The relative retention time of a compound is defined as the retention time (time from point of injection to point of maximum concentration in the detector cell) divided by the retention time of an internal standard. The internal standard is so chosen that its position can be positively identified in the chromatograph of the mixture since the relative retention times of the unidentified peaks must be based on the same internal standard as the relative retention times of the authentic compounds to be comparable. One of the first compounds to appear in the chromatogram of the mixture is usually chosen as the internal standard. The internal standard must not have a retention time so small in relation to that of the other components in the mixture that errors in its measurement cause unreasonably large errors in the calculation of relative retention times.

In the preliminary stages of the analysis of unknown mixtures by gas chromatography it is a distinct advantage to use a non-selective column. For such a column the retention time of a compound is dependent primarily on its boiling point rather than its chemical properties, polarity, and so on (37). A plot of relative retention times of available

authentic compounds suspected to be in the unknown mixture versus the corresponding boiling points will give a smooth curve. Dinneen and Decora (37) reported that when some liquid substrates were used on Tide a plot of the logarithm of relative retention time versus boiling point resulted in a linear relationship. The relative retention times of compounds authentic specimens of which are not available may be estimated from their boiling points using this graph. This procedure was used for all of the fractions analysed and, wherever possible, repeated with a second column.

It was apparent that some groups of compounds boiled over such a small temperature range that it would be necessary to make use of differences in properties other than boiling point to achieve chromatographic separation. The peaks found using a non-selective column that were suspected of representing mixtures of two or more compounds were re-chromatographed on a selective column that was shown to be capable of separating these mixtures.

ii. Identification by Infrared Spectroscopy

To substantiate further the tentative chromatographic identifications many of the peaks were collected for analysis by infrared spectroscopy. The infrared absorption spectrum of each major peak eluted was recorded and identification was attempted by comparison with the absorption spectra of the available authentic compounds as well as with the data reported in the literature (40, 41, 42, 43).

iii. Quantitative Analysis of the Steam Volatile Tar Bases using Vapour Phase Chromatography

The method of using the areas under the peaks to calculate

the relative abundance of each component in the chromatogram of a mixture is well known. Messner, Rosie and Argabright (45) found that relative detector response was independent of temperature, concentration of sample and carrier gas flow rate as long as these factors remained constant during the determination. They also reported that the areas under the curve can be converted to mole per cent using a correction factor for a homologous series of compounds.

In the ideal case, where each peak is symmetrical with no appreciable tailing or leading, well separated from neighboring peaks, and if all the material injected is eluted, very accurate quantitative results may be achieved. Even when a shoulder occurs on a peak, if it is well defined quantitative results may be obtained (46). Since rather incomplete chromatographic separation was achieved in this work exact quantitative results were not possible. Quantitative estimates were made for some of the lower boiling compounds by dividing the area of the individual peak in question by the total area under the curve representing the whole fraction. The concentration of a peak in each of the fractions was calculated in order to determine the abundance of that peak in the whole steam distillable basic fraction.

IV. Equipment Used for the Analysis

i. Vapour Phase Chromatography

(a) Chromatograph

A Beckman GC-2 vapour phase chromatography unit was used. The unit was equipped with the Beckman Dual Column Valve. With this arrangement the sample could be injected into either of two columns installed in the chromatograph. In the preliminary stages of the research this

made it possible to determine the optimum operating conditions for two columns without having to cool the machine and change the columns between runs. The Dual Column Valve also made it possible to collect peaks from one column as they were eluted and immediately inject them into another column.

The machine was equipped with a flash evaporator built in this laboratory. This consisted of a brass block as illustrated in Figure 2. The sample was deposited at the bottom of the vertical hole with a syringe. A 3/8" D. x 1/16" silicone rubber disk held in place by a Swagelok hex nut at the top of the block provided a leak-proof seal for the syringe needle. The ¼" hole bored in the top of the block served as a thermometer well. A length of heating tape (12") wound around the block and connected to an autotransformer was used to control the temperature of the evaporator.

Helium was used as the carrier gas. The flow rate was measured with a soap bubble flow meter attached to the exit tube from the detector cell.

(b) Columns

When the commonly employed solid supports (Celite, Chromosorb and firebrick) are used for the chromatography of pyridine compounds tailing frequently results (page 9). Tide, a commercial detergent manufactured by Procter and Gamble, was treated by the method of Dinneen and Decora (37) to prepare a solid support. Tide is manufactured by a spray drying process. Surfactants such as sodium alkylbenzene sulphonate and sodium alkyl sulphate are intimately mixed with the inorganic constituents (silicates, higher molecular phosphates and sodium sulphate). The detergent was first crushed and screened. The 40-60 mesh portion

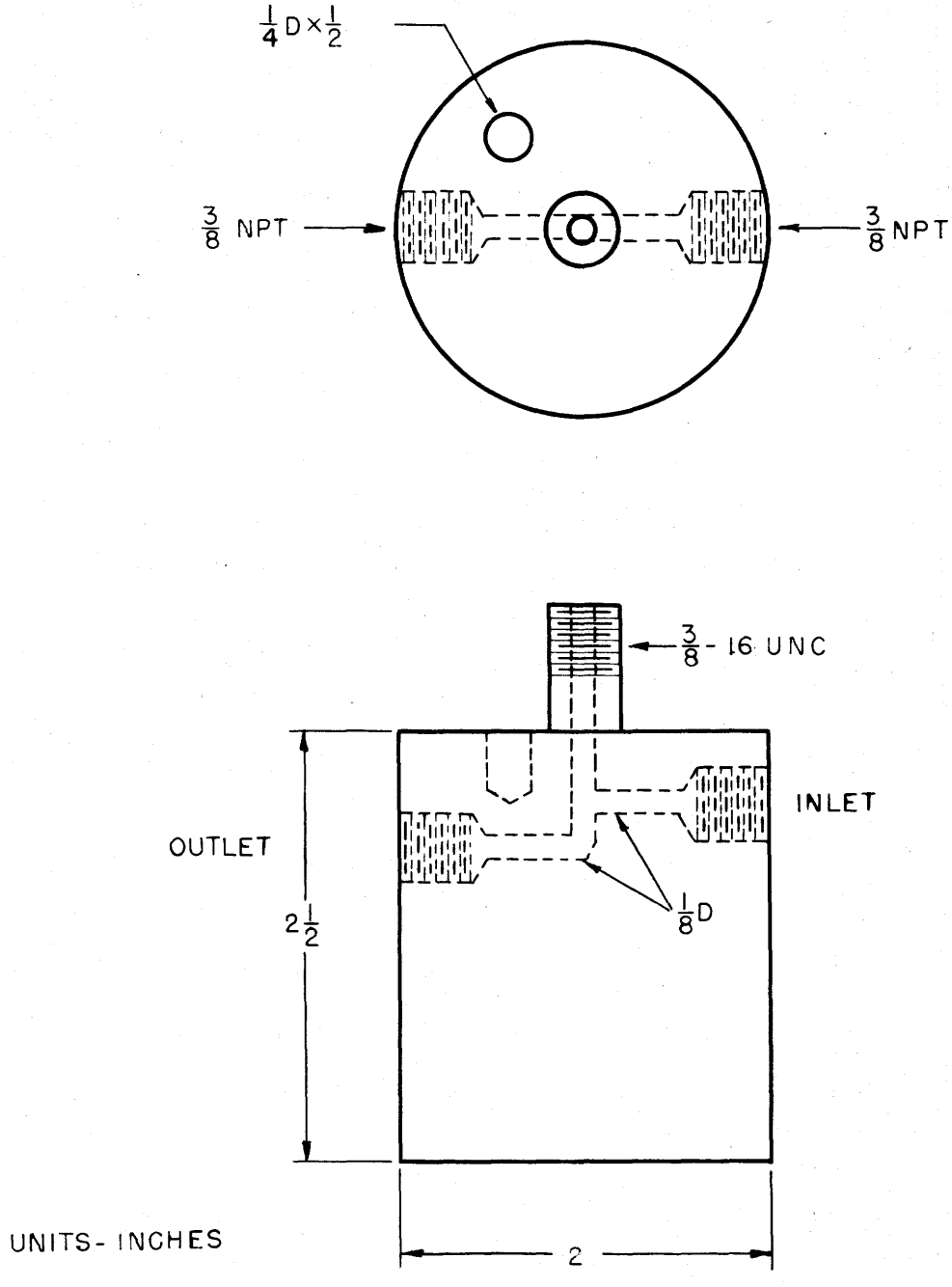

FIGURE 2 FLASH EVAPORATOR

was retained and heated at 190° for 24 hours. This was followed by extraction with petroleum ether (b.p. 40-60°) in a Soxhlet extractor for about 24 hours. The porous, mainly inorganic residue was dried at 110° and then screened once more. The 40-60 mesh portion was retained and used as a solid support.

In preparing columns using this support enough liquid substrate to give the desired concentration (expressed as grams of liquid substrate divided by grams of solid support x 100) was dissolved in a volume of the appropriate solvent approximately equal to half of the volume of the solid support being used. This liquid substrate solution was added to the solid support, thoroughly mixed and then the solvent was rapidly evaporated (boiling was avoided as the prepared Tide was fragile and tended to crumble). The packing was then dried at 110° and screened. The 40-60 mesh material was retained. A list of liquid substrates used is given below.

(1) Silicone Oil "Embaphase" - May and Baker Ltd.

(2) S.E.-30 (highly methylated silicone oil) - General Electric Co.

(3) Diphenyl phthalate.

(4) Apiezon-N - Edwards and Co., Toronto.

(5) L-699 (monohydroxyethyltrihydroxypropylethylenediamine) - National Aluminate Corp.

It was noted that, particularly with long Tide columns, the flow rate would decrease slightly as the column grew older. This was remedied by removing and re-screening the packing with special effort taken to remove the fine (<60 mesh) material. This resulted in more reliable retention times. Prepared Tide was quite fragile and it appeared

that any fine material that remained in the packing after screening would tend to pack and eventually restrict the gas flow.

It has been claimed in commercial bulletins that Fluoropak (a polymeric fluorocarbon) is a suitable solid support for the vapour phase chromatography of pyridine compounds. This material was obtained and columns using "Fluoropak 80" were prepared in much the same manner as those using the prepared Tide. It was found that 10 per cent is about the maximum concentration of liquid substrate that can be used with Fluoropak 80. Greater concentrations cause the packing to become too "wet" to pack. The prepared Tide would flow like a dry solid even after 25 per cent liquid substrate had been added.

All columns were packed in $\frac{1}{4}$ inch O.D. copper tubing. A mechanical vibrator was used to ensure consistent packing of the columns.

(c) Fraction Collectors

In many cases it was necessary to collect fractions eluted from the vapour phase chromatography columns either for infrared analysis or for further chromatographic analysis. To prevent any pressure change in the detector cell, which in turn would cause spurious signals to be sent to the recorder, a collection system must be designed to cause no back pressure. As in Cram's work (7), straight sections of 6 mm. glass tubing approximately 7 cm. in length were placed over the end of the exhaust tube from the detector cell during the interval that the recorder indicated that the peak of interest was being eluted. In addition a pipe cleaner was wrapped around the tube and wetted with a volatile solvent to help condense the lower boiling compounds. The tubes were corked and stored horizontally in a tray other than during the collection interval.

The infrared analysis of the condensed liquid was to be carried out on a liquid film. The liquid (5-10 μl.) had to be transferred to the sodium chloride plates of the infrared spectrophotometer without contamination. Plungers, in the form of cylinders having a diameter slightly larger than the internal diameter of the glass collection tubes, were cut with a cork borer from a sheet of silicone rubber 3/16 inches thick. These plungers were pushed down the collection tubes thus forcing the condensed material onto the sodium chloride plates for infrared analysis.

If the collected material was to be re-chromatographed, the plunger was forced only part way through the tube. The material clinging to the walls of the collector above the plunger was brought down to the surface of the plunger by centrifuging. The liquid could then be readily collected with a syringe for re-injection.

The amount of any one compound that can be collected from a single injection of a mixture depends on the relative abundance of that compound in the mixture that can be injected at one time. If a large volume of the mixture is injected the efficiency of separation becomes poor. Usually the maximum sample size was found to be 10-20 μl. and 3 to 10 separate injections were required to collect sufficient amounts of individual peaks for infrared analysis or re-chromatography.

ii. Spectroscopic Analysis

All spectra were measured on a Perkin-Elmer, Model 21, Recording Infrared Spectrophotometer using sodium chloride optics. All samples were measured as liquid films.

V. Source of Reference Compounds

Table VI

Reference Compounds

Compound	Source*	Compound	Source*
pyridine	An.	3-methylaniline	E.
2-methylpyridine	R.T.	4-methylaniline	B.D.H.
3-methylpyridine	R.T.	1,3-dimethylaniline	A.
4-methylpyridine	R.T.	2,3-dimethylaniline	A.
2,6-dimethylpyridine	R.T.	3,4-dimethylaniline	A.
2,5-dimethylpyridine	A.	quinoline	F.
2,4-dimethylpyridine	A.	2-methylquinoline	A.
2,3-dimethylpyridine	R.A.	7-methylquinoline	A.
3,5-dimethylpyridine	A.	8-methylquinoline	E.
3,4-dimethylpyridine	A.	2,8-dimethylquinoline	A.
2,4,6-trimethylpyridine	An.	2,4-dimethylquinoline	A.
2,3,6-trimethylpyridine	R.A.	4,6-dimethylquinoline	A.
3-ethylpyridine	G.	isoquinoline	An.
2-methyl-5-ethylpyridine	M.C.&B.	3-methylisoquinoline	A.
4-methyl-3-ethylpyridine	A.	indole	B.D.H.
aniline	An.	2-methylindole	A.
2-methylaniline	B.D.H.	2,3-dimethylindole	A.

*Chemical Supply House

A. - Aldrich Chemical Co.
An. - Anachemia Co.
B.D.H. - British Drug House
M.C.&B. - Matheson, Coleman and Bell Co.
R.T. - Reilly Tar and Chemical Co.
R.A. - Rutgerswerke-Aktiengesellschaft - Germany
E. - Eastman Kodak Co.
F. - Fisher Chemicals
G. - Courtesy Mr. Giam Choo Seng

EXPERIMENTAL RESULTS AND CONCLUSIONS

I. Qualitative Analysis of the Fractions Resulting from the Thermal Distillation of the Steam Volatile Tar Bases

i. Fraction One (b.p. 67-80°/27 mm.)

The following columns were prepared and used to analyse Fraction 1: 6' L-699 (10%) on Fluoropak, 5' Apiezon-N (25%) on Tide, 9' silicone oil (10%) on Tide, 14' silicone oil (10%) on Tide, 6' L-699 (10%) on Tide in series with a 6' diphenyl phthalate (10%) on Tide and a 10' L-699 (11%) on Tide in series with a 10' diphenyl phthalate (11%) on Tide. The 9' silicone oil (10%) on Tide column gave the best separation. A temperature of 130° and a flow rate of 20 ml./min. were found to give the best separation for Fraction 1 (Figure 3). Since pyridine was chosen as the internal standard it was necessary to determine which peak in the chromatogram of the fraction was pyridine. The chromatogram of Fraction 1, with a trace (about 5 per cent) of pyridine added, was compared with the chromatogram of pure Fraction 1 determined under the same conditions. The position of the pyridine peak was apparent from the relative increase in height of one particular peak. Authentic compounds were mixed with about 10 per cent pyridine and chromatographed under the same conditions as the unknown Fraction 1. The logarithms of the relative retention times of the authentic compounds were plotted against their boiling points (Figure 4). The points deviated only slightly from a straight line. From this graph it was apparent that some peaks could result from more than one compound. Tentative identities were assigned to the

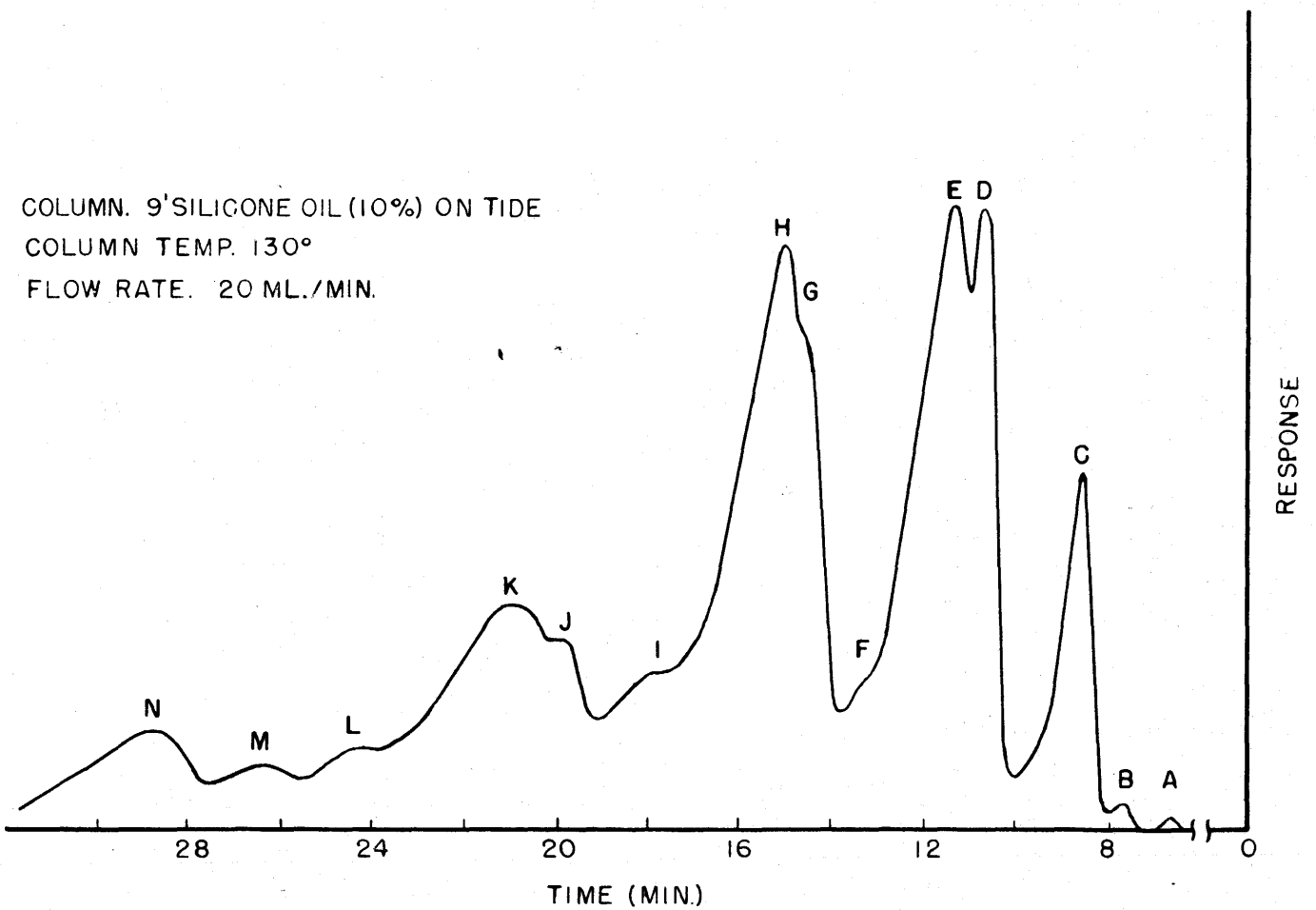

FIGURE 3. CHROMATOGRAM OF FRACTION I

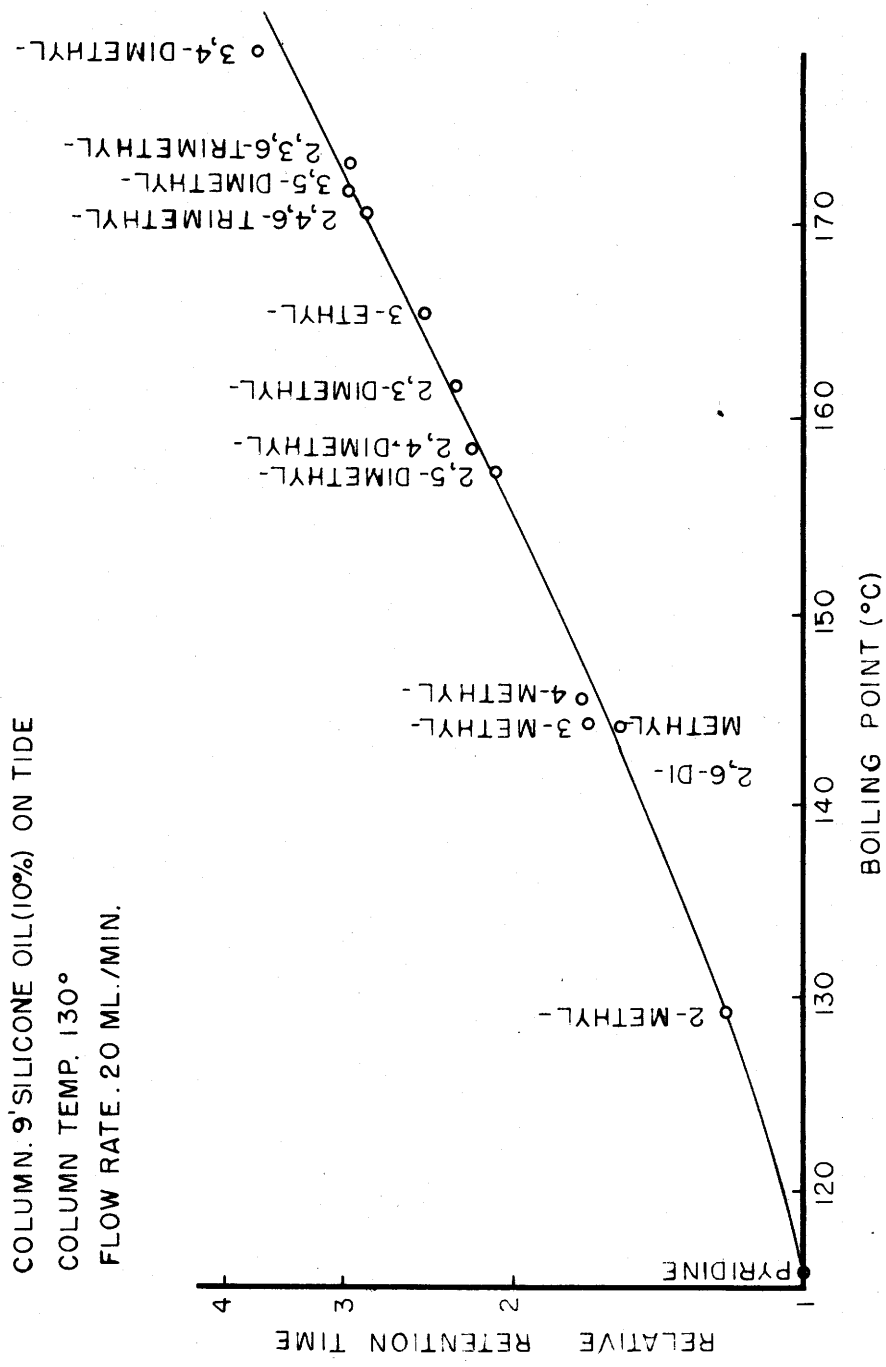

FIGURE 4

RELATIVE RETENTION TIMES OF SUBSTITUTED PYRIDINES

major peaks in the chromatogram of the fraction. Results are given in Table VII.

Table VII

Chromatographic Analysis of Fraction 1*

Peak*	Relative Retention Time	Possible Identity
A	1.00	pyridine
B	1.13	
C	1.25	2-methylpyridine
D	1.55	2,6-dimethylpyridine
E	1.68	3-methylpyridine 4-methylpyridine
F	1.98	
G	2.12	2,5-dimethylpyridine
H	2.22	2,4-dimethylpyridine 2,3-dimethylpyridine
I	2.62	3-ethylpyridine
J	2.97	2,4,6-trimethylpyridine
K	3.14	2,3,6-trimethylpyridine 3,5-dimethylpyridine
L	3.62	
M	3.93	3,4-dimethylpyridine
N	4.30	

*A 9' silicone oil (10%) on Tide column at 190° and flow rate of 20 ml./min. was used.

*Refer to Figure 3.

The degree of separation obtained began to deteriorate with this column so a second 9' silicone oil (10%) on Tide column was prepared and used to analyse Fraction 1 (Figure 5). Relative retention times were quite similar although not identical to those found using the first column. The compounds represented by the major peaks were collected and examined by infrared spectroscopy. By comparing these spectra to the spectra of available authentic compounds several peaks were identified. The results are shown in Table VIII. One of the major

Table VIII

Components of Fraction 1 Identified by Infrared Studies

Peak*	Compounds Present
B	2-methylpyridine
C	3-methyl-, 4-methyl- and 2,6-dimethylpyridine
F	2,5- and 2,4-dimethylpyridine
G	2,3-dimethylpyridine
J	2,3,6-trimethylpyridine

*Refer to Figure 5

absorption maxima in the spectra of the collected fractions appeared at 1700 cm^{-1}. It occurred in each of the collected fractions. The peak did not occur in the spectra of the authentic compounds. This peak is discussed further in Appendix B.

A few small peaks in the chromatogram of Fraction 1 remained unidentified. The relative retention times of the peaks whose

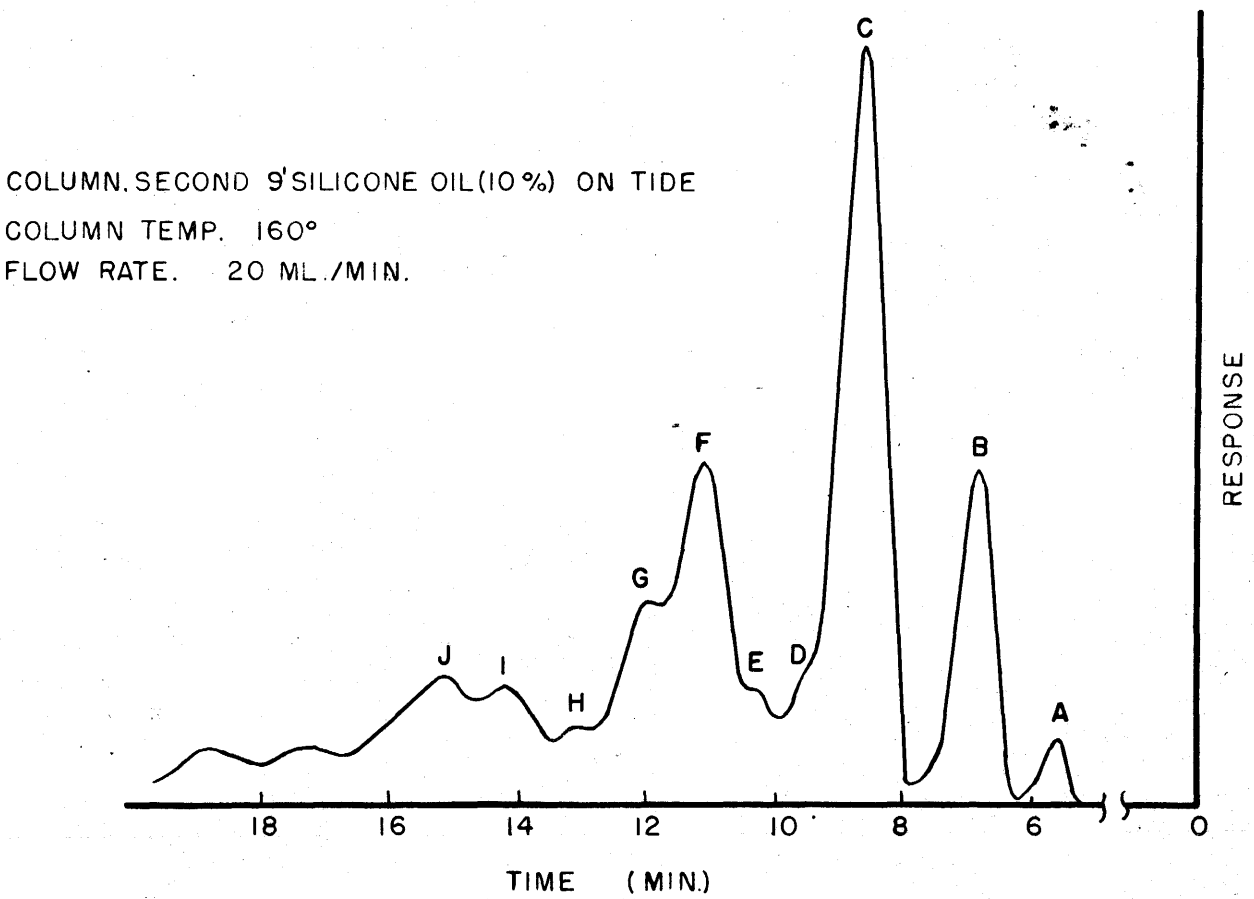

FIGURE 5. CHROMATOGRAM OF FRACTION I

identity had been determined by infrared spectroscopy were calculated from Figure 5 and used in plotting the graph shown in Figure 6. The relative retention times of the unidentified peaks were calculated from this same chromatogram. The relative retention times of those pyridines, for which no authentic specimens were available, were estimated from Figure 6 by using their reported boiling points. Peaks D, H and I were identified as 2-ethyl-, 3-ethyl- and/or 4-ethyl- and 2,4,6-trimethylpyridine respectively. This method eliminated errors in relative retention times that would arise from small errors in the measurement of retention times that occur when each of the authentic compounds is mixed with the internal standard and chromatographed separately.

The chromatographic analysis of Fraction 1 on the 9' silicone oil (10%) on Tide column (Figures 5 and 6) indicated that peak C could contain 3-methyl-, 4-methyl- and 2,6-dimethylpyridine and that peak F could contain 2,5- and 2,4-dimethylpyridine. Infrared analysis of the fractions corresponding to the two peaks showed that all of these compounds were present. A series column was prepared in which a 10' diphenyl phthalate (11%) on Tide column was joined to a 10' L-699 (11%) on Tide column (37). A mixture of 3-methyl-, 4-methyl-, 2,6-dimethyl-, 2,5-dimethyl- and 2,4-dimethylpyridine was completely resolved on this column. Peaks C and F were collected from the chromatography of Fraction 1 on the second 9' silicone oil (10%) on Tide column (Figure 5) and rechromatographed on the series column. Peak C contained approximately equal amounts of 3-methyl-, 4-methyl- and 2,6-dimethylpyridine and peak F contained 2,5- and 2,4-dimethylpyridine in approximately equal amounts.

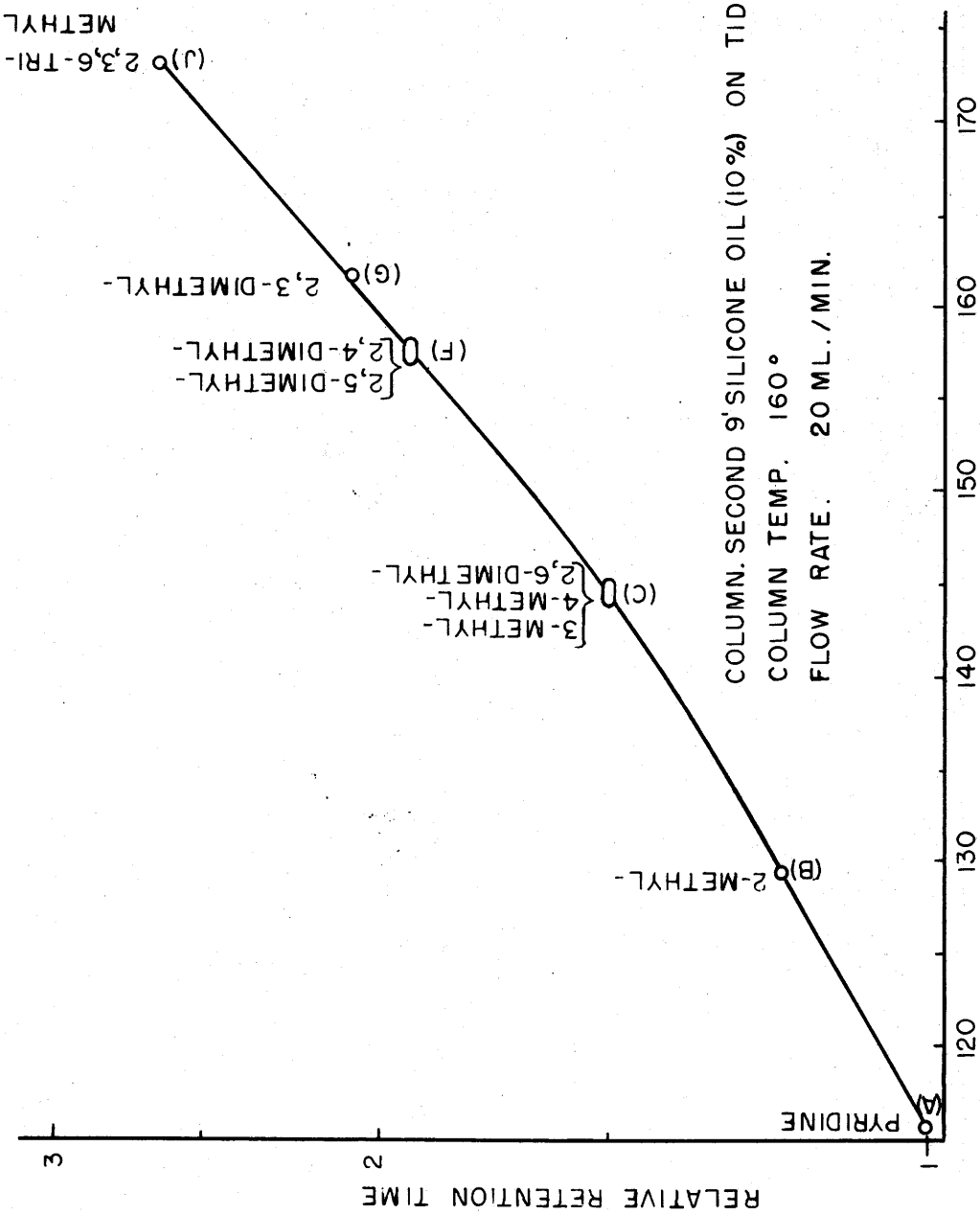

FIGURE 6

RELATIVE RETENTION TIMES OF SUBSTITUTED PYRIDINES

An attempt was made to use the series column to analyse the whole of Fraction 1. The lower boiling compounds were readily identified but the higher boiling components gave broad, indistinct peaks. The temperature was raised to 160° but it was apparent that at this temperature a considerable amount of liquid substrate was being removed from the column.

ii. Fraction Two (b.p. 80-121°/27 mm.)

The following columns were used in the analysis of Fraction 2: 6' L-699 (10%) on Tide, 6' L-699 (10%) on Tide in series with 6' diphenyl phthalate (10%) on Tide, 10' L-699 (11%) on Tide in series with 10' diphenyl phthalate (11%) on Tide, 6' silicone oil (10%) on Tide, 9' silicone oil (10%) on Tide, 15' silicone oil (10%) on Tide, 9' silicone oil (8%) on Tide and 5' Apiezon-N (25%) on Tide. The chromatographic separation of Fraction 2 was incomplete on all of the columns studied. Every chromatogram appeared to be a series of only partially separated peaks and shoulders. Separation of Fraction 2 was best using the same 9' silicone oil (10%) on Tide column that had been used for the analysis of Fraction 1 (Figure 7). Optimum conditions for separation were achieved when the column temperature was 130° and the flow rate was 60 ml./min.

It was necessary to determine the position of the pyridine peak in the resulting chromatogram. Using the same procedure that had been used for Fraction 1, a small trace of pyridine was added to Fraction 2. The relative increase in height of one peak in the resulting chromatogram indicated the position of the pyridine peak. Further information was obtained by superimposing the chromatogram of Fraction 1 on the chromatogram of Fraction 2 obtained under the same conditions.

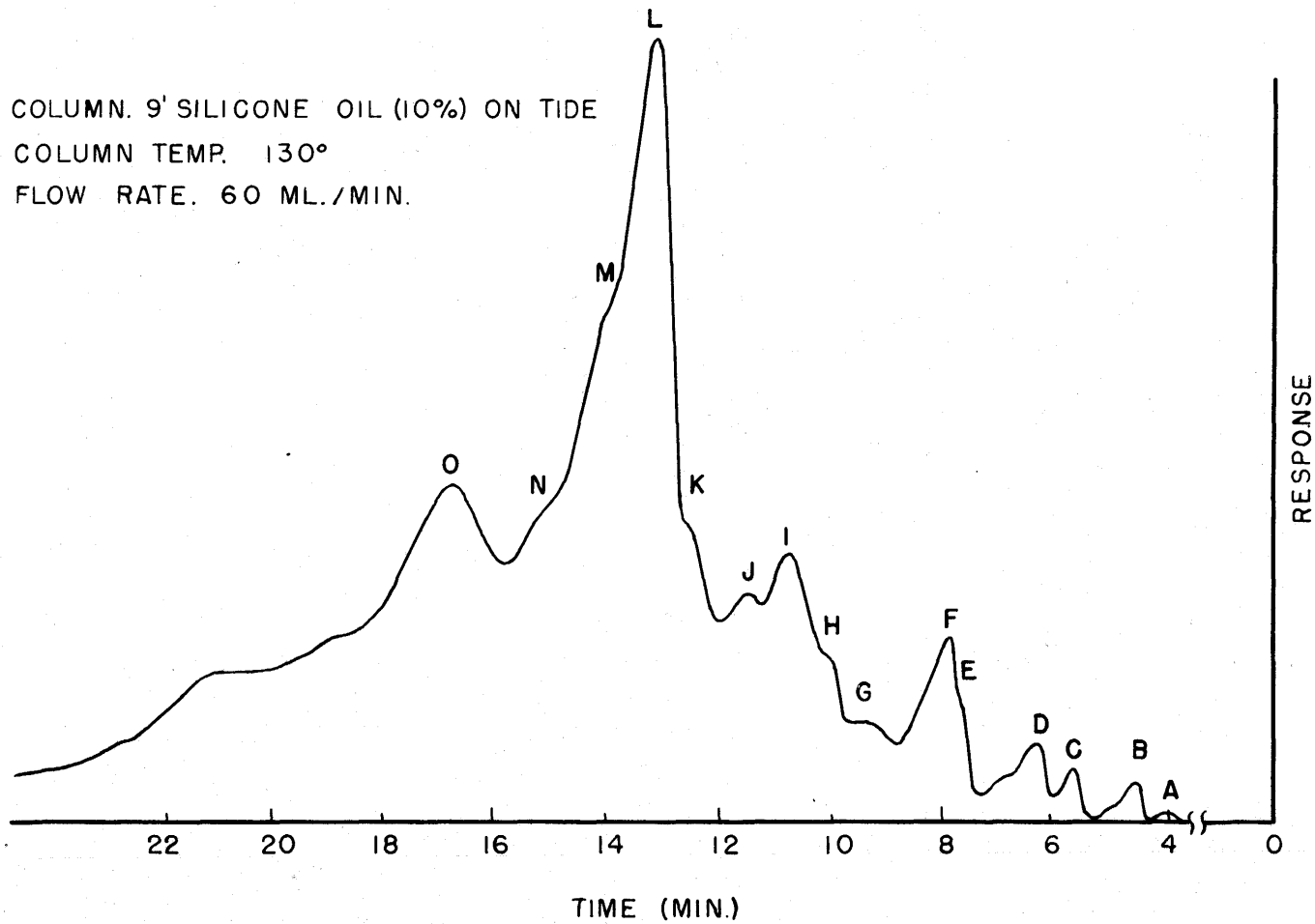

FIGURE 7. CHROMATOGRAM OF FRACTION 2

Comparison of the retention times showed that all of the peaks in Fraction 1 corresponded to peaks in the lower boiling part of Fraction 2. Although relative abundances in the two fractions were different it was possible to assign identities to all the components of Fraction 2 that had been previously identified in Fraction 1.

All of the authentic compounds that were available that might occur within the boiling point range of Fraction 2 were chromatographed. Their relative retention times were calculated (Table IX) and compared to those of the unidetified peaks in Fraction 2 (Table X). A tentative identification of several compounds was thus made. Within the boiling point range of this fraction many compounds could be expected (see Appendix A). From the incomplete separation obtained by chromatography it was evident that many closely boiling compounds existed in this fraction. Since only a few authentic specimens were available the interpretation of the results of the chromatographic analysis was difficult.

A second chromatographic analysis was carried out using a 12' Apiezon-N (10%) on Tide column. Although separation was not as complete as that obtained using the silicone oil column, relative retention time data indicated the presence of those compounds previously identified using the silicone oil column.

Using the 9' silicone oil (10%) on Tide column several fractions were collected. The infrared absorption spectrum of each was recorded. It was noted that for the collected samples the absorption maxima in the 10 to 15 micron region were small and indistinct. No positive identifications could be effected by comparing these spectra

Table IX

Relative Retention Times of Authentic Compounds*

Compound	Relative Retention Time	Compound	Relative Retention Time
2,4,6-trimethylpyridine	2.94	3,4-dimethylpyridine	3.62
aniline	3.04	2-methylaniline	4.38
2,3,6-trimethylpyridine	3.06	4-methylaniline	4.89
3,5-dimethylpyridine	3.10	3-ethyl-4-methylpyridine	5.24
5-ethyl-2-methylpyridine	3.34		

*A 9' silicone oil (10%) on Tide column at 130° and flow rate of 60 ml./min. was used.

with those of authentic compounds. It was concluded that the chromatographic separation was not adequate to provide fractions of sufficient purity to give good infrared absorption spectra. It is of interest to note that the absorption maximum that occurred at 1700 $cm.^{-1}$ in the material collected from the chromatography of Fraction 1 was also found in material collected from Fraction 2.

The principal peak (peak L, Figure 7) in the chromatogram of Fraction 2 represented a relatively large portion (about 2 per cent) of the steam volatile tar bases. All of the Fraction 2 material was used in an unsuccessful attempt to collect and rechromatograph enough of the compound or group of compounds represented by this peak to provide a quantitative elemental analysis. Further attempts to obtain this material are outlined in Appendix C.

Table X

Chromatographic Analysis of Fraction 2*

Peak*	Relative Retention Time	Possible Identity
A	1.00	pyridine
B	1.34	2-methylpyridine
C	1.67	2,6-dimethylpyridine
D	1.86	3-methylpyridine 4-methylpyridine
E	2.25	2,5-dimethylpyridine
F	2.32	2,4-dimethylpyridine 2,3-dimethylpyridine
G	2.73	3-ethylpyridine
H	2.95	2,4,6-trimethylpyridine
I	3.12	2,3,6-trimethylpyridine 3,5-dimethylpyridine aniline
J	3.34	5-ethyl-2-methylpyridine
K	3.63	3,4-dimethylpyridine
L	3.79	
M	4.08	
N	4.36	2-methylaniline
O	4.86	4-methylaniline

*A 9' silicone oil (10%) on Tide column at 130° and flow rate of 60 ml./min. was used.

*Refer to Figure 7. Peaks A to G identified by comparison with Fraction 1.

iii. Fraction Three (b.p. 121-156°/27 mm.)

Separation of the components of Fraction 3 was attempted on the following columns: 9' silicone oil (8%) on Tide, 12' Apiezon-N (10%) on Tide, 16' silicone oil (10%) on Fluoropak, 12' silicone oil (10%) on Fluoropak, 9' silicone oil (10%) on Fluoropak, 15' silicone oil (10%) on Tide, 9' silicone oil (10%) on Tide, 6' Apiezon-N (25%) on Tide and 6' L-699 (10%) on Fluoropak. The first three of the above columns gave the best separation. The analysis was first carried out on the 16' silicone oil (10%) on Fluoropak column (Figure 8). Optimum conditions were a column temperature of 190° and a flow rate of 35 ml./min. The principal peak in Fraction 3 (Peak A, Figure 8) had the same retention time as quinoline and was later proved to be quinoline by infrared spectroscopic analysis. Quinoline was chosen as the internal standard.

The available authentic compounds that could be expected to appear in this fraction were chromatographed. It was apparent from relative retention time data that peaks A, B and C (Figure 8) were quinoline, isoquinoline and 2-methylquinoline respectively. The infrared analysis of these three peaks supported the results obtained using chromatography. Peak E was identified as 4-methylquinoline by comparing its infrared spectrum with absorption data reported in the literature (41).

The chromatographic analysis was repeated using a 9' silicone oil (8%) on Tide column. Once again the presence of quinoline, isoquinoline and 2-methylquinoline was indicated.

The fraction was then analysed on the 12' Apiezon-N (10%) on Tide column (Figure 9). Conditions were: column temperature of 190°

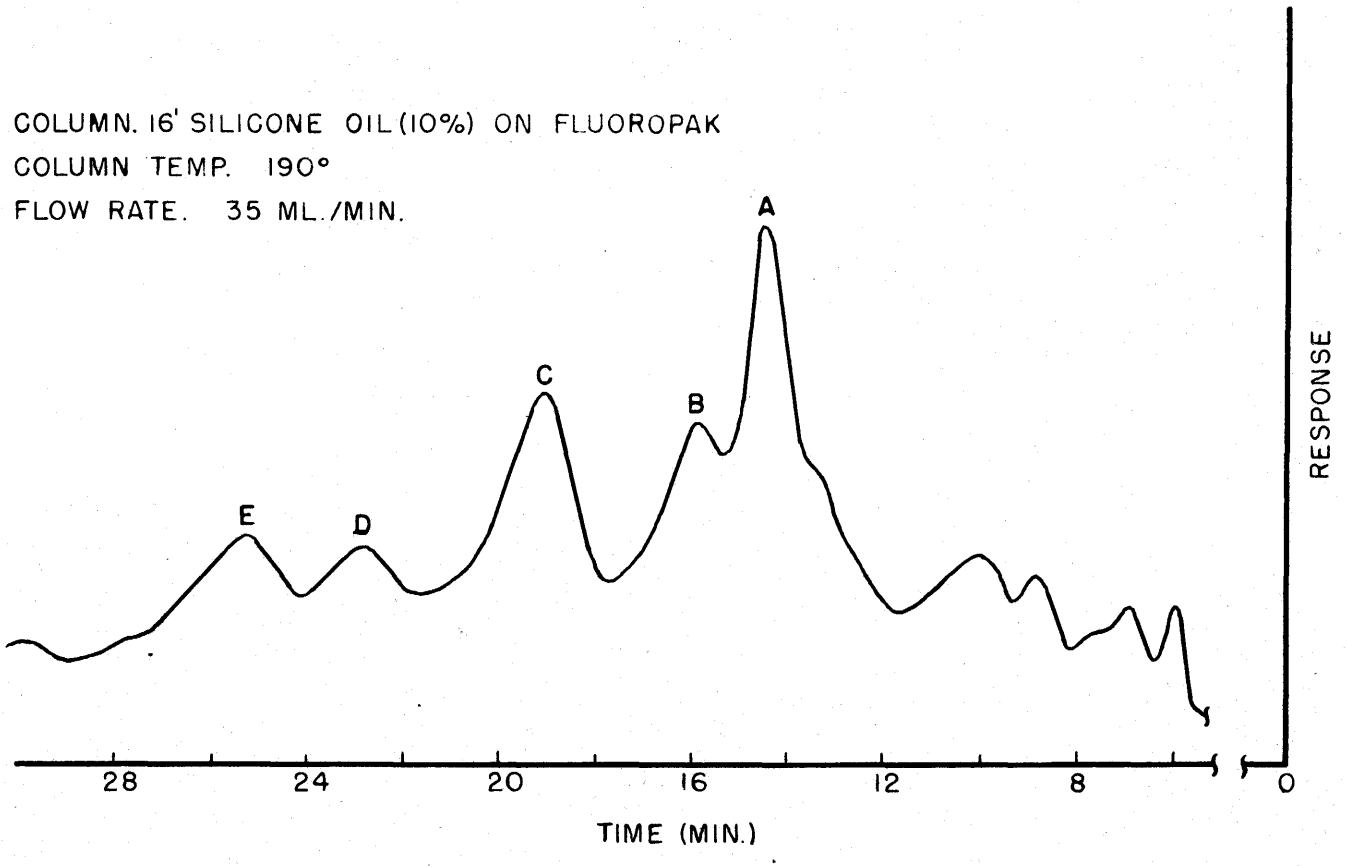

FIGURE 8. CHROMATOGRAM OF FRACTION 3

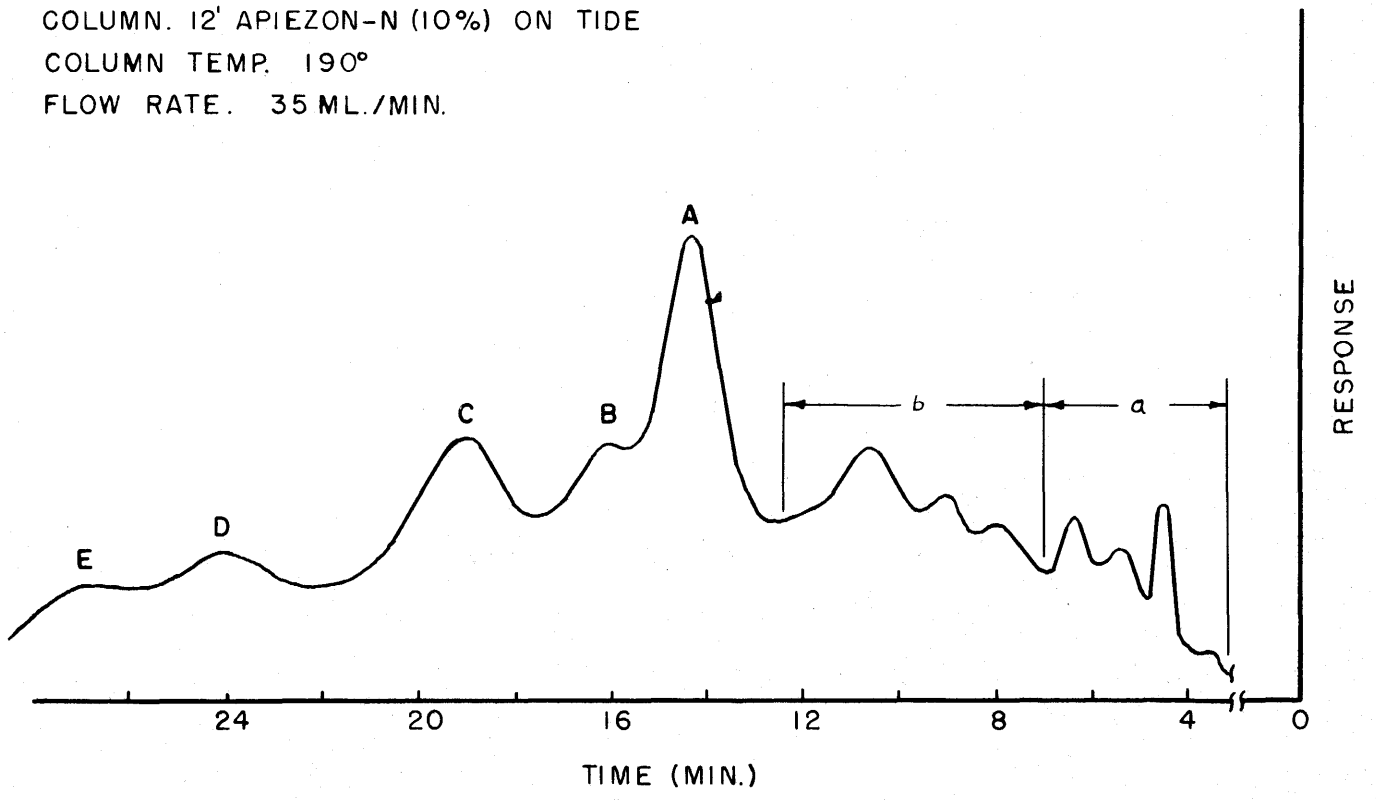

FIGURE 9. CHROMATOGRAM OF FRACTION 3

and flow rate of 35 ml./min. A graph of the logarithm of relative retention time vs. boiling point was prepared for the authentic specimens (Figure 10). The points did not fall close enough to a smooth curve to permit the prediction of relative retention times for compounds for which authentic specimens were not available. The results of the chromatographic analysis of Fraction 3 are given in Table XI.

Table XI

Chromatographic Analysis of Fraction 3*

Peak†	Relative Retention Time	Possible Identity
A	1.000	quinoline
B	1.122	isoquinoline
C	1.33	2-methylquinoline
D	1.67	7-methylquinoline and/or 1-methylisoquinoline
E	1.88	2,8-dimethylquinoline

*A 12' Apiezon-N (10%) on Tide column at 190° and flow rate of 35 ml./min. was used.

†Refer to Figure 9.

It was noted that on the Apiezon-N column indole had the same retention time as quinoline, but that on the 9' silicone oil (10%) on Tide column the two compounds were well separated. Peak A (Figure 9) was collected from the Apiezon-N column and re-chromatographed on the silicone oil column. No indole peak was found.

Two low boiling portions of Fraction 3 (a and b, Figure 9)

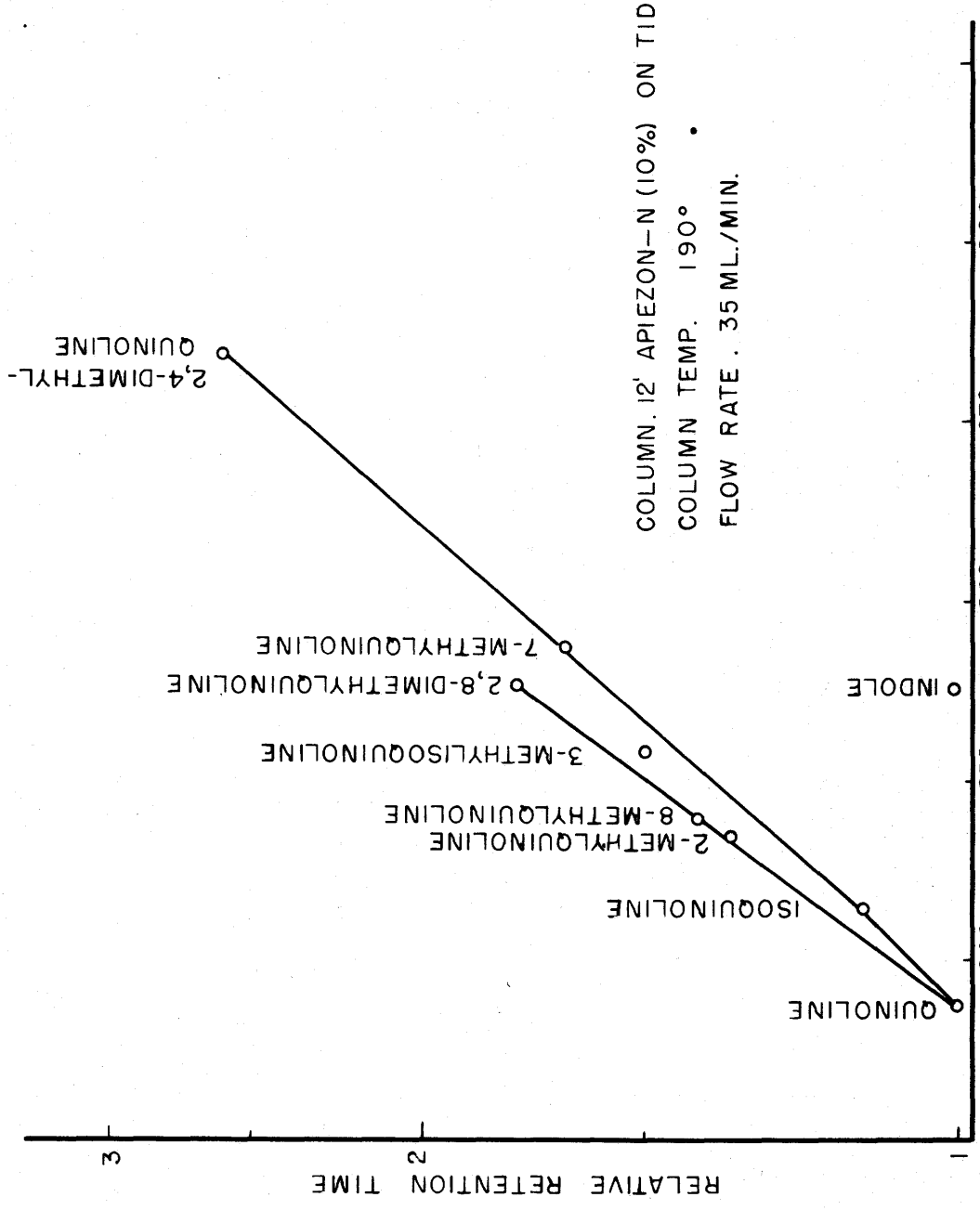

FIGURE 10

RELATIVE RETENTION TIMES OF SUBSTITUTED QUINOLINES

were collected from the Apiezon-N column and re-chromatographed on the 16' silicone oil (10%) on Fluoropak column. Two of the peaks in "a" were identified by their relative retention times as aniline and a mixture of the methylanilines. This supports the results found for Fraction 2. The infrared analysis of peaks B, C, D and E (Figure 9) was carried out. Peak D was not identified but B, C and E were found to be isoquinoline, 2-methylquinoline and 4-methylquinoline respectively. These results are the same as those obtained using the 16' silicone oil (10%) on Fluoropak column.

iv. Fraction Four (b.p. 156-166°/27 mm.)

The analysis of Fraction 4 was attempted on four columns: 16' silicone oil (10%) on Fluoropak, 6' S.E. 30 (4%) on Chromosorb W, 9' silicone oil (8%) on Tide and 12' Apiezon-N (10%) on Tide. The 16' silicone oil (10%) on Fluoropak column gave the best separation of the components of Fraction 4 (Figure 11). The operating conditions used were a temperature of 220° and a flow rate of 35 ml./min. Dinneen and Decora (37) reported that pyridine compounds tailed severely if Chromosorb were used as the solid support. It is interesting to note that quinoline compounds also tailed considerably when the 6' S.E. 30 (4%) on Chromosorb column was used.

The chromatogram of Fraction 3 was superimposed on the chromatogram of Fraction 4, both being recorded under the same operating conditions. By comparing retention times it was possible to identify the peaks that had been identified previously in Fraction 3. By this means peaks A, B, C and E (Figure 11) were identified as quinoline, isoquinoline, 2-methylquinoline and 4-methylquinoline respectively.

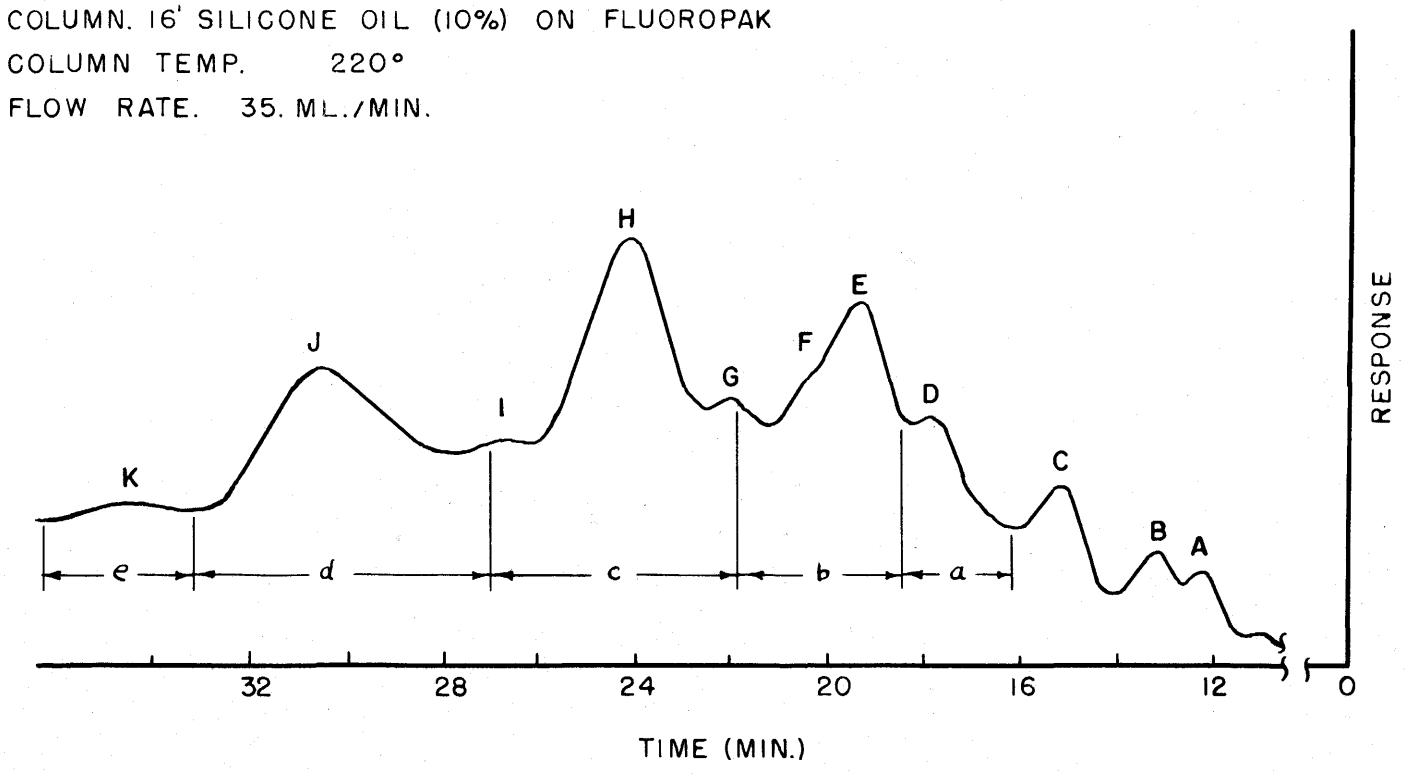

FIGURE II. CHROMATOGRAM OF FRACTION 4

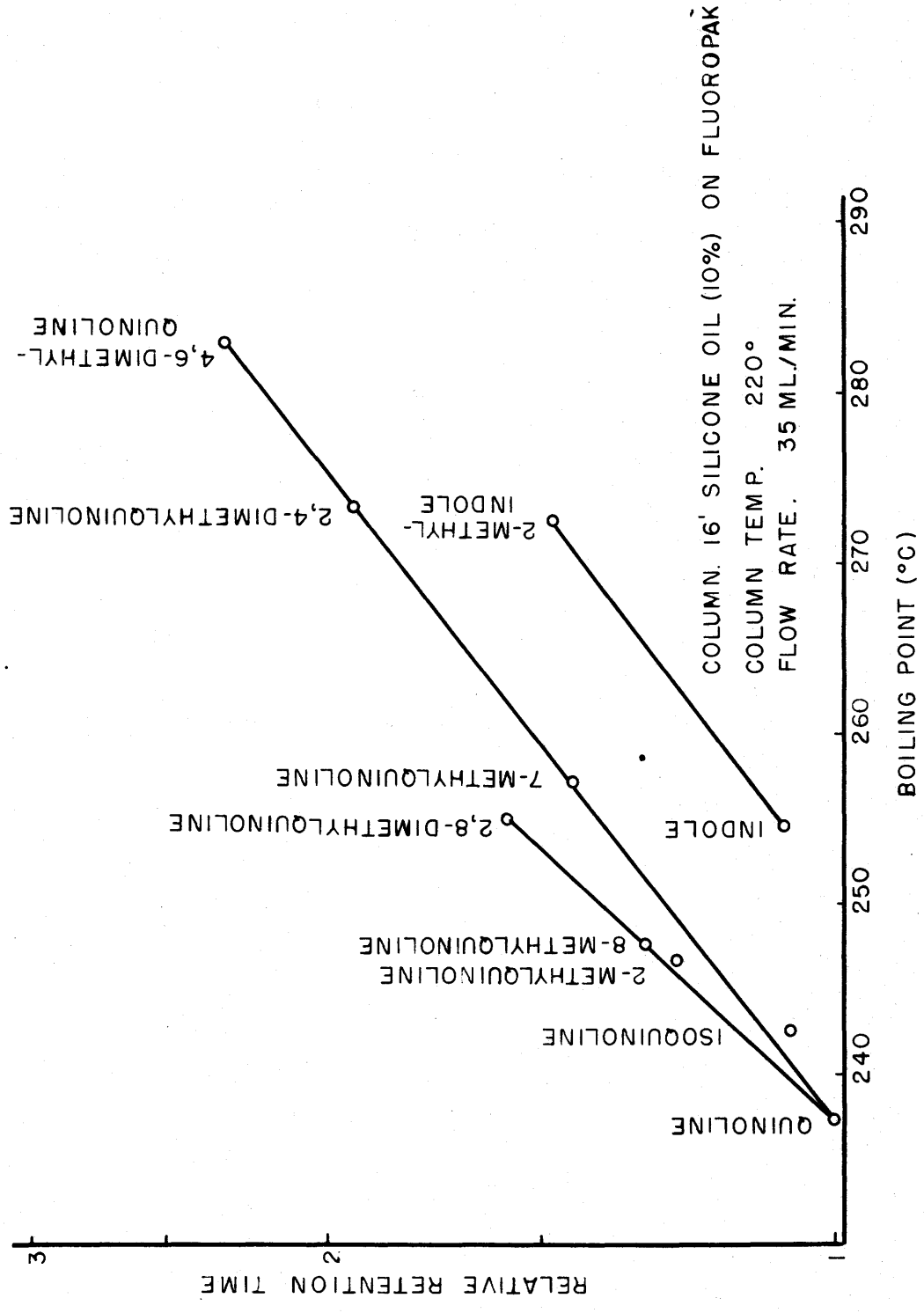

FIGURE 12

RELATIVE RETENTION TIMES OF SUBSTITUTED QUINOLINES

The available authentic compounds in this boiling point range were chromatographed. A plot of the logarithm of relative retention time vs. boiling point was made (Figure 12). The majority of the quinolines fell on a straight line but 2-methyl-, 8-methyl- and 2,8-dimethylquinoline fell slightly above the line. The indoles chromatographed fell below the curve. It would be expected that coal tar basic material in the boiling point range of this fraction would contain quinolines, isoquinolines and indoles. It would not be possible to predict accurately the relative retention times of such compounds from their boiling points using this graph. Since so few of the many possible basic compounds were available, it was apparent that chromatography would be of little value for this fraction. Tentative chromatographic identifications were made, however. The results are listed in Table XII.

An attempt was made to collect the compounds corresponding to the peaks in the chromatogram of Fraction 4 and analyse them by infrared spectroscopy. When samples of sufficient volume to make collection possible (15-20 μl.) were injected, chromatographic separation became poor. To obtain peaks of greater purity for infrared analysis the Fraction 4 material was chromatographically separated into five fractions (a, b, c, d and e, Figure 11). Each of these fractions was re-chromatographed and the individual peaks were collected. Only the major peaks, E, H and J (Figure 11) yielded enough material for infrared analysis. Using the infrared absorption spectra of methylquinolines reported in the literature (41, 42) an attempt was made to identify these three peaks. Peak J was not identified but E and H proved to be 4-methyl- and 2,4-dimethylquinoline respectively.

Table XII

Chromatographic Analysis of Fraction 4*

Peak†	Relative Retention Time	Possible Identity
A	1.000	quinoline
B	1.080	isoquinoline
C	1.243	2-methylquinoline
D	1.465	
E	1.59	4-methylquinoline
F	1.69	
G	1.81	
H	1.99	2,4-dimethylquinoline
I	2.22	4,6-dimethylquinoline
J	2.52	
K	2.84	

*A 16' silicone oil (10%) on Fluoropak column at 220° and flow rate of 35 ml./min. was used.

†Refer to Figure 11. Peaks A, B, C and E identified by comparison with Fraction 3.

v. Fractions Five (b.p. 166-182°/27 mm.), Six (b.p. 182-190°/27 mm.) and Seven (heated to char)

The components appearing in Fractions 5, 6 and 7 were too high boiling to be analysed by vapour phase chromatography. The lack of reference compounds in this high boiling point range added to the difficulty of identification of these compounds.

II. Quantitative Analysis of the Steam Volatile Tar Bases Using Vapour Phase Chromatography

Considerable doubt arose as to the reproducibility of the results of the steam distillation and chemical separation procedures involved in the preliminary stages of this project (see Appendix C). In many cases chromatographic separation of the basic material was incomplete. It was felt that the use of the more exact techniques (45, 46) for quantitatively interpretingchromatograms was not worthwhile.

Both the areas under the individual peaks as well as the area of the whole chromatogram were measured using a planimeter. The peak area divided by the total area was considered to be the weight fraction of that compound in the fraction being analysed. In order for this procedure to be essentially valid two assumptions had to be made. Firstly the sample was considered to be completely eluted from the column so that the total area of the chromatogram actually represented the whole fraction. This assumption was justifiable since after each of the fractions was eluted the detector response returned to zero and remained there. The neutral liquid substrates used would not be expected to permanently retain any of the compounds. Secondly it was assumed that relative detector response was identical for all of the compounds in any one fraction. This was reasonably justified since both Fraction 1 and Fraction 2 contained primarily pyridines and Fraction 3 contained primarily quinolines and the relative response for each member of a series of homologous compounds is quite similar (45).

The weight per cent of each peak that had been previously

identified was calculated for each fraction. From this data the weight per cent of each of these peaks could be determined for the whole steam distillable basic fraction. The peaks that were known to contain more than one compound (peaks C and F, Figure 5) had been separated on other columns so the relative abundance of each of the constituents could be determined. The results of the quantitative analysis are given in Table XIII.

Table XIII

Quantitative Analysis of the Steam Distillable Tar Bases

Compound	Weight Per Cent*
pyridine	0.21
2-methylpyridine	1.29
3-methylpyridine	1.50
4-methylpyridine	0.71
2,6-dimethylpyridine	1.53
2,5-dimethylpyridine	1.08
2,4-dimethylpyridine	1.02
2,3-dimethylpyridine	1.22
2,4,6-trimethylpyridine	0.91
2,3,6-trimethylpyridine	1.92
quinoline	2.37
isoquinoline	1.79
2-methylquinoline	2.32
Total	17.87

*Based on the steam volatile basic fraction which comprised 0.70% of the whole tar.

SUMMARY

Saskatchewan lignite tar, obtained by the Parry low temperature carbonization process (1), was steam distilled from a neutral solution. The organic material was extracted with ether from the distillate. After the ether was removed the steam-volatile tar was extracted with aqueous alkali to remove the tar acids (phenolic compounds) and then extracted with acid to remove the tar bases (primarily pyridines and quinolines). The remaining unextracted material was the neutral (primarily hydrocarbon) fraction. The tar bases were divided into seven fractions by thermal distillation. The four lower boiling fractions were analysed using vapour phase chromatography. Comparison of the relative retention times of the peaks in the unknown fractions with those of authentic compounds was used to identify tentatively several compounds. The materials represented by the major peaks in the unknown fractions were collected and analysed using infrared spectroscopy. Comparison of these spectra with the spectra of authentic specimens substantiated further many of the identifications made using vapour phase chromatography. The following components were identified using vapour phase chromatography and infrared spectroscopy. Quantitative estimates of the identified peaks were made from the chromatograms.

Compound	Weight Per Cent*
pyridine	0.21
2-methylpyridine	1.29
3-methylpyridine	1.50
4-methylpyridine	0.71

Contd.

2,6-dimethylpyridine	1.53
2,5-dimethylpyridine	1.08
2,4-dimethylpyridine	1.02
2,3-dimethylpyridine	1.22
2,4,6-trimethylpyridine	0.91
2,3,6-trimethylpyridine	1.92
quinoline	2.37
isoquinoline	1.79
2-methylquinoline	2.32
4-methylquinoline*	
2,4-dimethylquinoline*	

*Based on the steam-volatile basic fraction which comprised 0.70% of the whole tar.

*Chromatographic separation was not sufficient to calculate the abundance of these compounds.

The following compounds were tentatively identified using vapour phase chromatography. Infrared analysis was not carried out on the material corresponding to these peaks.

2-ethylpyridine

3-ethylpyridine
4-ethylpyridine

5-ethyl-2-methylpyridine

3,4-dimethylpyridine

aniline

2-methylaniline
3-methylaniline
4-methylaniline

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* Consulted in abstract form only.

Appendix A

Coal Tar Bases Reported by Oberkobusch

(Brenstoff-Chemie, 40, 145 (1959))

Compound	b.p./760 mm.
pyridine	115.3°
2-methylpyridine	129.4
3-methylpyridine	144.2
4-methylpyridine	145.4
2,6-dimethylpyridine	144.1
2,5-dimethylpyridine	157.2
2,4-dimethylpyridine	158.5
2,3-dimethylpyridine	161.6
3,5-dimethylpyridine	171.6
3,4-dimethylpyridine	178.9
2,4,6-trimethylpyridine	170.5
2,3,6-trimethylpyridine	173.0
2,3,5-trimethylpyridine	186.8
2,4,5-trimethylpyridine	189.8
2,3,4-trimethylpyridine	193
3,4,5-trimethylpyridine	211.4
2-ethylpyridine	148.7
3-ethylpyridine	165.3
2,3,4,6-tetramethylpyridine	204
2,3,5,6-tetramethylpyridine	
2,3,4,5-tetramethylpyridine	233
4-ethyl-2-methylpyridine	179
6-ethyl-2-methylpyridine	161.5
2,3-cyclopentenopyridine	199.4
3,4-cyclopentenopyridine	211.8
6-methyl-2,3-cyclopentenopyridine	211.9
2-phenylpyridine	277.0
4-phenylpyridine	280.5
pyrrole	130
indole	254.7
3-methylindole	266.4
7-methylindole	267.6
5-methylindole	269.8
4-methylindole	270.9
2-methylindole	272.8
7-azaindole	272.0
aniline	184.4
4-methylaniline	200.4
2-methylaniline	200.7
3-methylaniline	203.3

Compound	b.p./760 mm.
2,4-dimethylaniline	214°
2,5-dimethylaniline	218
3,5-dimethylaniline	220
2,3-dimethylaniline	222
quinoline	237.3
2-methylquinoline	246.9
8-methylquinoline	247.8
3-methylquinoline	259.6
7-methylquinoline	257.6
6-methylquinoline	258.6
5-methylquinoline	262.7
4-methylquinoline	265.2
2,8-dimethylquinoline	255.2
6,8-dimethylquinoline	268.4
2,6-dimethylquinoline	
2,7-dimethylquinoline	
2,4-dimethylquinoline	273.5
2,3-dimethylquinoline	274.9
4,6-dimethylquinoline	283.1
4,7-dimethylquinoline	283.9
2,6,8-trimethylquinoline	275.3
2,4,8-trimethylquinoline	278.8
2,4,6-trimethylquinoline	289.1
1,2,3,4-tetramethylquinoline	251
isoquinoline	242.8
3-methylisoquinoline	251.4
1-methylisoquinoline	255.2
1,3-dimethylisoquinoline	262.4
α-naphthylamine	301
β-naphthylamine	306
4-azafluorene	314.5
1,2,3,4-tetrahydroacridine	328.3
7,8-benzoquinoline	340.2
acridine	343.9
9,10-dihydroacridine	349
phenanthridine	349.5
5,6-benzoquinoline	350
carbazole	353
2-methyl-5,6-benzoquinoline	355
2-methylcarbazole	363
α-carboline	363.6
3-methylcarbazole	365
2-methylacridine	365.1
7-methylcarbostyril	380
2-azafluoranthene	394
13-azafluoranthene	396
1-azapyrene	407.6
4,4',5',5-benzcarbazole	408.2
2,3-benzo-4-azafluorene	410
3,4-benzacridine	434
phenanthridone	438
1,2-benzacridine	438
1,2-benzocarbazole	450
quinindoline	450
2,3-benzocarbazole	455
1-oxy-1,2-dihydro-2-azapyrene	480

Appendix B

The Presence of a 1700 $cm.^{-1}$ Band in the Infrared Spectra of Lignite Tar Bases

It was noted that the infrared absorption spectrum of each of the collected chromatographic peaks from Fractions 1 and 2 contained a strong absorption maximum at 1700 $cm.^{-1}$. The spectra of the corresponding authentic compounds did not contain this peak. At first it was suspected that this peak resulted from some impurity arising during the course of chromatography or during the collection procedure. A synthetic mixture containing equal volumes of 2-methyl-, 2,5-dimethyl- and 2,3,6-trimethyl-pyridine was prepared and chromatographed. The peaks were collected and their infrared absorption spectra were recorded. The 1700 $cm.^{-1}$ peak was not present. The infrared absorption spectrum of whole Fraction 1 did, however, show strong absorption at 1700 $cm.^{-1}$. It would seem that the material causing this absorption maximum was present in the original distillate fractions of the steam volatile tar bases. No acceptable explanation of this peak can be offered at this time.

Appendix C

Analysis of a Second Sample of Tar Bases Obtained from Saskatchewan Lignite

The compound(s) represented by the principal peak in the chromatogram of Fraction 2 (peak L, Figure 7) could not be identified by either vapour phase chromatography or infrared analysis. An attempt was made to secure enough of the material corresponding to this peak for quantitative elemental analysis. A second sample of the basic fraction was isolated, from the same low temperature carbonization lignite tar, by Mr. C. Chambers in these laboratories. Essentially the same steam distillation and chemical separation procedures had been used to obtain this sample. The sample was fractionated by him into five distillate fractions according to the same procedure as that outlined on page 17. Each of these fractions was chromatographed on the 16' silicone oil (10%) on Fluoropak column and compared to the similarly obtained chromatograms of Fractions 1, 2 and 3 obtained by the author's original isolation procedure. The chromatographic results indicated that the five fractions obtained from the tar bases isolated by Mr. Chambers contained no components with boiling points higher than quinoline and that the relative abundancesof several peaks were quite different to those in Fractions 1, 2 and 3 reported in this thesis. The relative abundance of the large peak that had been found in Fraction 2 was too small in Mr. Chambers' sample to be collected.

Slight differences in the steam distillation and chemical separation procedures as carried out by Chambers and the author were probably the cause of the different relative abundances.

The results of the author's steam distillation and chemical separation procedures are compared with those of both Cram and Chambers in the following table. Cram's results are very close to those of the author while Chambers' are in considerable disagreement. It is felt by the author that the contradictory results in the analysis of Chambers' tar bases do not constitute reason for doubting the reproducibility of this work

Analysis of Saskatchewan Lignite Tar*

Fraction	Percentage of Tar		
	Chambers	Cram	Author
Steam volatile tar bases	0.52	1.29	0.70
Steam volatile neutral oil	16.8	21.00	21.84
Steam volatile tar acids	37.6	4.52	5.57
Steam volatile alkali and ether soluble material	-	-	1.27
Water	30.0	28.7	30.0
Non steam volatile material	15.1	44.4	40.6
Total	100.0	100.0	100.0

*On the basis of wet tar, as received.