Gas-Liquid Chromatographic Separation and Spectrometric Identification of Nitrogen Bases in Hydrocracked Shale Oil Naphtha

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A tar-base concentrate from a hydrocracked shale oil naphtha was separated by gas-liquid partition chromatography using nonpolar and polar columns. Final cuts were analyzed by mass, infrared, and nuclear magnetic resonance spectrometry. Fifty individual compounds were identified and eight additional structures are proposed as possible components of the concentrate. Alkylpyridines comprised about 64% of the bases and alkylanilines about 33%; the rest of the bases were quinoline and small quantities of cycloalkanopyridines. Substitution patterns for both the alkylpyridines and alkylanilines showed that α substitution was favored over β or γ, and γ was favored over β.

As part of an investigation into the composition and properties of shale oil and its components, the Bureau of Mines determined the composition of the tar bases extracted from a shale oil naphtha produced by recycle hydrocracking of a crude shale oil. The conditions under which this naphtha was produced are reported by Cottingham and Carpenter (*1*). Practically, this analysis is valuable for determining the nature of a material which could become a by-product of shale oil refining. From a theoretical standpoint, it is possible to use the data to draw some conclusions about the role of nitrogen compounds in the hydrocracking process. The work described in this paper is a continuation of characterizations of shale oil naphthas previously reported by this laboratory (*2–4*).

A method for obtaining the composition of naphtha-boiling-range nitrogen bases is presented. In general, the analysis was carried out by preparing a tar-base concentrate, separating the components by gas-liquid partition chromatography (GLPC), and identifying the components spectrometrically.

The GLPC separation was carried out by chromatographing samples on both polar and nonpolar columns. The retention volume of a nitrogen base will differ greatly on a polar and a nonpolar column, particularly for a compound having an alkyl substituent adjacent to the nitrogen (*5, 6*). Separation of such compounds may be enhanced by trapping unresolved groups of compounds on a nonpolar column and rechromatographing them on a polar column. This technique was found particularly useful in preparing final cuts large enough for spectrometric analysis.

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Although the spectrometric identification of organic compounds is a well-established procedure (*7*), some ingenuity was frequently required in the interpretation of poor spectra or the spectra of mixtures. For this reason a number of specific examples of the identifications are shown to illustrate the analysis.

EXPERIMENTAL PROCEDURES

Apparatus. The chromatograph was a Wilkins Model A-90P using helium as carrier gas. The columns used in the GLPC separations are described in Table I. Spectrometric analyses were performed with a Perkin-Elmer Model 521 infrared spectrometer, a Consolidated Electrodynamics Corp. 21–103 mass spectrometer, and a Varian Model A-60 nuclear magnetic resonance (NMR) spectrometer. A few experiments were performed using the gas chromatograph connected to a Bendix Model 14-107 time-of-flight (TOF) mass spectrometer. Accessories for dealing with very small samples were frequently employed, particularly for NMR spectrometry.

Preparation Tar-Base Concentrate. Shale oil naphtha, produced by hydrocracking and containing about 1% by volume of basic nitrogen compounds (*1*), was extracted with dilute sulfuric acid. The extract was adjusted to pH 4 with dilute caustic to minimize decomposition and the mixture was steam-distilled for a short period to remove volatile neutral oils. The residue was cooled, made basic, and steam-distilled to remove the bases. The distillate was treated with potassium carbonate and extracted with pentane. The extract was dried over potassium hydroxide, and the solvent was evaporated with a stream of dry nitrogen. About 5 grams of bases were concentrated for the GLPC separation.

Separation Procedure. The procedure was designed to separate the major components of the tar-base concentrate into characterizable portions. The concentrate was first separated into four narrow-boiling fractions on the SE-30 column (column 1) described in Table I. The first two fractions were separated into characterizable cuts using the diglycerol column (2). The last two fractions each required two gas chromatographic separations to achieve characterizable cuts, and these separations used either of the nonionic detergent columns (3 or 4).

To obtain satisfactory separations, it was necessary to acid- and base-wash the solid supports prior to coating them. Additional resolution for all four columns was obtained by an *in situ* silanization. Two 10-μl injections of a 50 vol. % benzene solution of hexamethyldisilazane were made with the column oven at 100 °C and the gas flow at about 10 ml per minute. For the GLPC of basic compounds, this technique of silanization gave columns with performance equal to that of columns packed with presilanized supports.

Fractions were collected from successive injections kept small enough to permit good resolution. Traps were cooled in dry ice, while collecting fractions and were kept cold prior to analysis.

Instrumental Procedures. Mass spectrometric (MS) analysis was used routinely on most final cuts. Low-voltage spectra were used to identify parent ions and high-voltage spectra were useful for determining substitution patterns. Pyridines could not be distinguished from anilines by the MS analysis used. Infrared analyses were obtained on most of the

(1) P. L. Cottingham and H. C. Carpenter, *Ind. Eng. Chem. Process Design Develop.*, **6**, 212 (1967).
(2) G. U. Dinneen, R. A. Van Meter, J. R. Smith, C. W. Bailey, G. L. Cook, C. S. Allbright, and John S. Ball, *Bur. Mines Bull.* **593** (1961).
(3) H. H. Heady, L. G. Adams, and G. U. Dinneen, *Bur. Mines Rept. Invest.* **5662** (1960).
(4) R. A. Van Meter, C. W. Bailey, J. R. Smith, R. T. Moore, C. S. Allbright, I. A. Jacobson, Jr., V. M. Hylton, and J. S. Ball, Anal. Chem., **24**, 1758 (1952).
(5) J. S. Fitzgerald, *Australian J. Appl. Sci.*, **12**, 51 (1961).
(6) J. Janak and M. Hrivnac, *J. Chromatog.*, **3**, 297 (1960).
(7) R. M. Silverstein and G. Clayton Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, 1963.

Table I. Chromatographic Columns

Column No.[a]	Support[b]	Length, meters	Stationary phase	Loading, wt. %	Max. useful temp., °C
1	Gas-chrom P[c]	3	SE-30	20	250
2	Gas-chrom P[c]	6	Diglycerol	15	120
3	Chromosorb G[d]	6	Tween 20	5	200
4	Chromosorb G[d]	6	Triton X305	5	220

[a] All columns made from 0.25-inch-o.d. aluminum tubing, silanized *in situ* after packing and prior to use.
[b] All supports acid- and base-washed.
[c] 60–80 mesh.
[d] 70–80 mesh.

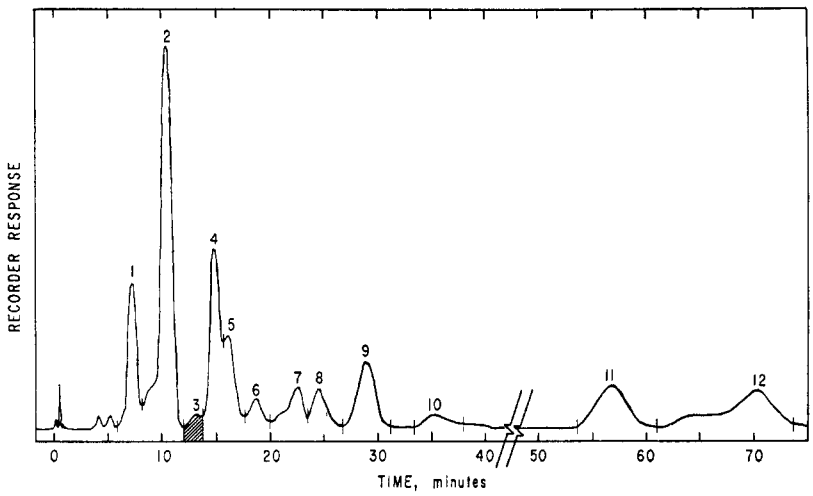

Figure 1. Chromatogram of fraction 2
Cut numbers correspond to those of Table III

cuts and were particularly valuable in determining the presence of anilines. Carbon tetrachloride was used as the solvent for both infrared and NMR analyses; and because the bases gradually degraded in this solvent, final cuts were not diluted until just prior to analysis. The 60-MHz NMR analyses gave the most valuable information on molecular structure. Even in mixtures, two or three unambiguous identifications were made in some cases. Microtubes and a computer of average transients were used to obtain useful spectra of very small cuts. The direct use of GLPC to identify compounds was possible only for the lower boiling materials, where retention data of known compounds are available (*5*, *6*, *8*). The relative quantities of cuts were obtained by integrating the chromatograms; although response factors and internal standards were not used, this quantification was considered adequate for the purpose of this investigation.

IDENTIFICATION OF COMPOUNDS

Compound identifications were based on the combined use of GLPC and spectrometric data. The four examples given below were selected to show the utility of the instrumental techniques:

Identification of 2-Butylpyridine in Fraction 2. Figure 1, the chromatogram of fraction 2, was obtained by use of the diglycerol column listed in Table I. The dividing lines indicate the cut points used in trapping the cuts and are numbered for use below. Cut 3 (the shaded area in Figure 1) was identified from its mass spectrum, which was obtained by connecting the TOF mass spectrometer directly to the gas chromatograph, because the amount of material in the cut was too small for conventional trapping. This spectrum is compared with the mass spectrum of 2-pentylpyridine in Table II. The similarities of the listed, fragment-ion amounts suggest that the unknown material is a 2-substituted, straight-chain alkylpyridine, and the molecular ion indicates C_4 alkyl substitution.

Table II. Mass Spectra of Fraction 2 Cut 3 and 2-Pentylpyridine

m/e	Relative intensities[a] Fraction 2 cut 3	2-Pentylpyridine[b]
93	100	100
106	18	23.0
107	9	6.31
120	11	21.5
121	4	2.61
133	4	...
134	17	1.42
135	12	0.15
148	...	1.60
149	...	1.54

[a] Intensities normalized to *m/e* 93 peak.
[b] API uncertified spectrum.

Identification of 2-Methylaniline in Fraction 2 Cut 11. The retention time and the mass spectrum of this cut suggested that the compound was 2-methylaniline. The infrared spectrum of the cut, compared with an authentic sample, supported this identification with the assignment of the doublet centered about 2.9 microns attributed to a primary amino group. The NMR spectrum of this cut (Figure 2) does not show the expected, slightly broad singlet of the amino protons at about 3.3. This signal is actually present in the NMR spectrum as a very broad band extending from about 2.5 to 4.0 ppm. The band is more easily seen from the integration of the curve, also shown in Figure 2. This integration indicates the presence of two protons between 2.5 and 4.0 ppm. The broadening of the amino signal was probably caused by proton exchange with impurities accumulated in

(8) M. A. Hughes, *J. Appl. Chem. (London)*, **12**, 450 (1962).

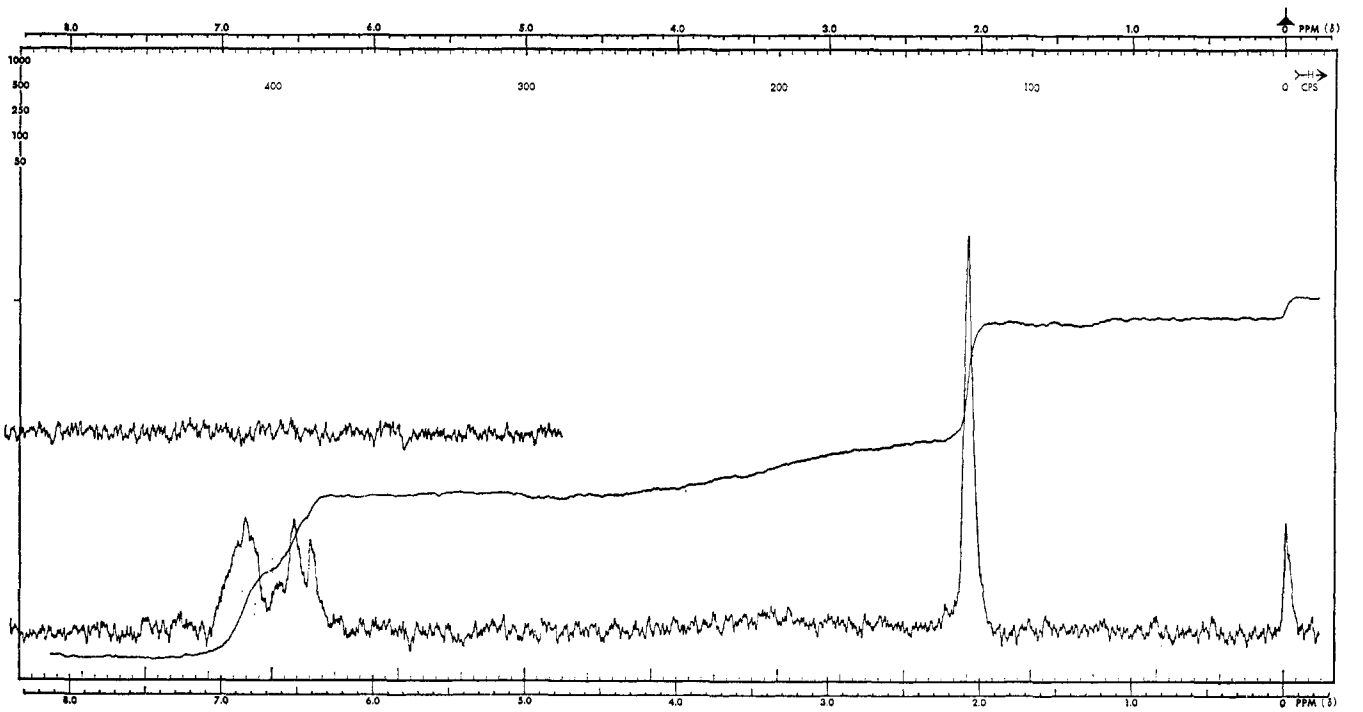

Figure 2. 500-Hz sweep width NMR spectrum of fraction 2 cut 11, identified as 2-methylaniline

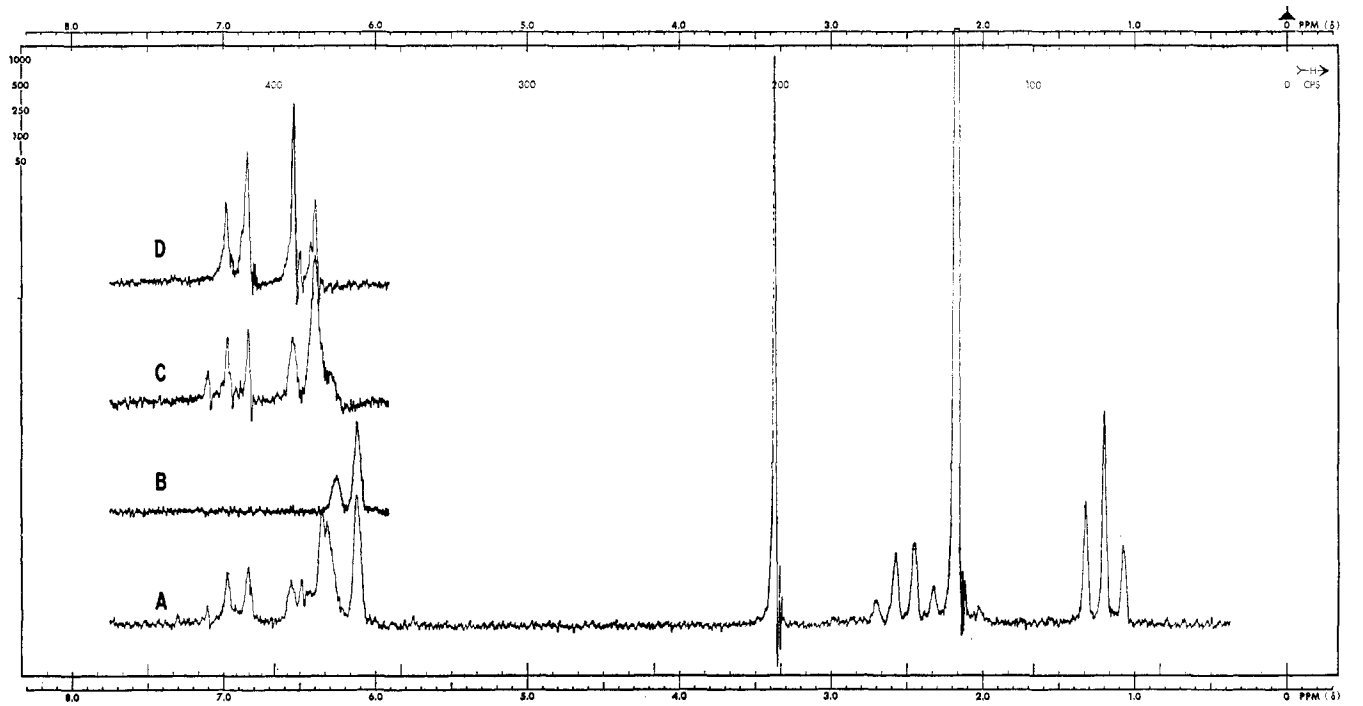

Figure 3. 500-Hz sweep width NMR spectra

A. Fraction 3 cut 5
Aromatic regions of:
B. 3,5-Dimethylaniline
C. 3-Methylaniline
D. 4-Methylaniline

GLPC trapping. Because this NMR band was often difficult to interpret, infrared spectra were valuable in firmly establishing the presence of the amino group. MS analysis could not distinguish anilines from pyridines.

Identification of Three Isomeric Anilines in Fraction 3 Cut 5. The infrared spectrum of the cut indicated the presence of an amino group and the low-voltage mass spectrum showed a molecular ion at *m/e* 121. The shape of the chromatographic peak indicated the presence of three compounds, one of which was tentatively identified as 3,5-dimethylaniline from its retention time. The NMR spectrum (Figure 3) indicates N-H protons at 3.38 ppm and an alkyl singlet at 2.18 ppm that can be assigned to 3,5-dimethylaniline. The other alkyl signals at 1.21 and 2.53 ppm suggest the presence of an ethyl group on an aromatic nucleus. This ethyl group is shown to contain the unresolved signals from both 3- and 4-ethylanilines by examining the aromatic region of the spectrum. The make-up of this part of the spectrum can be shown to

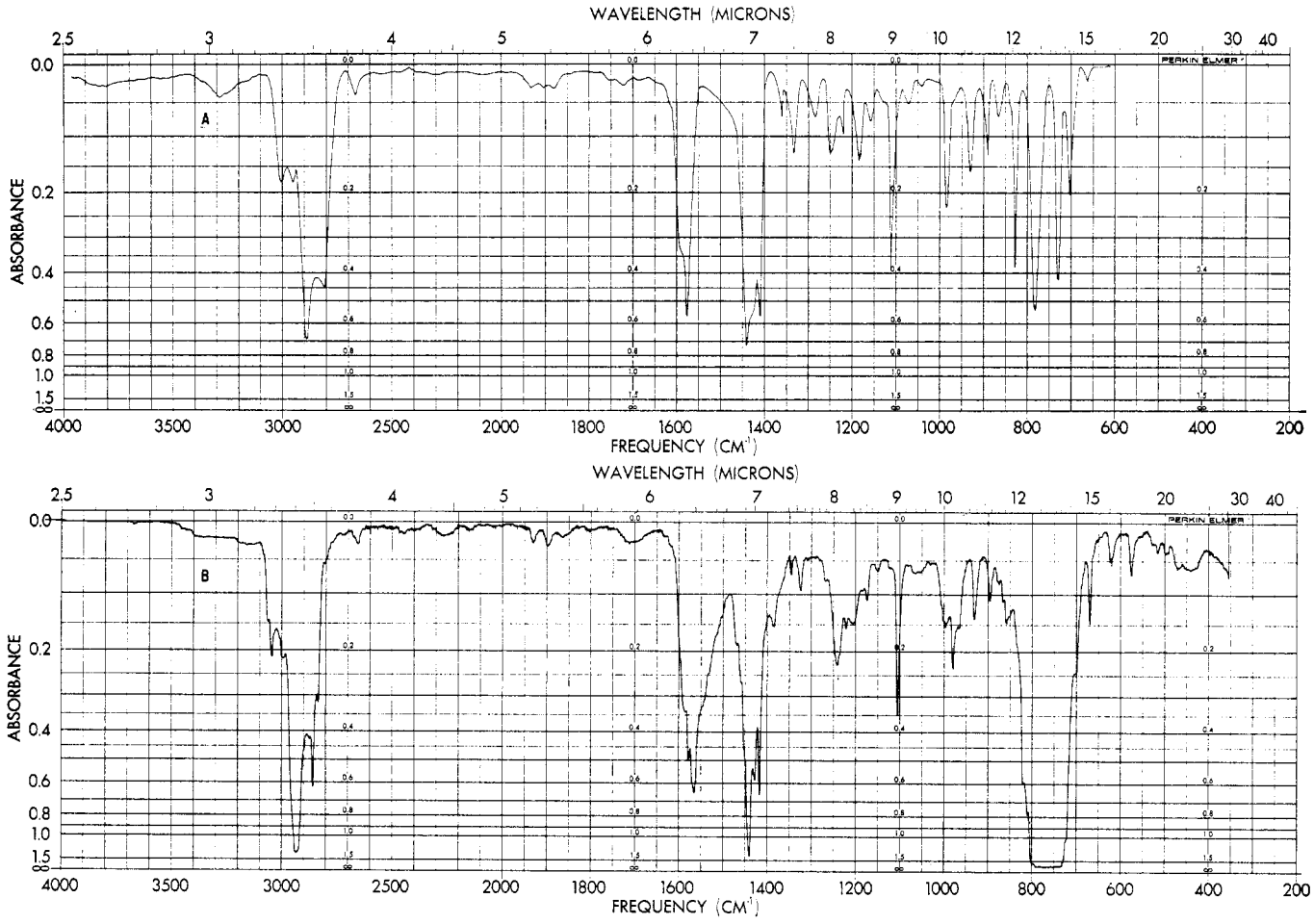

Figure 4. Infrared spectra

Upper (A). **5,6,7,8-Tetrahydroquinoline neat**
Lower (B). **Fraction 4 cut 3 in CCl_4 solution**

be derived from addition of the spectra of the three compounds in Figure 3. It was concluded that fraction 3 cut 5 was composed of 3,5-dimethylaniline, 3-ethylaniline, and 4-ethylaniline.

Identification of a Tetrahydroquinoline in Fraction 4 Cut 3. Figure 4 shows the infrared spectra of fraction 4 cut 3 and of 5,6,7,8-tetrahydroquinoline (*9*). The spectrum of the cut was run in CCl_4 solution and the spectrum of the pure standard was run neat. Although the unknown spectrum contains substantial solvent bands, there is good agreement between these two spectra in the regions of 3.4, 6.5, and 9.0 microns. The agreement between these two spectra plus supporting MS and NMR data was considered conclusive evidence of the presence of 5,6,7,8-tetrahydroquinoline in the nitrogen-base concentrate.

RESULTS AND DISCUSSION

The results of the analyses are listed in Table III. The compounds identified are tabulated by chromatographic cut. The techniques used to identify a particular structure are also indicated. Some compounds are proposed without sufficient information for positive identification (fraction 1 cut 3). In other cases where identification could not be made, substitution patterns are indicated to show the trends that exist (fraction 3 cut 1).

The alkylpyridines in the C_1 to C_3 range accounted for only 10% of the total tar-base concentrate. The substitution pattern for these pyridines showed that 80% of the molecules have alkyl substitution α to the nitrogen, 60% β, and 60% γ. Pyridine itself was not detected and 2-methylpyridine was the only one of the three monomethylpyridines identified.

The alkylpyridines in the C_4 to C_7 range accounted for 54% of the concentrate, with the major part of these molecules having C_4- and C_5-substitution. While these data do not allow a rigorous assignment of substitution patterns in this molecular weight range, inspection of Table III shows that not one of the identified pyridines in this range lacked substitution α to the nitrogen and that only three C_4 to C_7 pyridines lacked substitution γ to the nitrogen: 2-methyl-6-propylpyridine, 2-butylpyridine, and 2,3-diethyl-6-isopropylpyridine. On the other hand, there were only four compounds having substitution β to the nitrogen: 2,3,4,6-tetramethylpyridine, 2,3-diethyl-6-isopropylpyridine, 2,4,5-trimethyl-6-ethylpyridine, and 2,5,6-trimethyl-4-ethylpyridine.

The substitution pattern exhibited by the lighter molecular weight pyridines is even more pronounced in the C_4 to C_7 range—that is, most compounds were of the 2,4,6-type of substitution with very little 3- or 5-substitution. The alkyl chains of these pyridines tended to be short, only two compounds having chains longer than three carbon atoms. The substitution tended toward multiple short chains rather than a few long chains. This finding is similar to recent work reported on petroleum (*10*).

In addition to alkylpyridines, two other types of heterocyclic

(9) E. Godar and R. P. Mariella, *J. Amer. Chem. Soc.*, **79**, 1402 (1957).

(10) H. V. Drushel and A. L. Sommers, ANAL. CHEM., **38**, 10 (1966).

Table III. Basic Nitrogen Compounds Identified in Tar Bases from Hydrocracked Shale Oil Naphtha

Cut No.	Wt % of tar bases	Compound identified	Analytical technique: MS Parent ion	MS Fragment ion	IR	NMR	GLPC
		Fraction 1[a]					
1	0.19	2-Methyl-6-ethylpyridine	×	×			×
2	0.04	2,6-Dimethylpyridine	×	×			×
3	0.26	2-Ethylpyridine[b]	×	×			×
		2-Methyl-6-isopropylpyridine	×	×			
4	0.31	2-Methylpyridine	×				×
		2,4-Dimethyl-6-ethylpyridine[b]	×				×
5	4.05	2-Ethyl-5-methylpyridine	×	×		×	
		2,3,6-Trimethylpyridine	×	×		×	×
		2,4,6-Trimethylpyridine	×			×	×
6	1.57	2-Ethyl-4-methylpyridine	×		×		
7	0.37	2,5-Dimethylpyridine	×				×
		3-Methylpyridine[b]	×				×
		2,4-Dimethylpyridine	×				×
		2-Methyl-5-ethylpyridine	×				×
8	1.76	2-Methyl-4-ethylpyridine	×		×		×
9	0.84	3,5-Dimethylpyridine	×		×		×
10	0.44	3,4-Dimethylpyridine	×		×		×
11	0.89	Aniline	×		×		×
	0.18	Not identified					
		Fraction 2[a]					
1	1.89	2,4-Dimethyl-6-isopropylpyridine	×	×	×	×	
2	7.09	2-Methyl-6-propylpyridine (trace)	×	×			
		2,4-Dimethyl-6-ethylpyridine	×	×	×	×	
3	0.25	2-Butylpyridine	×	×			×
4	4.44	2,6-Dimethyl-4-ethylpyridine	×	×	×	×	
5	1.38	2,4-Diethylpyridine	×	×		×	
6	0.71	2-Methyl-4-isopropylpyridine	×	×		×	
7	1.40	4-Propylpyridine[b]	×	×		×	×
		2,3,5-Trimethylpyridine	×	×			×
8	1.09	3-Methyl-5-ethylpyridine	×	×		×	
9	1.80	2,4,5-Trimethylpyridine	×	×		×	×
10	0.79	2,3,4-Trimethylpyridine	×	×			×
11	2.37	2-Methylaniline	×	×	×	×	×
12	3.29	3-Methylaniline	×	×	×	×	×
		4-Methylaniline	×	×	×	×	×
		Fraction 3[a]					
1	16.32	2,6-Diethyl-4-methylpyridine	×	×	×	×	
		2,4-Dimethyl-6-isopropylpyridine[b]	×	×	×	×	
		2,6-Dimethyl-4-propylpyridine[b]	×	×	×	×	
		Mixed 2,4,6-methyl-ethylpyridines[c]	×	×	×	×	
2	11.89	Mixed C_4 and C_5 pyridines[c]	×				
		2-Methyl-6-ethylaniline	×	×	×	×	
		2,3,4,6-Tetramethylpyridine	×	×	×	×	×
3	7.02	2-Ethylaniline	×	×	×	×	×
		2,6-Dimethylaniline (trace)	×			×	×
4	3.06	2,4-Dimethylaniline	×	×	×	×	×
5	2.99	3,5-Dimethylaniline	×	×	×	×	×
		3-Ethylaniline	×	×	×	×	×
		4-Ethylaniline	×	×	×	×	×
6	0.50	2,3-Dimethylaniline	×	×	×	×	×
7	0.82	3,4-Dimethylaniline	×	×		×	×
		3,4,5-Trimethylpyridine	×	×		×	
		Fraction 4[a]					
1	2.15	2,4-Diethyl-6-isopropylpyridine	×	×		×	
		2,3-Diethyl-6-isopropylpyridine	×	×		×	
		2-Ethyl-4-methyl-6-propylpyridine[b]	×	×		×	
2	6.16	2-Methyl-4-ethyl-6-propylpyridine[b]	×	×		×	
		2,4-Dimethyl-6-pentylpyridine	×	×		×	
		2,4,5-Trimethyl-6-ethylpyridine	×	×		×	
		2,5,6-Trimethyl-4-ethylpyridine[b]	×	×		×	
		Mixed C_6 and C_7 pyridines[c]	×	×		×	
3	2.27	2,4,6-Trimethylaniline	×			×	
		5,6,7,8-Tetrahydroquinoline	×	×	×	×	
		Methyl-5,6,7,8-tetrahydroquinoline[c]	×	×		×	
		5,6,7,8-Tetrahydroisoquinoline[b]	×	×		×	
4	5.91	2-Propylaniline	×	×	×	×	
5	1.03	2-Methyl-5-ethylaniline	×	×		×	
6	1.18	Quinoline	×	×		×	
7	1.30	Mixed methylethylanilines[c]	×			×	

[a] Fraction 1 is 10.9%, fraction 2 is 26.5%, fraction 3 is 42.6%, fraction 4 is 20.0% of total bases. [b] Proposed compound. [c] Most likely substitution patterns indicated to show trends.

tar bases were identified: quinoline and tetrahydroquinolines (cycloalkanopyridines). Cycloalkanopyridine types have been reported in coal (*11*) and similar structures have been found in petroleum (*12, 13*). The combined quantity of quinoline and cycloalkanopyridines amounted to about 3% of the nitrogen-base concentrate.

The anilines, which make up about 33% of the tar-base concentrate, are of interest because their presence has not been reported in raw shale oil naphtha (*2, 4*). They may be assumed to be produced in the hydrocracking process by rupture of the heterocyclic ring—for instance, 2-ethylaniline and 2-propylaniline might result from the reductive cleavage of indole and quinoline which are known compounds in shale oil. This is supported by hydrogenation of petroleum fractions that contain known bases (*10, 14*). Inspection of the aniline data in Table III shows aniline and ring-substituted alkylanilines through C_3. The substitution pattern for the alkylanilines shows that 90% of the aniline molecules have substitution α to the location of the amino group, 15% β substitution, and 25% γ substitution. The preponderance of α substitution is even more notable for the C_1 to C_3 anilines than for the C_1 to C_3 pyridines.

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(11) Clarence Karr and Ta-Chuang Lo Chang, *J. Inst. Fuel*, **31**, 522 (1958).
(12) C. F. Brandenburg and D. R. Latham, *J. Chem. Eng. Data*, **13**, 391 (1968).
(13) H. V. Drushel and A. L. Sommers, ANAL. CHEM., **38**, 19 (1966).
(14) G. K. Hartung, D. M. Jewell, O. A. Larson, and R. A. Flinn, *J. Chem. Eng. Data*, **6**, 477 (1961).

Features of the Modified Covell Method for Computation of Total Absorption Peak Areas in Complex Gamma-Ray Spectra

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This article describes results of an investigation of the features of the modified Covell method for comparison of the total absorption peak areas in nondestructive activation analysis. Principles of the method have been described in an earlier publication. Either a small computer or an ordinary calculator can be used. The method proposed gives a better evaluation of the precision of the peak area in a complex gamma-ray spectrum than the traditional method of Covell. The predominance of this method over that of Covell is demonstrated especially in the case of a high ratio of the height of baseline to the peak height—i.e., for small peaks appearing on a high background.

IN RECENT YEARS a number of elegant, often very sophisticated, algorithms based on the least squares method or on the stripping method have been published to analyze complex gamma-ray spectra. The principle of the algorithms is an assumption that a library of standard spectra is at hand. In connection with this, the programs written for these methods are possible and profitable only on large computers. Unfortunately, many small activation analysis laboratories either have no possibility of using such computers, or their access to them is very limited (*1*).

Algorithms of methods have also been described in which the objects of the mathematical analysis are total absorption peaks (TAP) in gamma-ray spectra. In these methods, no library of standard spectra is involved, appreciably reducing the requirements in regard to the computation technique; nevertheless, the execution of such procedures as the mathematical smoothing of apparatus spectra, the control of TAP, or the examining of the first derivative of TAP is impossible without the use of a computer.

If an activation analysis laboratory has neither a computer nor access to one, then the elaboration of a small number of spectra must be performed by simple technical means. Because of this, the development of simple methods of analysis of gamma-ray spectra is of real value.

The method discussed, a comparison of TAP area in nondestructive activation analysis, was proposed in an earlier publication (*2*). The principle of this method is based on an appropriate modification of the known formula of Covell (*3*).

The basic advantages of the method are the rapidity and simplicity of calculations and a better evaluation of precision of the TAP area in a complex gamma-ray spectrum as compared to Covell's method. The present method can be applied (like Covell's method) using only an ordinary calculator or a small computer.

During the last two years the new method has been used in a laboratory practice for the interpretation of scintillation spectra of gamma radiation. A few new features of the method have been observed based on experimental data.

In order to know all features of the method, systematic numerical studies were carried out. By means of a computer the TAP was generated for the various peak half-widths and the various ratios of the height of the baseline to the peak height. The calculated precision of the peak areas was compared to both Covell's method and the present method.

(1) K. Liebscher and H. Smith, ANAL. CHEM., **40**, 1999 (1968).
(2) Sl. Sterliński, ANAL. CHEM., **40**, 1995 (1968).
(3) D. F. Covell, *ibid.*, **31**, 1785 (1959).