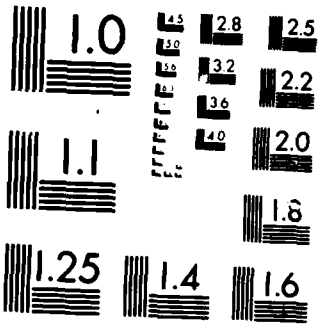
AD-A165 402 LC-(1)H NMR CHARACTERIZATION STUDIES OF TRICYCLIC AROMATICS AND OLEFINS I..(U) VIRGINIA POLYTECHNIC INST AND STATE UNIV BLACKSBURG DEPT OF C.. T E BLASS ET AL. 1/1

UNCLASSIFIED 18 FEB 86 N00014-82-K-2057 F/G 7/4 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

AD-A165 402

LC-^{1}H NMR CHARACTERIZATION STUDIES OF TRICYCLIC AROMATICS AND OLEFINS IN DIESEL FUELS

FINAL REPORT

February 1986

DTIC
ELECTE
MAR 1 7 1986
S D
D

DTIC FILE COPY

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

86 2 19 028

2

LC-^{1}H NMR CHARACTERIZATION STUDIES OF TRICYCLIC AROMATICS AND OLEFINS IN DIESEL FUELS

FINAL REPORT

February 1986

By

T. E. Glass, W. R. Bebout, K. A. Caswell, L. Allen and H. C. Dorn*
Virginia Polytechnic Institute and State University
Department of Chemistry
Blacksburg, VA 24061-0699

DTIC
ELECTE
MAR 1 7 1986
S D
D

Prepared for:

Naval Research Laboratory
4555 Overlook Avenue
Washington, DC
Under Contract No. N00014-82-K-2057

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Virginia Polytechnic Institute and State University 6b. OFFICE SYMBOL (If applicable) 999444	7a. NAME OF MONITORING ORGANIZATION U.S. Naval Research Laboratory
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Blacksburg, VA 24061-0699	7b. ADDRESS (City, State, and ZIP Code) Code 6180 Washington, DC 20375-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Naval Research Lab. 8b. OFFICE SYMBOL (If applicable) 251950	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER NRL Contract N00014-82-K-2057
8c. ADDRESS (City, State, and ZIP Code) Code 6180 Washington, DC 20375-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 62765N PROJECT NO. TASK NO. ZF-65-571-005 WORK UNIT ACCESSION NO 61-0079

11. TITLE (Include Security Classification)
LC-^{1}H NMR Characterization Studies of Tricyclic Aromatics and Olefins in Diesel Fuels (Unclassified)

12. PERSONAL AUTHOR(S)
T.E.Blass, W.R.Bebout, K.A.Caswell, L.Allen and H.C.Dorn*

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 9/82 TO 12/31/85	2/18/86	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Diesel Fuels, Chemical Characterization, Tricyclic Aromatics, Olefins, Wt. % Data, LC-^{1}H NMR

19. ABSTRACT (Continue on reverse if necessary and identify by block number) Approx.

New analytical approaches for determination of: (1) tricyclic aromatics, (2) alkenes, and weight % data in Naval diesel fuels are described. Tricyclic aromatics are detected and characterized at concentrations as low as ~0.25% in diesel fuels. Various analytical approaches for characterizing alkenes in diesel fuels are also explored, including: (1) chromatographic separation of the alkene fraction in diesel fuels by $AgNO_3$ impregnated chromatographic columns, and (2) a ^{19}F NMR tagging method characterizing alkenes. Finally, a calculative method for conversion of LC-^{1}H NMR molar data to weight % data for each chromatographic fraction in a fuel is described.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL R. N. Hazlett	22b. TELEPHONE (Include Area Code) 202-767-3559 22c. OFFICE SYMBOL 251950

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

TABLE OF CONTENTS

		Page
I.	Work Statement	1
II.	The Development of an Analytical Approach to Quantitate Tricyclic Aromatics in Diesel Fuels	2
III.	The Development of an Analytical Approach to Quantitate Unconjugated and Conjugated Alkenes in Diesel Fuels	5
IV.	The Development of a Calculative Method to Convert Molar and Average Molecule ^{1}H NMR Derived Data to Weight % Data	10
V.	References	14
VI.	Tables	15
VII.	Figures	22
VIII.	Appendix	38
	1. Copy of LC-^{1}H NMR Program (in BASIC CODE)	38

Accesion For
NTIS CRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By ltr. on file
Distribution /
Availability Codes
Dist | Avail and / or Special
A-1 | 23

WORK STATEMENT

1. The development of an analytical approach to quantitate tricyclic aromatics in diesel fuels.

2. The development of an analytical approach to quantitate alkenes in diesel fuels.

3. The development of an analytical approach to quantitate conjugated alkenes in diesel fuels.

4. The development of a calculative method to convert molar and average molecule ^1H NMR derived data to weight % data.

I. The Development of an Analytical Approach to Quantitate Tricyclic Aromatics in Diesel Fuels

In this phase of the study attention focused on extending the LC-^{1}HNMR (1-5) approach to the characterization of tricyclic aromatics in typical fuel samples (e.g., diesel fuels). We previously established that the normal phase liquid chromatographic columns* normally employed in the LC-^{1}HNMR approach are usually adequate to allow separation of tricyclic aromatics. The major limitation is the sensitivity of the ^{1}H NMR detector in the LC-^{1}H NMR approach. For example, tricyclic aromatics at concentrations below ~0.5% in the fuel are difficult to detect and quantitate utilizing LC-^{1}HNMR. In the first year of this study, considerable effort was directed at improvements in the LC-^{1}H NMR flow cell design (7,8). However, operation of superconducting NMR solenoids at higher field strengths (e.g., 9.4T, ^{1}H at 400 MHz) is a more direct way of alleviating this sensitivity problem. With the present 4.7T (200 MHz) LC-^{1}H NMR system sensitivity limits of ~0.25% for the tricyclic aromatics appears reasonable.

The average composition method (5) which was previously limited to alkanes, monocyclic aromatics, and dicyclic aromatics has now been expanded to include tricyclic aromatics. The "average structure" expressions for fluorenes and phenanthrenes parallels the expressions previously derived for the monocyclic and dicyclic aromatic fractions (5). The normalization equation for fluorenes has the same form as that for naphthalene (see 2 below), the constant for phenanthrene is given by equation (1) below.

$$N^P = (C^P_{un} + C^P_{sub})/10 \qquad [1]$$

* For example, Whatman-9 silica gel PAC column (500 mm x 9 mm i.d.)

$$N^F = (C^f_{un} + C^f_{sub})/8 \quad [2]$$

Both fluorenes and phenathrenes have four bridgehead carbons (equations 3 and 4).

$$C^f_{BH} = (C^f_{un} + C^f_{sub})/2 \quad [3]$$

$$C^p_{BH} = (C^p_{un} + C^p_{sub})/2.5 \quad [4]$$

The proton spectral region for the case of alkyl substitution in fluorenes and phenanthrenes is determined in a similar manner to the previously described method for naphthalenes(5). In the case of fluorene, alkyl substitution at the methylene bridge between aromatic rings wasn't considered. The bridging methylene is reported as a part of the methylene carbon α to an aromatic ring ($C^f_{\alpha CH_2}$). The expression for determining the bridging methylene is shown below.

$$C^f_{BM} = (C^f_{un} + C^f_{sub})/8 \quad [5]$$

As in the cases for monocyclic and dicyclic aromatics the equations assume that no branching exists past the α position. All substituted carbons are then determined in the same manner as previously reported (5).

The fractional aromaticity equation has been expanded to include tricyclic aromatics (fa^f and fa^p).

$$fa = fa^m + fa^d + fa^f + fa^p \quad [6]$$

The fraction of total carbon in each chromatographic peak (relative to the entire sample) has also been changed to reflect the presence of tricyclics

(F^f_{totalC} and F^p_{totalC}). The value for the alkane fraction is still obtained by difference.

$$F^a_{totalC} = 1-F^m_{totalC} - F^d_{totalC} - F^f_{totalC} - F^p_{totalC} \quad [7]$$

During the last 2-3 years, we have reported tricyclic aromatic data for various fuels based on the above procedure (9). In order to test the level of agreement of this approach as well as establish the lower limits of detection, a fuel (85-06) not containing appreciable levels (>0.25%) of tricyclic aromatics was purposely doped with 1% (w/w) fluorene and phenanthrene. Figures 1a-e and 2a-e illustrate the LC-^{1}H NMR profiles for fuel (85-06) in the absence and presence, respectively, of 1% (v/v) fluorene and phenanthrene. It is clear that the only difference in these figures (Figure 1 vs 2) is the additional peaks in Figures 2d and 2e attributable to fluorene and phenanthrene. Tables I and II provide the average molecule data for fuel 85-06 (doped and undoped) which also indicate reasonably good agreement. However, impurities in the alkane region appear to slightly alter the average molecule properties for monocyclic and dicyclic fractions for the two separate experiments. More importantly, the measured weight % data values of 1.1 and 1.1 for the phenanthrene and fluorene are in excellent agreement with the doped levels of 1.0% for each, respectively. It should also be noted that the average molecule data for both tricyclics contain background ^{1}H NMR signals in the alkyl region (0.5 - 2 ppm). Once again, these data suggest alkyl contributions to the average tricyclic molecule data which are obviously not present. However, the level of agreement is still quite remarkable for fuels at the 1% level. Furthermore, all C^x_{total} and F^x_{total} values indicate a high level of agreement for the two experiments (see Tables I and II).

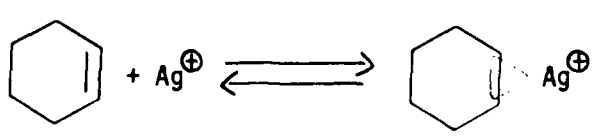
In a second experiment, fuel (85-06) was also doped at the 0.5% level. Figure 3 illustrates the corresponding (S/N) levels for this sample for the

fluorene "slice" of the LC-^{1}H NMR profile. This is also compared with the previously doped sample at the 1% level. From this data we estimate that with present instrumentation, the limits of detection for tricyclic aromatics is ~0.25%. Finally, it should be noted the 0.5% level provided measured values of 0.6% and 0.7% for fluorene and phenanthrene, respectively. These values are in fair agreement, especially in view of the background problem noted above. Representative parameters for tricyclic aromatics are illustrated in Figure 4. A copy of the modified program for inclusion of tricyclic aromatics is also given in Appendix I.

II. The Development of an Analytical Approach to Quantitate Unconjugated and Conjugated Alkenes in Diesel Fuels

Various research groups have suggested methods to chemically characterize and identify alkenes in fuels. However, new analytical methodology is still highly desirable. There are two major problems in characterizing the alkene content in fuels. Typically, most fuels exhibit low alkene concentrations (i.e., <1%) and chromatographic separation from other chemical classes (e.g., alkanes and monocyclic aromatics) is difficult to achieve. The latter problem is undoubtedly the more formidable one. Therefore, we focused attention on this problem during the first phase of this study.

It is well known that $Ag^{\oplus}$ ion can reversibly complex with alkenes as illustrated below for cyclohexene.



Various chromatographic separations of alkenes have been reported in the literature(10-12) for $AgNO_3$ impregnated chromatographic columns. Thus, one would anticipate that $AgNO_3$ chromatographic columns might allow efficient separation of alkenes from other hydrocarbon classes in fuels (e.g., alkanes and monocyclic aromatics). The specific experiments performed in this phase of the study are outlined below.

A. Attempted Separation of the Alkene Fraction in Fuels by $AgNO_3$ Impregnated Chromatographic Columns

The experiments outlined below utilized a simple model mixture which hopefully, simulates the chromatographic properties of a typical fuel. The model mixture contained isoctane, 1-methylnapthalene, xylene, and 1-hexene at mole percent concentrations of 90.1, 6.6, 2.2 and 1.0, respectively. A 1 gram sample of this model mixture was loaded on an open tubular chromatographic column containing 50 g of silica gel* with 5% $AgNO_3$. The eluting solvent was a 50/50 mixture of hexane and benzene. The chromatographic fractions were monitored by static ^1H NMR**. In this case, serious chromatographic overlap occurred, since the 1-hexene was present in both the isooctane and later eluting m-xylene fraction. Various experimental conditions were also changed in the hope of affecting a better chromatographic separation (vide infra).

1. A lower loading level (0.1 g of model mixture/50 g of support) was tried.

* The initial experiments utilized silica gel containing 5% $AgNO_3$ (w/w). However, silver nitrate levels as high as 15% (w/w) were also tried. The typical methods for preparing these silver nitrate impregnated silica gel columns have been previously described(8-10).

** The ^1H NMR peaks at ~5 ppm were used to monitor the presence of 1-hexene.

2. A less volatile alkene (1-octene) was substituted for 1-hexene in the model mixture, however, chromatographic separation was still not achieved with this new model mixture.

3. An even simpler model mixture containing only 1% 1-octene and 99% isoctane was subjected to chromatographic separation. A load level of 0.1 g on 50 g of support (5% $AgNO_3$ on silica gel) was used in the same manner as previously described. However, significant chromatographic overlap of the isoctane and 1-octene fractions still occurred.

4. Alternative solvents were also examined including freon-113 and pentane.

In all experiments above, separation of the alkenes (1-hexene or 1-octene) from the alkane (isoctane) and monocyclic aromatic (m-xylene) fraction was not achieved.

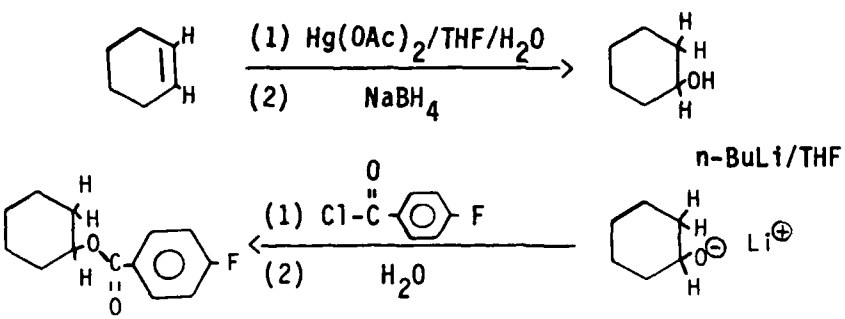
In summary, we are not exactly certain why a "class" separation of alkenes was not achieved with open tubular $AgNO_3$ impregnated silica gel columns, since the literature certainly suggests the feasibility of this approach. However, the high percentage of alkanes (e.g., isoctane) appear to chromatographically tail into the alkene fraction, thereby, preventing a clear separation.

In addition to the experiments described above, HPLC silica gel columns were also impregnated with $AgNO_3$. However, results similar to the case of the open tubular columns were observed. Namely, a separation of the isoctane and 1-octene fractions was not achieved.

B. Development of a ^{19}F NMR Tagging Method for Concentrating and Characterizing Alkenes

In view of the limited success in achieving a chromatographic class separation of alkenes (vide supra), other studies aimed at concentrating and characterizing alkenes present in fuels were examined. To date, the best approach we have found consists of four steps: (1) chemical conversion of the alkenes to alcohols in the fuels, (2) concentration of the alcohols by

precipitation with n-butyl lithium, (3) conversion of the alkoxide salts to p-fluorobenzoate esters, and (4) characterization of the p-fluorobenzoate esters by ^{19}F NMR. Although the number of steps in this procedure appears to be excessive, nevertheless, the entire procedure can be accomplished in four to eight hours. In addition, several steps may eventually be combined. In a typical experiment, 10 µl of cyclohexene was diluted in 50 ml of n-hexane (0.02%v/v). This model system was then treated with 50 ml of HPLC grade tetrahydrofuran (THF), 5 ml of water and 2 g of mercuric acetate ($Hg(OAc)_2$). After formation of the coresponding oxymercuration products, a basic water solution of $NaBH_4$ was added to reduce the oxymercuration products to the coresponding alcohols (13). After drying over anhydrous $MgSO_4$, the organic phase was treated with n-butyl lithium to precipitate the lithium alkoxide salts. After filtration (concentration by removal of nonreacting hexane) the lithium alkoxide salts were treated with p-fluorobenzoyl chloride in THF to prepare the corresponding p-fluorobenzoate ester derivatives. The entire reaction scheme is illustrated below for cyclohexene:



The final step in the procedure is characterization of the p-fluorobenzoate esters by ^{19}F NMR. In the future, LC-^{19}F NMR could be used for even better separation and characterization of the various alkenes in a given fuel. It should be noted also that a given fuel could be initially treated with n-butyl lithium to separate and characterize any alcohol and/or phenol

components in the fuel <u>before</u> conversion of the alkenes to the corresponding alcohols via the oxymercuration procedure.

To illustrate the approach, Figure 5 is the ^{19}F NMR spectrum for the p-fluorobenzoate ester of the dilute alkene sample characterized in the manner described above. Peaks #2 and #3 in Figure 5 are the signals due to the ^{19}F chemical shift ($CFCl_2CFCl_2$,Freon-113) and quantitation (ααα-trifluoroacetophenone) reference, respectively. In addition, peaks #4 and #5 are the ^{19}F NMR signals due to the derivatizing agent (p-fluorobenzoyl chloride) and the hydrolysis product (p-fluorobenzoic acid), respectively. Of particular importance, peak #6 is the derivative peak of interest for cyclohexanol. In other studies, it has been observed that peaks due to derivatives of other classes (e.g., phenols, amines, etc.) do not overlap in the region of interest for p-fluorobenzoate ester derivatives of alcohols (14). However, we have found that traces of alcohols in the solvents used in the procedure (e.g., THF) are also derivatized unless very high purity solvents are employed and/or precautions are taken to exclude these alcohol impurities.

In order to further test the procedure, an actual fuel sample was also examined (Fuel 80-63). Utilizing the same procedure described (50 ml of fuel), Figure 6 is the ^{19}F spectrum for the p-fluorobenzoate derivatives of this fuel sample. Peaks #5 and #6 in this spectrum are assigned to unreacted p-fluorobenzyl chloride and p-fluorobenzoic acid, respectively. However, the small peak #7 (~0.0013%) is in the appropriate region for diols (e.g., 2,3-butanediol, δ_F=-38.27 ppm, ref. 14a). Furthermore, peak #8 (~0.14%, based on peak #2) is in the appropriate region for secondary alcohol derivatives and could resu7lt from olefins in Fuel 80-63 (14a). However, it should be cautioned that although all attempts were made to exclude alcohol impurities

from the solvents employed, a second possibility is that peak #8 could be due to solvent impurities at this low level (~0.14%). The peak at 43.15 ppm (Peak #9) is indicative of a secondary amine (e.g., diisopropyl amine, δ_F=-43.14 ppm). Peak #10 is a foldover peak and is not a derivative peak.

In conclusion, the results above are promising. However, a number of potential pitfalls need to be examined before this approach can be used to quantitate the alkene content in a given fuel.

III. The Development of a Calculative Method to Convert Molar and Average Molecule ^{1}H NMR Derived Data to Weight % Data

The original average molecule program (5) has now been modified to calculate weight % data for each chromatographic fraction. Three different approaches were examined for the determination of weight % data. In the following discussion, the various equations and terms follow the format we used in a previously published paper (5). In addition several definitions are reported in Table III.

Method 1

In this method, the average number of moles for C^m_{total} and C^d_{total} are readily obtained from the "average molecule" approach (e.g., see ref. 5, eq. 16 and 18). In addition, the average molecular weights are also determined by this approach (e.g., see ref. 5, eg. 16 and 19). In a similar fashion C^f_{total} and C^p_{total} are also readily determined (see Section I of this report). Thus, W^m, W^d, W^f and W^p are readily calculated, since the average number of moles and molecular weights are known for these fractions. Next, the fraction of total carbon in the alkane fraction is obtained by difference from the following equation.

$$F^a_{totalC} = 1 - F^m_{totalC} - F^d_{totalC} - F^f_{totalC} - F^p_{totalC} \qquad [8]$$

It should be noted that F^m_{totalC}, F^d_{totalC}, F^f_{totalC}, and F^p_{totalC} are all derived quantities from the average molecule approach, if carbon aromaticity data is obtained from the ^{13}C spectrum (see eq. 20, 21 and 22 in ref. 5). The total alkane carbon content (C^a_T) can then be calculated since all the quantities in the right-hand side of eq. 8 below are then known.

$$C^a_T = \frac{(F^a_{totalC})(C^m_{total} + C^d_{total} + C^f_{total} + C^p_{total})}{(F^m_{totalC} + F^d_{totalC} + F^f_{totalC} + F^p_{totalC})} \qquad [9]$$

To obtain the weight% for the alkane fraction <u>we assume</u> an <u>average weight per alkane carbon and attached hydrogen atoms of 14.2</u>. This value assumes a C_{12} linear hydrocarbon; assuming other chain lengths and/or branched alkanes will change this number slightly (e.g., C_5H_{12} - $C_{15}H_{32}$ values range from 14.40 - 14.13).

$$W^a = (C^a_{total})\ (14.2) \qquad [10]$$

The weight % alkane, monocyclic, dicyclic, etc., fractions are then easily obtained.

$$W^{total} = W^a + W^m + W^d + W^t + W^p \qquad [11]$$

$$WP^x = W^x / W^{total} \times 100 \qquad [12]$$

The major limitation of Method 1 is the assumption of 14.2 for the average weight per alkane carbon and attached hydrogens. In addition, the C^a_T values critically depend on accurate f^a values normally obtained from quantitative ^{13}C NMR data.

<u>Method 2</u>

In this method C^m_{total}, C^d_{total}, C^f_{total} and C^p_{total} are obtained in the same manner as Method 1. However, C^a_{total} is obtained in a different manner.

Specifically, the H^a_{CH}, $H^a_{CH_2}$, and $H^a_{CH_3}$ regions of the alkane fraction are integrated in the manner previously reported (See Figure 2, ref. 5). Next, absolute moles of each carbon-type are calculated.

$$C^a_{CH_3} = \frac{H^a_{CH_3} K(V^a)}{3} \qquad [13]$$

Similar equations can be written for $C^a_{CH_2}$ and C^a_{CH} terms with denominators of 2 and 1, respectively. Thus, C^a_T can then be obtained from the following equation:

$$C^a_T = C^a_{CH} + C^a_{CH_2} + C^a_{CH_3} \qquad [14]$$

At this point, W^a, W^{total} and WP^x are then readily calculated.

$$W^a = (C^a_{CH_3})\ (15) + (C^a_{CH_2})(14) + (C^a_{CH})(13) \qquad [15]$$

The major drawback with this approach is the exclusion of quaternary alkane carbons in the total weight W^a (or WP^a) for the alkane fraction.

Method 3

In this method the density of the original fuel is experimentally determined. Then, for a given LC-^{1}H NMR injection volume (e.g., 100 µl) the total weight (W^{total}) of fuel injected is known. Thus W^a can be calculated by difference from eq. 10 where W^d, W^f and W^p are obtained in the same manner as Methods 1 and 2. A limitation of this method is the need for an external density measurement of the fuel as well as errors associated with the use of the loop injector for the LC-pump system.

Comparison of Methods 1-3 for Weight % Determination Using LC-^{1}H NMR Data

In order to test the accuracy of Methods 1-3, LC-^{1}H NMR, ^{13}C FTNMR, and density data were obtained for "model mixture C" (15). This is the same model mixture which was previously employed (5) to test the accuracy of the average molecular approach (see Table II, ref. 5). In Table IV, the average weight % data are reported for model mixture C using Methods 1-3 and are compared with the known values. Of the three methods, Method 1 compares favorably with the known values. Whereas, Method 2 has a lower value for WP^a in comparison with the known value. This is consistent with the fact that model mixture C contains an appreciable quantity (200.40g) of isooctane and is the only alkane hydrocarbon in this model mixture which contains a quaternary carbon atom. It should be recalled that a major drawback in utilizing Method 2 is the inability of this approach to "count" quaternary carbons in the weight percent determination for the alkane fraction (WP^a). Method 3 appears to give only approximate values, however, further tests of the reliability and precision of this method should be undertaken. This method crucially depends on a separate density determination <u>and</u> accurate injection of a known volume of a given fuel.

In conclusion, Method 1 appears to provide reasonably accurate weight percent data (WP^a, WP^n, WP^d, etc.). We normally employ Method 1 to obtain weight percent data (See program in the Appendix). For example, in Table V typical weight percent data for various fuels are reported. Nevertheless, a more accurate method for obtaining weight percent data is still desired. In this regard, a recent paper (16) describing a method for on-line density measurements could ultimately be used in conjunction with the LC-^{1}H NMR approach.

REFERENCES

1. J. F. Haw, T. E. Glass and H. C. Dorn, Anal. Chem., 53, 2327-2332 (1981).

2. J. F. Haw, T. E. Glass and H. C. Dorn, Anal. Chem., 53, 2332-2336 (1981).

3. J. F. Haw, T. E. Glass and H. C. Dorn, J. Magn. Reson. 49, 22-31 (1982).

4. R. N. Hazlett, H. C. Dorn, T. E. Glass, Magnetic Resonance. Introduction, Advanced Topics and Applications to Fossil Energy, 709-720 (1984). Publisher.

5. J. F. Haw, T. E. Glass and H. C. Dorn, Anal. Chem., 55, 22-27(1983).

6. H. C. Dorn, Anal. Chem., 56, 747A (1984).

7. T. E. Glass and H. C. Dorn, J. Magn. Reson., 51,527-530 (1983).

8. T. E. Glass and H. C. Dorn, J. Magn. Reson. 52, 518-522, (1983).

9. For example, see report for Naval Research Contract (N0014-84-C-2428), September 1984-September 1985.

10. J. C. Suantoni, H. R. Garber, B. F. Davis, J. Chromatog., Sci. 13, 367 (1975).

11. R. R. Heath, J. H. Tumlinson, R. E. Doolittle, and A. T. Proveaux, J. Chromatog., Sci. 13, 380 (1975).

12. R. R. Heath and P. E. Sonnet, J. Liq. Chromatog., 3, 1129 (1980).

13. H. C. Brown, P. J. Geoghegan, Jr., J. Amer. Chem. Soc., 89, 1522 (1967).

14. (a) M. P. Spratt and H. C. Dorn, Anal. Chem., 56, 2038 (1984).
    (b) M. P. Spratt, Y. Meng, and H. C. Dorn, Anal. Chem., 57, 76 (1985).
    (c) M. P. Spratt, D. Armistead, E. Motell, and H. C. Dorn, Anal. Chem., 57, 354 (1985).

15. H. J. Albert and R. W. Wood, Rev. Sci., Instrum, 55, 589 (1984).

16. Although weight % data for only model mixture C are presented in this report, additional models and samples which more closely mimic Naval diesel fuels are currently being studied.

TABLE I

LC-^{1}H NMR Average Molecule Properties for Fuel 85-06 Spiked With 1% Fluorene and 1% Phenanthrene

FUEL: (85-06 Doped with 1% Fluorene and 1% Phenanthrene by wt.)
SOURCE: NAVAL RESEARCH LABORATORY

STATIC NMR DATA:	^{13}C Aromaticity FX-60	^{13}C Aromaticity FX-200	^{1}H Aromaticity FX-60	^{1}H Aromaticity FX-200	AVG. N-ALKANE LENGTH
		.131	NA		

LC-^{1}H NMR QUANTITATIVE DATA:

AVERAGE STRUCTURAL PARAMETERS FOR MONOCYCLIC AROMATIC FRACTION	$^{m}*C_{un}$	$^{m}*C_{sub}$	$^{m}*C_{\alpha CH_3}$	$^{m}*C_{\alpha CH_2}$	$^{m}*C_{\alpha CH}$	$^{m}*C_{\alpha tet}$	$^{m}*C_{CH_2>\alpha}$	$^{m}*C_{CH_3>\alpha}$	$^{m}\overline{MW}$	^{m}ADS
	3.79	2.21	1.46	0.60	0.01	0.14	2.52	0.61	152.1	2.21
AVERAGE STRUCTURAL PARAMETERS FOR DICYCLIC AROMATIC FRACTION	$^{d}*C_{un}$	$^{d}*C_{sub}$	$^{d}*C_{BH}$	$^{d}*C_{\alpha CH_3}$	$^{d}*C_{\alpha CH_2}$	$^{d}*C_{\alpha CH}$	$^{d}*C_{CH_2>\alpha}$	$^{d}*C_{CH_3>\alpha}$	$^{d}\overline{MW}$	^{d}ADS
	6.55	1.45	2.00	1.36	0.09	0.00	0.10	0.09	151.2	1.45
AVERAGE STRUCTURAL PARAMETERS FOR FLUORENE FRACTION	$^{f}*C_{un}$	$^{f}*C_{sub}$	$^{f}*C_{BH}$	$^{f}*C_{\alpha CH_3}$	$^{f}*C_{\alpha CH_2}$	$^{f}*C_{\alpha CH}$	$^{f}*C_{CH_2>\alpha}$	$^{f}*C_{CH_3>\alpha}$	$^{f}\overline{MW}$	^{f}ADS
	7.74	0.26	4.00	0.22	1.04	0.00	0.34	0.04	175.1	0.26
AVERAGE STRUCTURAL PARAMETERS FOR PHENANTHRENE FRACTION	$^{p}*C_{un}$	$^{p}*C_{sub}$	$^{p}*C_{BH}$	$^{p}*C_{\alpha CH_3}$	$^{p}*C_{\alpha CH_2}$	$^{p}*C_{\alpha CH}$	$^{p}*C_{CH_2>\alpha}$	$^{p}*C_{CH_3>\alpha}$	$^{p}\overline{MW}$	^{p}ADS
	9.78	0.22	4.00	0.12	0.11	0.00	0.28	0.11	186.59	0.22

FUEL:
SOURCE: 85-06, 1% Doped

ABS. NO. MOLES OF CARBON & FRACTIONAL AROMATICTY DATA	ALKANES		MONOCYCLIC AROMATICS				DICYCLIC AROMATICS			
	C^a_{total}	F^a_{total}	$C^m_{Artotal}$	C^m_{total}	f^m_a	F^m_{total}	$C^d_{Artotal}$	C^d_{total}	f^d_a	F^d_{total}
	.005000	.789	.000567	.001073	0.83	.156	.000180	.000210	.026	.031

FLUORENES				PHENANTHRENES				
$C^f_{Artotal}$	C^f_{total}	f^f_a	F^f_{total}	$C^p_{Artotal}$	C^p_{total}	f^p_a	F^p_{total}	f_a
.000073	.000083	.011	.012	.000079	.000081	.012	.012	.13

COMMENTS:

Solvent contamination peak appears at 5.72 ppm

OTHER PHYSICAL DATA:	SMOKE POINT[1]	FREEZING POINT[2]	ELEMENTAL ANALYSIS[3] C	H	H (by NMR)	AROMATICITY[4] (Volume %)

TABLE II

LC-^{1}H NMR Average Molecule Properties for Fuel 85-06

FUEL: 85-06

SOURCE: NAVAL RESEARCH LABORATORY

STATIC NMR DATA:	^{13}C Aromaticity FX-60	^{13}C Aromaticity FX-200	^{1}H Aromaticity FX-60	^{1}H Aromaticity FX-200	AVG. N-ALKANE LENGTH
		0.126	NA		

LC-^{1}H NMR QUANTITATIVE DATA:

AVERAGE STRUCTURAL PARAMETERS FOR MONOCYCLIC AROMATIC FRACTION	^{m} $*C_{un}$	^{m} $*C_{sub}$	^{m} $*C_{\alpha CH_3}$	^{m} $*C_{\alpha CH_2}$	^{m} $*C_{\alpha CH}$	^{m} $*C_{\alpha tet}$	^{m} $*C_{CH_2>\alpha}$	^{m} $*C_{CH_3>\alpha}$	^{m} $\overline{MW}$	^{m} ADS
	3.58	2.42	1.52	0.700	0.05	0.15	2.03	0.75	150.70	2.42
AVERAGE STRUCTURAL PARAMETERS FOR DICYCLIC AROMATIC FRACTION	^{d} $*C_{un}$	^{d} $*C_{sub}$	^{d} $*C_{BH}$	^{d} $*C_{\alpha CH_3}$	^{d} $*C_{\alpha CH_2}$	^{d} $*C_{\alpha CH}$	^{d} $*C_{CH_2>\alpha}$	^{d} $*C_{CH_3>\alpha}$	^{d} $\overline{MW}$	^{d} ADS
	6.28	1.72	20	1.62	0.10	0	0.00	0.10	153.6	1.72
AVERAGE STRUCTURAL PARAMETERS FOR FLUORENE FRACTION	^{f} $*C_{un}$	^{f} $*C_{sub}$	^{f} $*C_{BH}$	^{f} $*C_{\alpha CH_3}$	^{f} $*C_{\alpha CH_2}$	^{f} $*C_{\alpha CH}$	^{f} $*C_{CH_2>\alpha}$	^{f} $*C_{CH_3>\alpha}$	^{f} $\overline{MW}$	^{f} ADS
	0	0.00	0	0.00	0.00	0.00	0.00	0.00	0	0
AVERAGE STRUCTURAL PARAMETERS FOR PHENANTHRENE FRACTION	^{p} $*C_{un}$	^{p} $*C_{sub}$	^{p} $*C_{BH}$	^{p} $*C_{\alpha CH_3}$	^{p} $*C_{\alpha CH_2}$	^{p} $*C_{\alpha CH}$	^{p} $*C_{CH_2>\alpha}$	^{p} $*C_{CH_3>\alpha}$	^{p} $\overline{MW}$	^{p} ADS
	0	0	0	0	0	0	0	0	0	0

FUEL:
SOURCE: 85-06

ABS. NO. MOLES OF CARBON & FRACTIONAL AROMATICTY DATA	ALKANES		MONOCYCLIC AROMATICS				DICYCLIC AROMATICS			
	C^a_{total}	F^a_{total}	$C^m_{Artotal}$	C^m_{total}	f^m_a	F^m_{total}	$C^d_{Artotal}$	C^d_{total}	f^d_a	F^d_{total}
	0.004	0.782	0.000552	0.001031	0.100	0.187	0.000142	0.000168	0.026	0.031

FLUORENES				PHENANTHRENES				
$C^f_{Artotal}$	C^f_{total}	f^f_a	F^f_{total}	$C^p_{Artotal}$	C^p_{total}	f^p_a	F^p_{total}	f_a
0	0	0	0	0	0	0	0	0

COMMENTS:

OTHER PHYSICAL DATA:	SMOKE POINT[1]	FREEZING POINT[2]	ELEMENTAL ANALYSIS[3] C	H	H (by NMR)	AROMATICITY[4] (Volume %)

TABLE III

W^a = weight of the alkane fraction

W^x = weight of an aromatic fraction (x = m,d,f, or p)

W^{total} = total weight of all chromatography fractions

WP^x = weight percent of a chromatography fraction (x = a,m,d,f, or p)

F^x = The fraction of total carbon in each chromatographic fraction (i.e., $F^a_{total} + F^m_{total} + F^d_{total} + F^f_{total} + F^p_{total} = 1$

C^x_{total} = The total carbon in a given fraction (i.e., alkane, monocyclic, dicyclic, phenanthrene, or fluorene fractions)

F^a = The carbon aromaticity for the total sample (i.e., the total aromatic carbon ($C_{Ar(total)}$) divided by total carbon (C_{total})

$\overline{MW}_C$ = molecular weight of a quaternary carbon

$\overline{MW}_{CH}$ = molecular weight of a methine group

$\overline{MW}_{CH_2}$ = molecular weight of a methylene group

$\overline{MW}_{CH_3}$ = molecular weight of a methyl group

Table IV

Weight Percent Data for Model Mixture C Utilizing Methods 1-3[1]

Model Mixture C	WP^a	WP^m	WP^d
(Method 1)	90.87	6.94	2.19
(Method 2)	87.81	6.94	2.19
(Method 3)	89.88	7.70	2.43
(Known Values)	91.02	6.65	2.33

[1] Model C was prepared by mixing 13.29 g of n-butylbenzene, 18.47 g of n-pentane, 10.16 g of m-xylene, 13.07 g of tetralin, 95.70 g of n-nonane, 56.20 of hexadecane, 200.40 g of isooctane, 43.65 g of n-hexane, 85.67 g of dodecane, and 12.80 g of napthalene. The known values above are based on this composition data. Also, the text should be consulted for a complete description of Methods 1-3. In addition, it should be noted that WP^f and WP^p are zero for this model mixture.

Mixture 3 is a poor choice for two reasons in relationship to U. S. Navy fuels: (1) Components are too low M.Wt. in several cases (particularly C_5 and i-C_8) and volatiles are easily lost; (2) i-C_8 is not representative - the amount of quarternary carbons would never be this high.

TABLE V

Weight Percent

FUEL	ALKANE	MONOCYCLIC AROMATICS	DICYCLIC AROMATICS	FLUORENES	PHENANTHRENE
NRL 83-7	65.08	25.37	8.60	.94	.002
NRL 83-8	69.08	18.87	8.90	2.64	.51
NRL 83-9	64.61	20.67	11.59	2.30	.83
NRL 83-10	58.31	34.15	6.77	.76	.002
NRL 83-12	69.10	17.85	10.68	1.22	1.25
NRL 83-14	69.13	19.52	8.41	2.59	.35
NRL 83-17	69.42	21.59	7.26	1.26	.47
NRL 83-19	68.57	16.45	12.02	1.53	1.43
NRL 83-22	64.74	16.31	15.52	2.76	.67
NRL 83-23	61.68	21.84	13.37	1.47	1.65
NRL 83-24	52.08	19.79	20.42	5.04	2.67
NRL 83-26	58.96	24.52	11.49	3.35	1.68
NRL 83-27	70.44	17.99	7.84	2.69	1.04
NRL 83-30	75.36	15.46	7.20	1.35	.63
NRL 83-36	59.79	21.47	15.36	2.58	.81
NRL 83-37	65.19	18.61	11.69	3.14	1.37

FIGURE 1a

LC-^{1}H NMR Profile of Fuel 85-06
Doped with 1% Fluorene and 1% Phenanthrene
Alkane Files
Separation on a Whatman M9 10/25 PAC Column
Solvent Used: Freon 113/$CDCl_3$: 95%/5%
HMDS Added 0.05%
Each of Files 1-12 represents .5ml elution volume

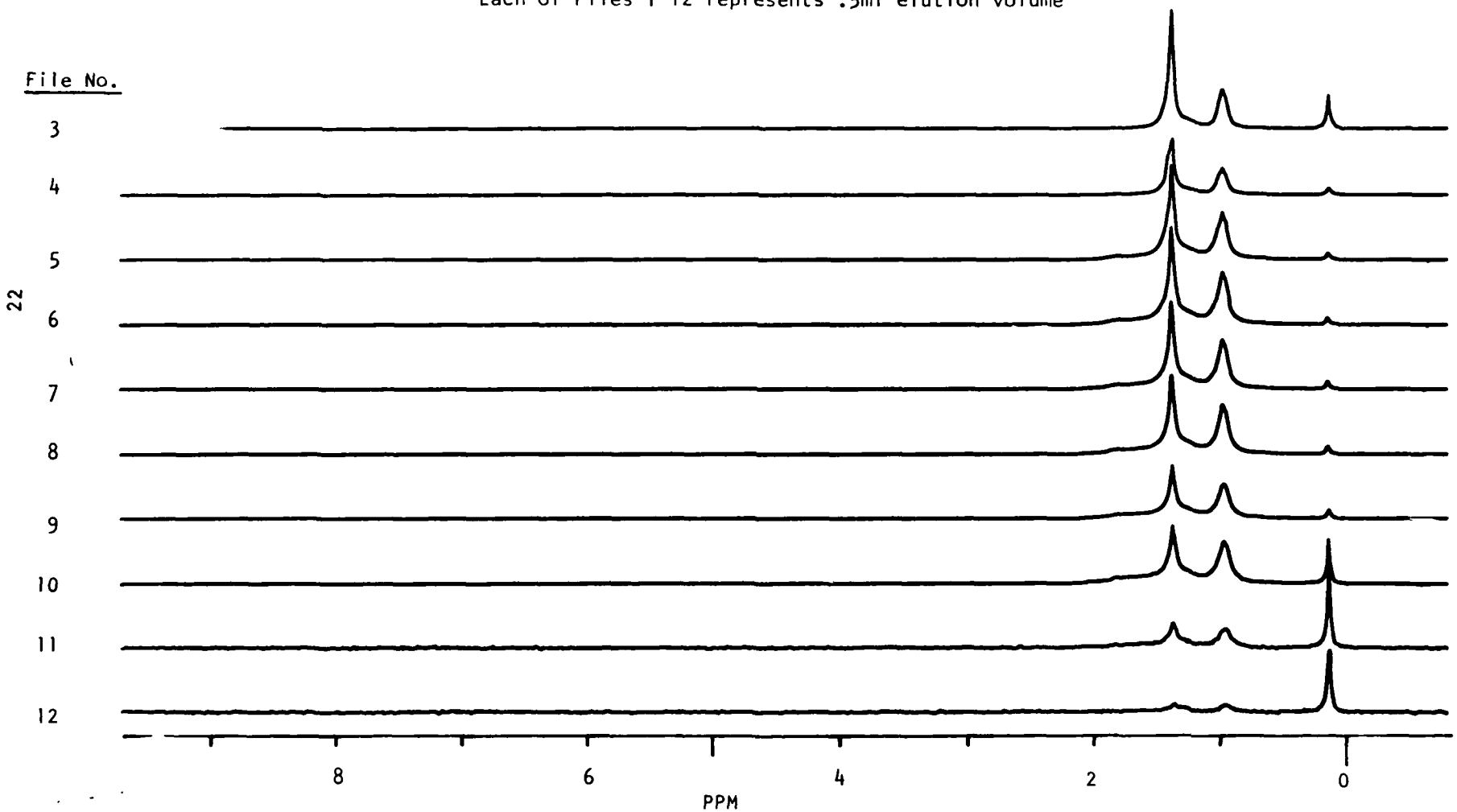


FIGURE 1b

LC-NMR Profile of Fuel 85-06, 1% Doped
Monocyclic Aromatic Files
Each of Files 13-27 represents 1 ml elution volume

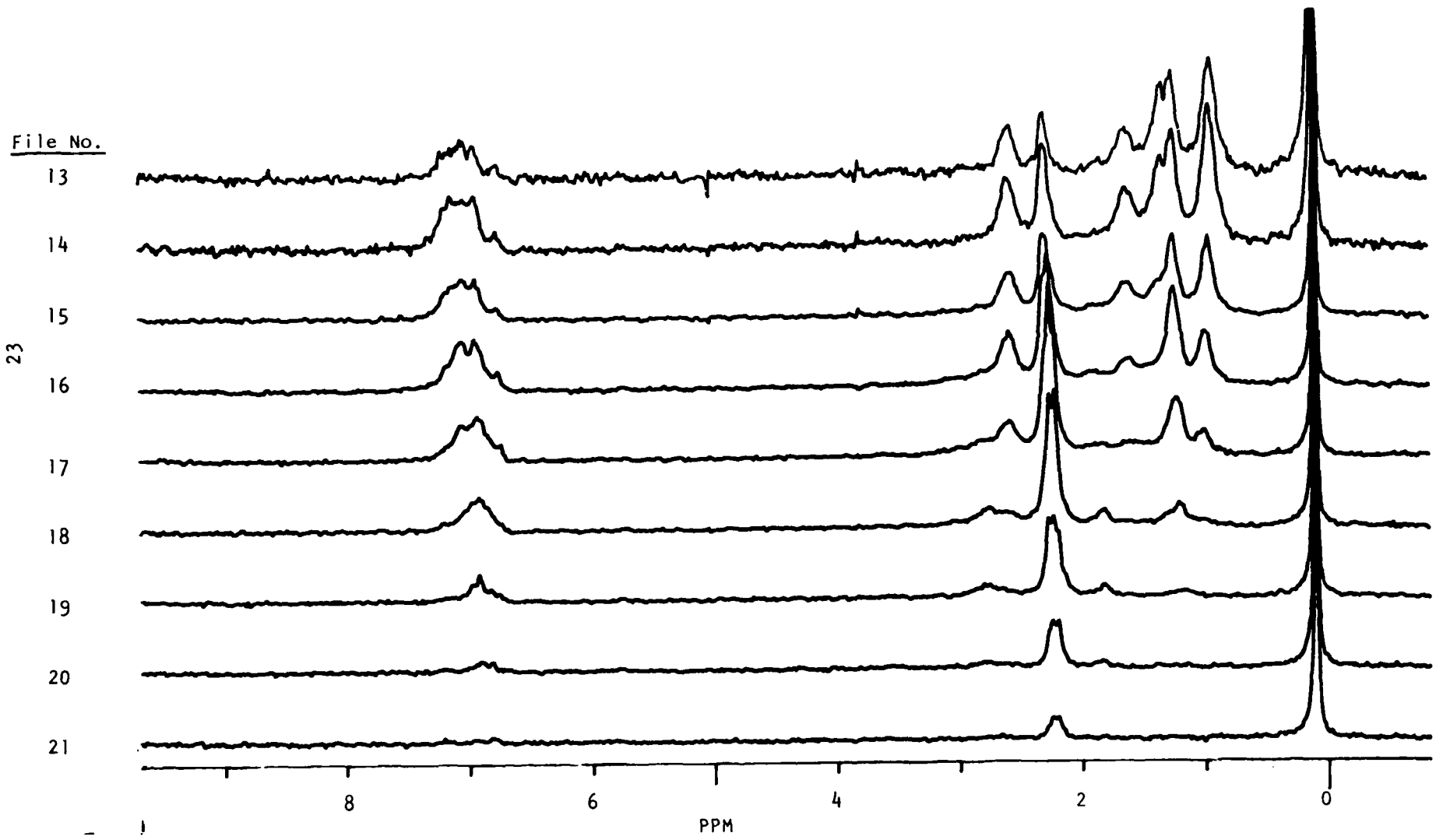


FIGURE 1c

LC-^{1}H NMR Profile of Fuel 85-06, 1% Doped
Dicyclic Aromatic Files
Each of Files 28-45 represents 2 ml elution volume

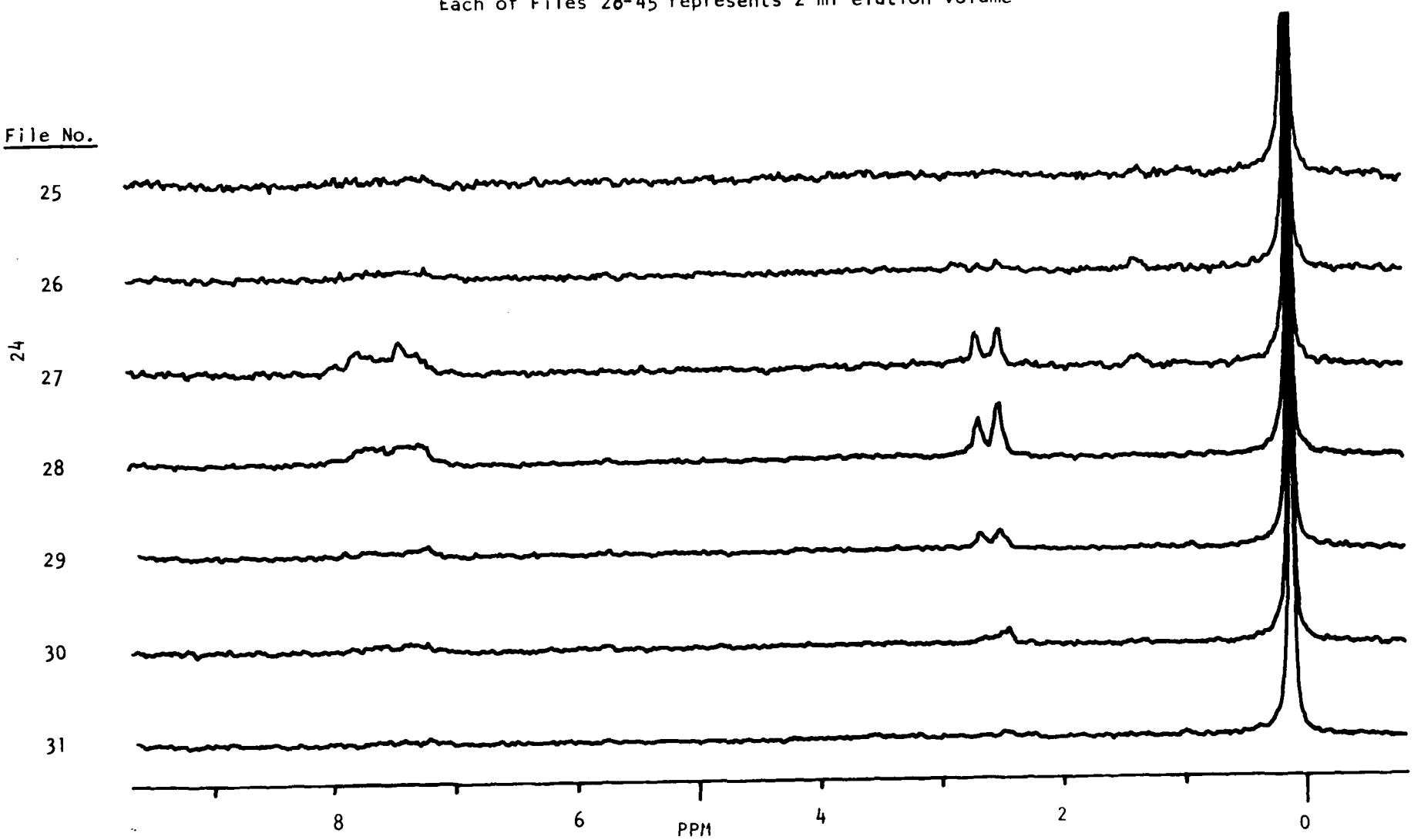


FIGURE 1d

LC-NMR Profile of Fuel 85-06, 1% Doped
Fluorene Files
Each of Files 28-45 represents 2ml elution volume

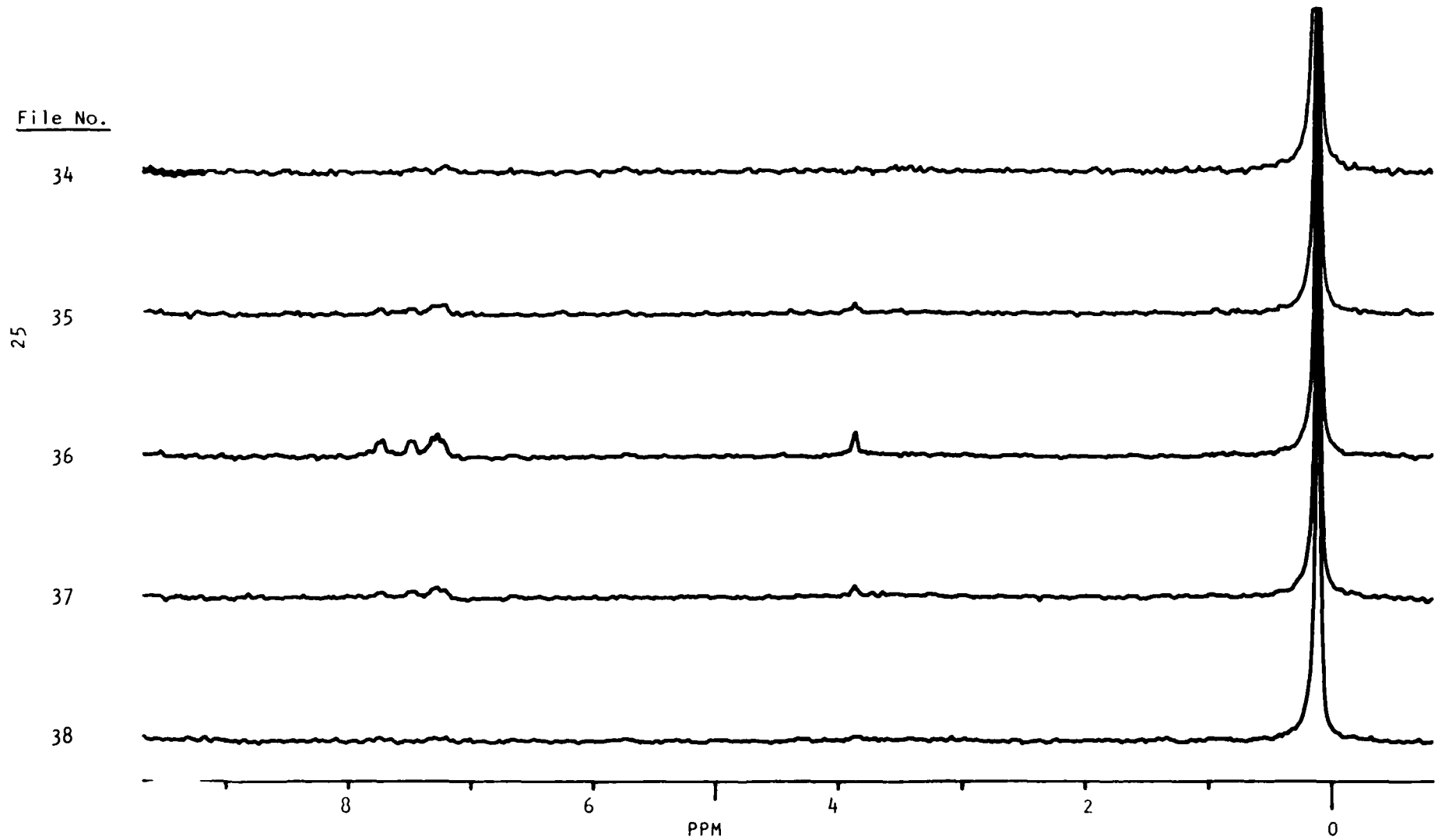


FIGURE 1e

LC-NMR Profile of Fuel 85-06, 1% Doped
Phenanthrene Files
Each of Files 28-45 represents 2ml elution volume

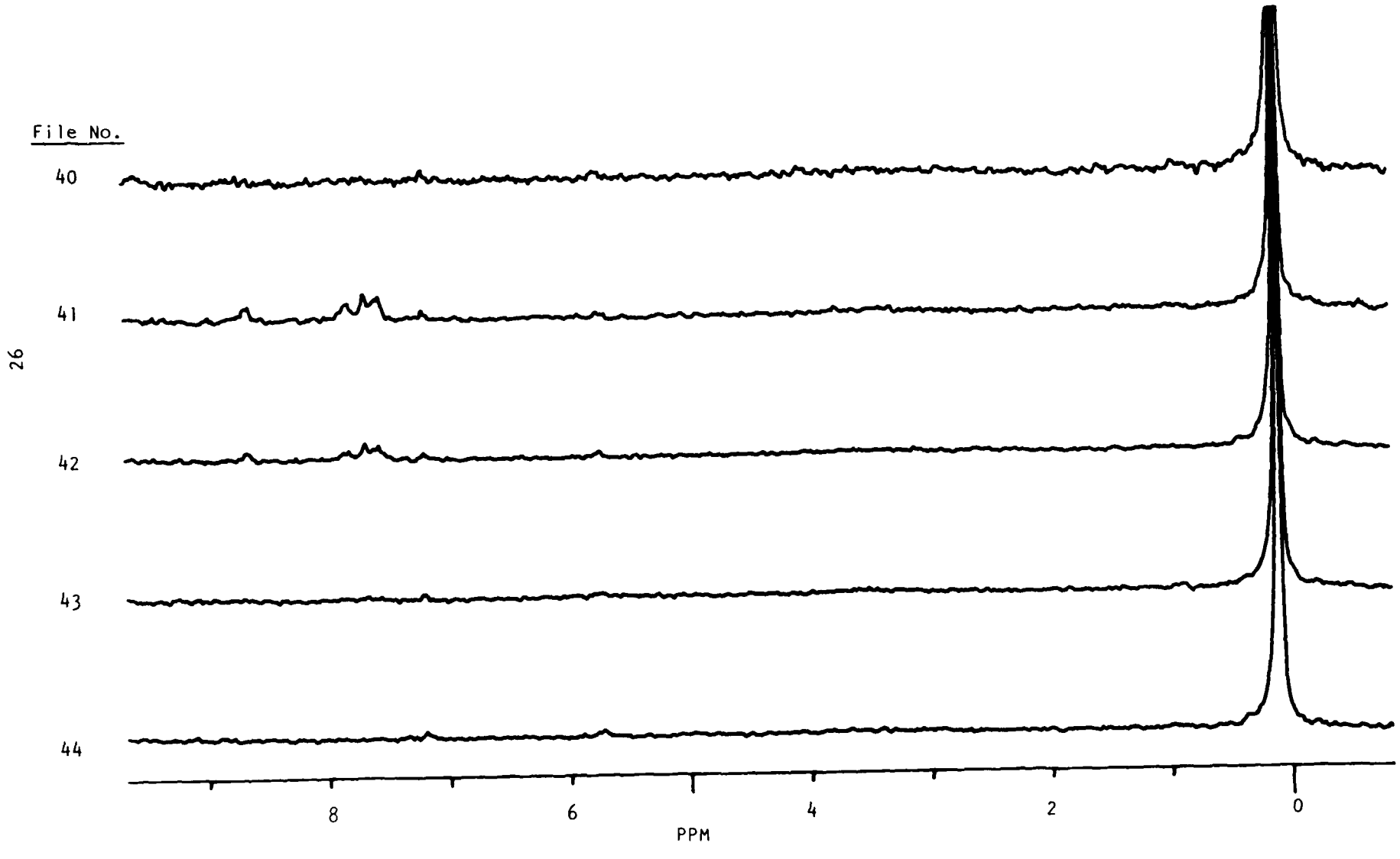


FIGURE 2a

LC-^{1}H NMR Profile of Fuel 85-06
Alkane Files
Separation on a Whatman M9 10/25 PAC Column
Solvent Used: Freon 113/$CDCl_3$: 95%/5%
HMDS Added 0.05%
Each of Files 1-12 represents .5ml elution volume

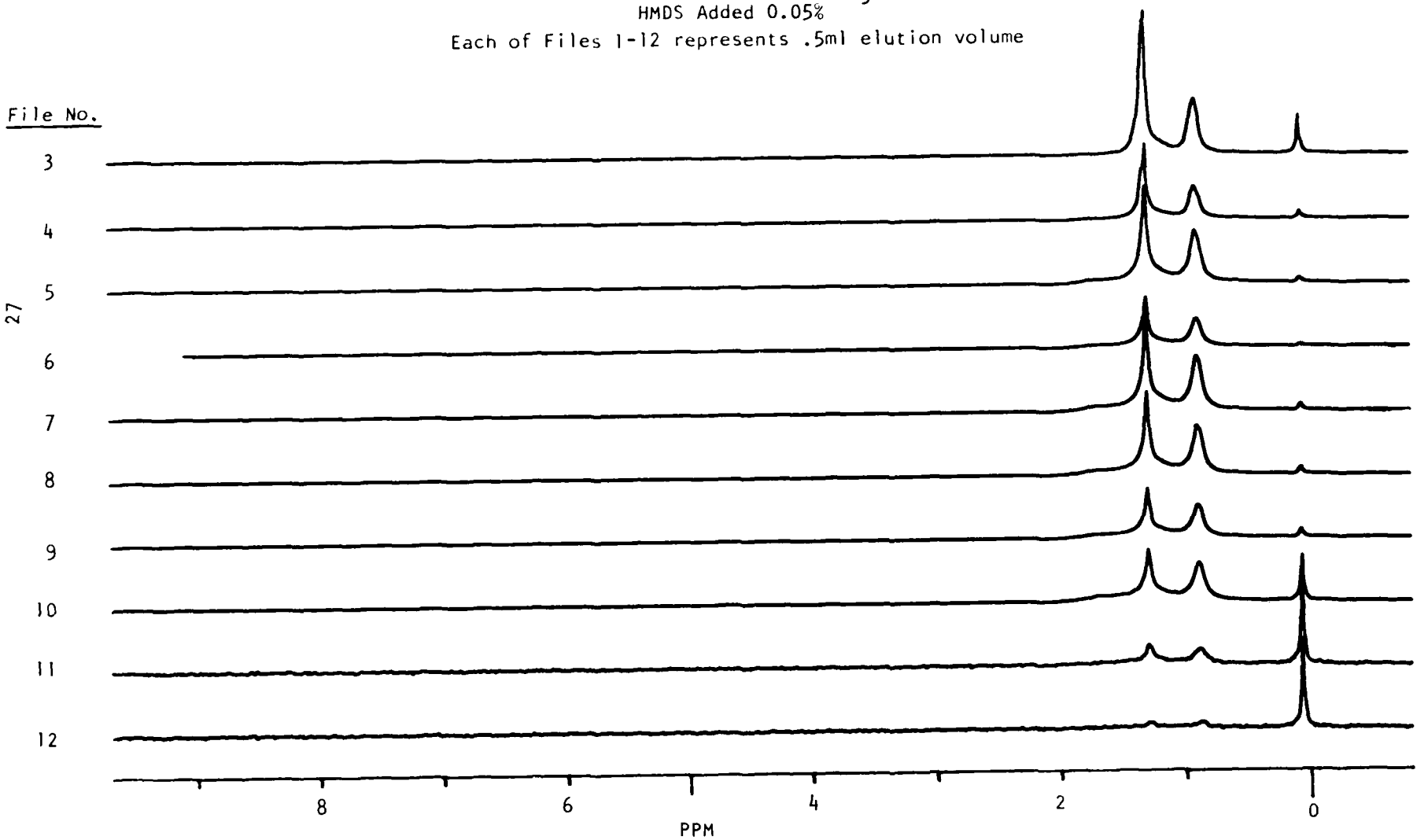


FIGURE 2b

LC-NMR Profile of Fuel 85-06
Monocyclic Aromatic Files
Each of Files 13-27 represents 1 ml elution volume

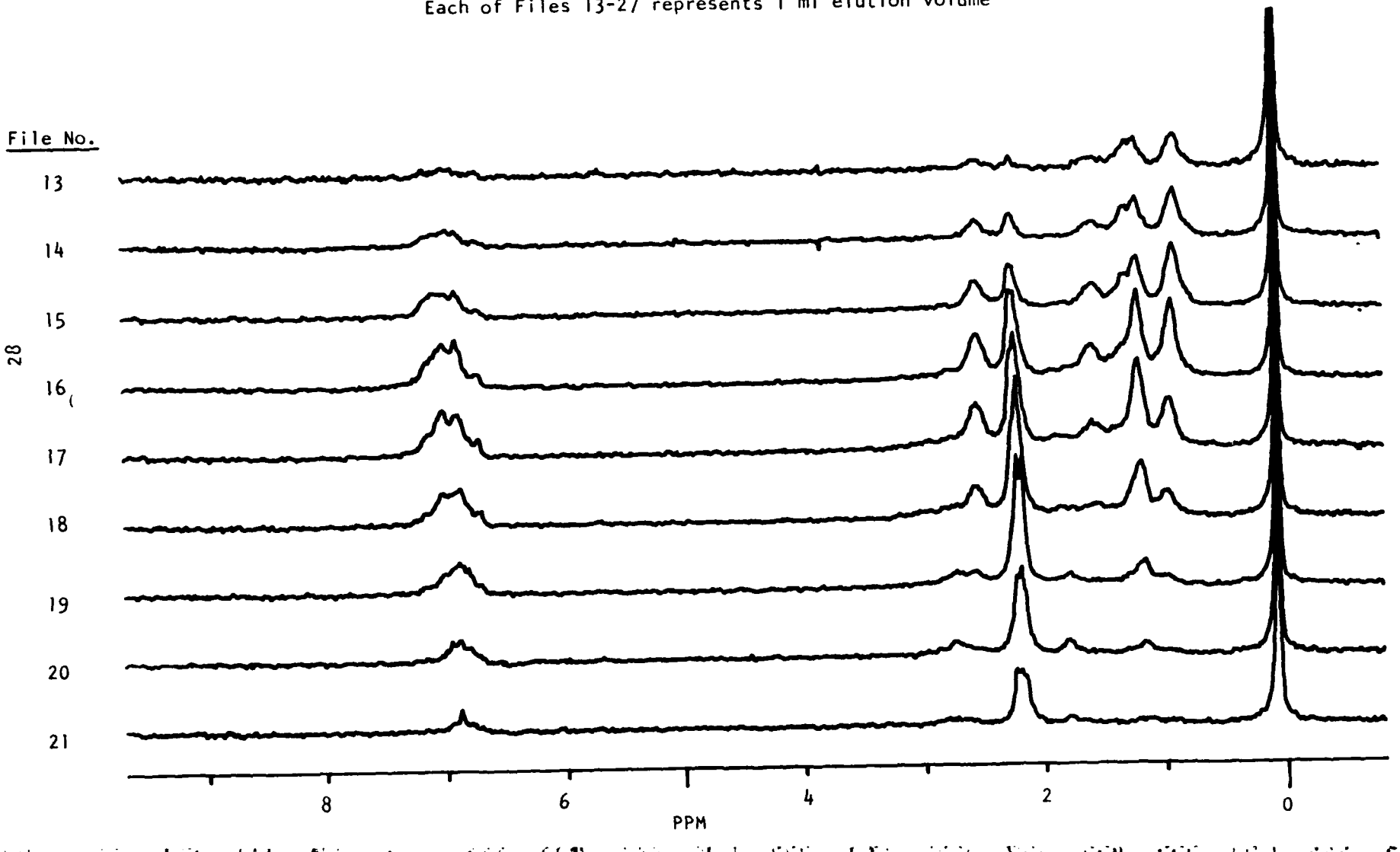


FIGURE 2c

LC-^{1}H NMR Profile of Fuel 85-06
Dicyclic Aromatic Files
Each of Files 28-45 represents 2 ml elution volume

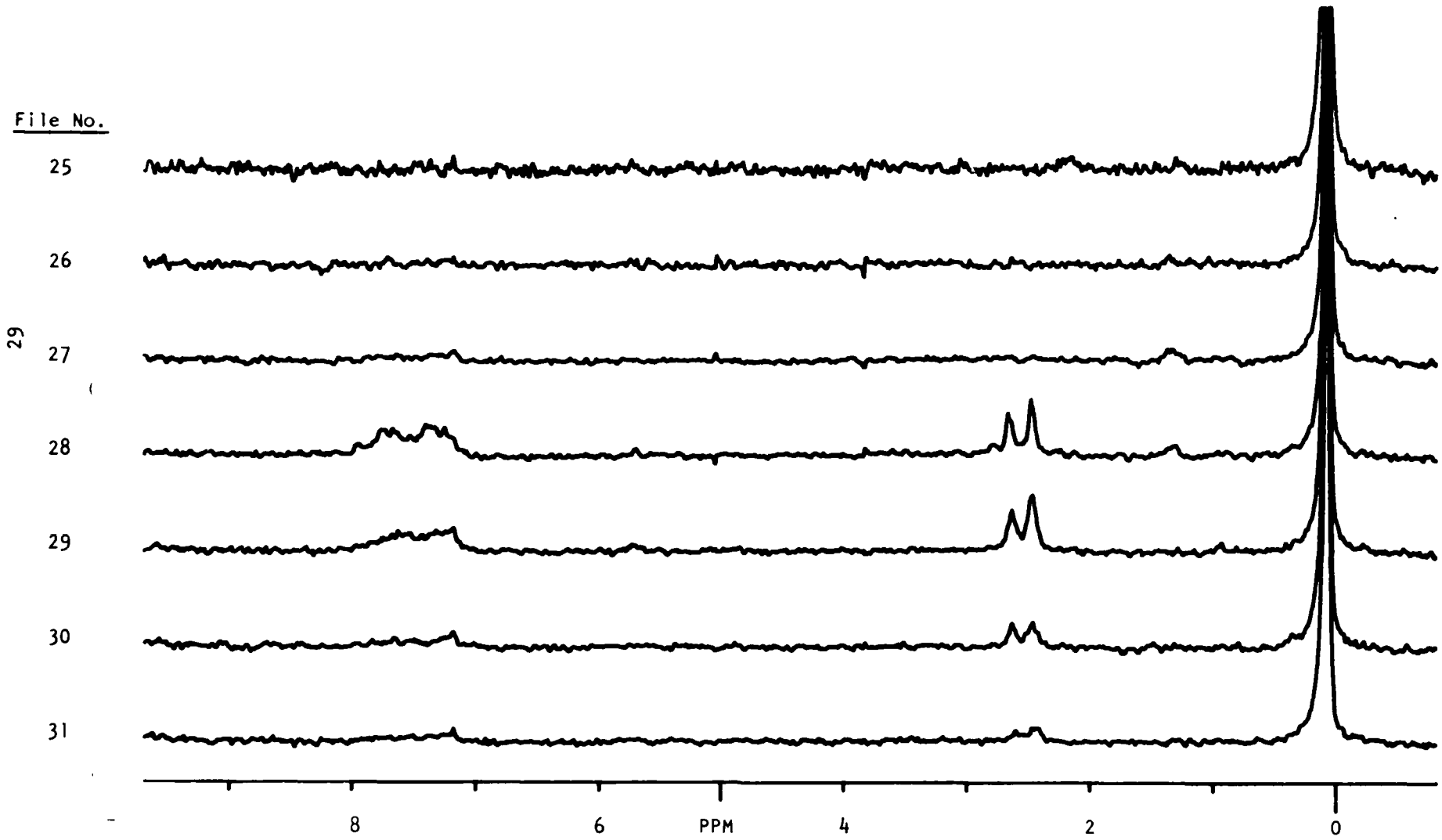


FIGURE 2d

LC-NMR Profile of Fuel 85-06
Fluorene Files
Each of Files 28-45 represents 2ml elution volume

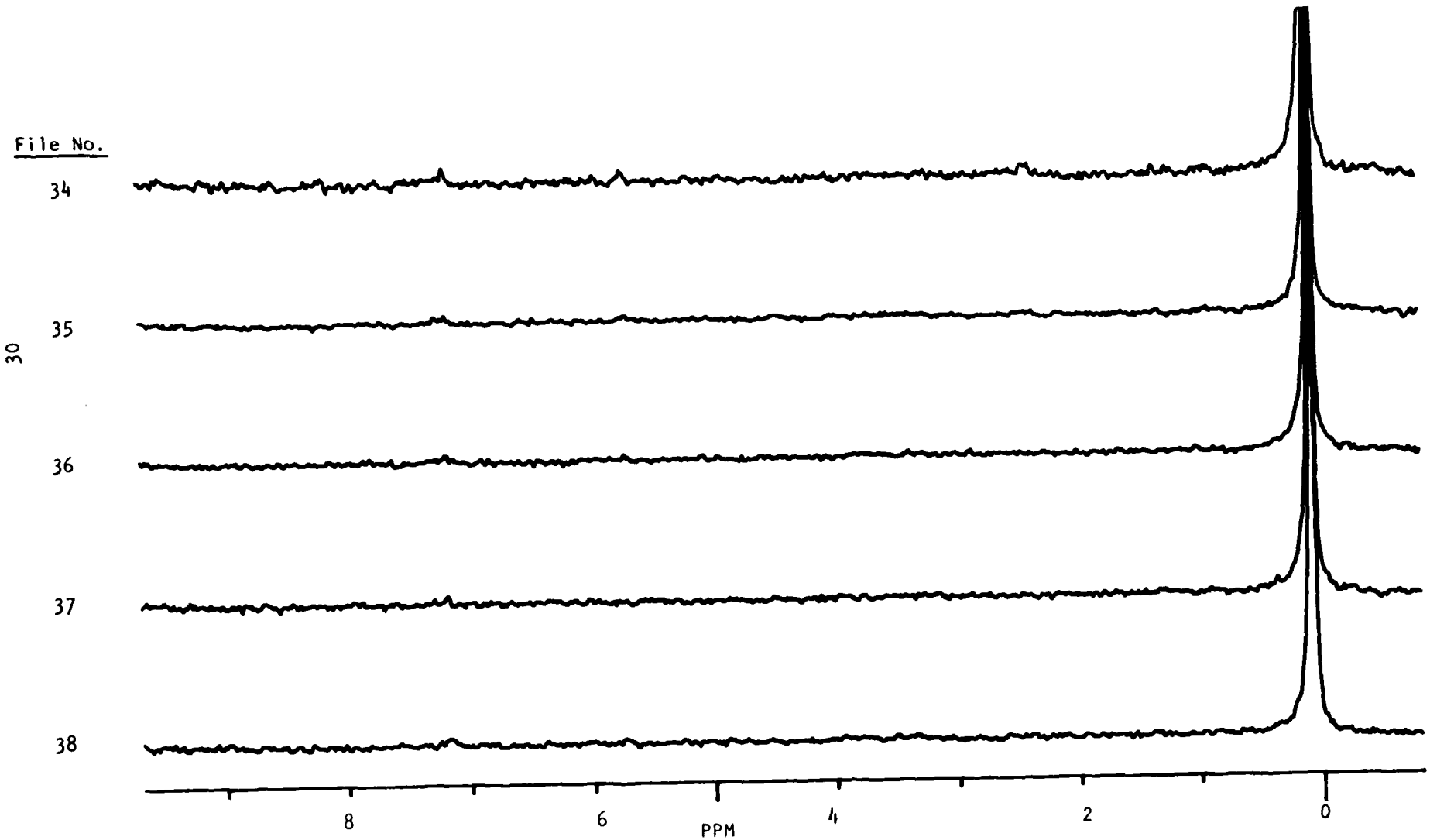


FIGURE 2e

LC-NMR Profile of Fuel 85-06
Phenanthrene Files
Eac of Files 28-45 represents 2ml elution volume

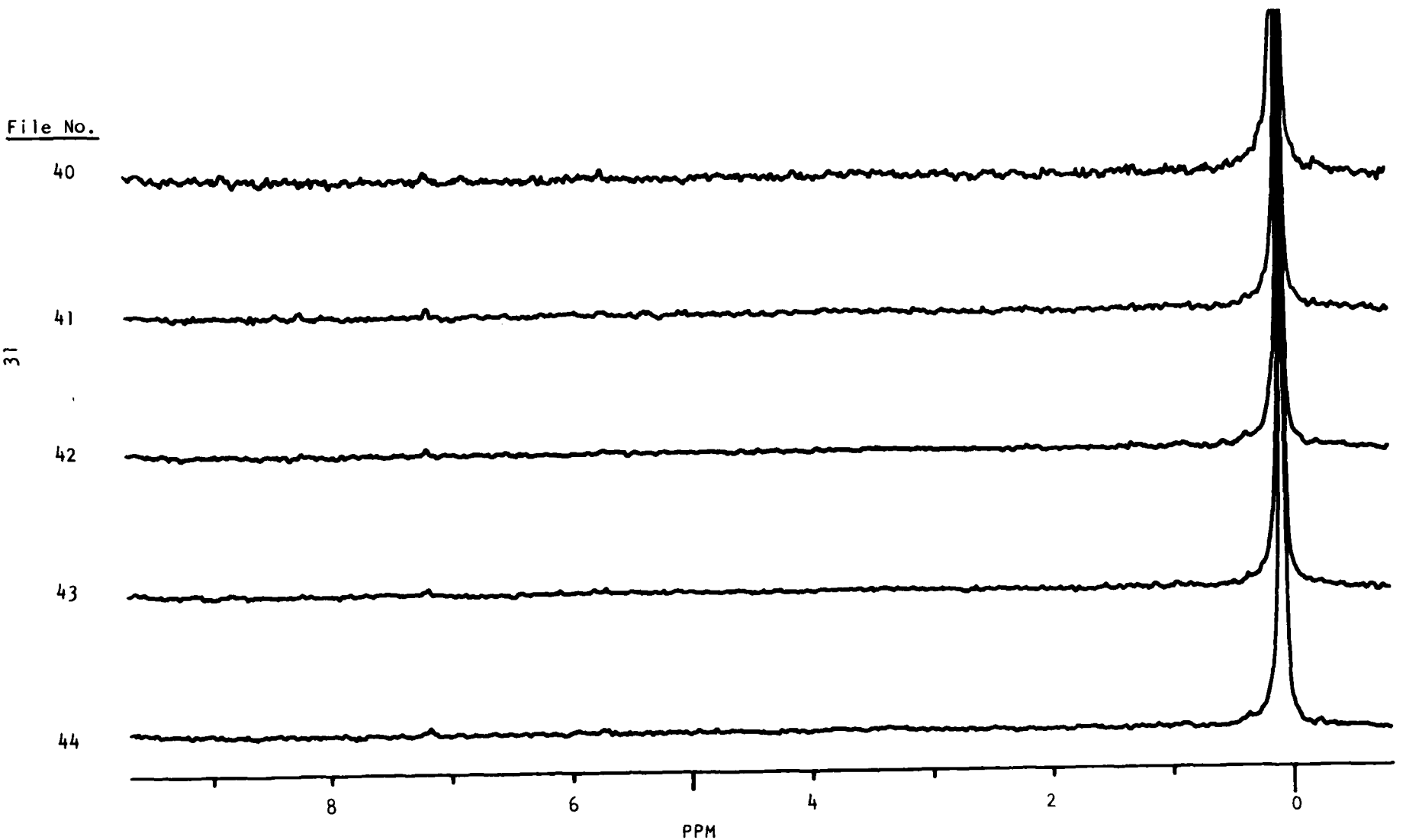
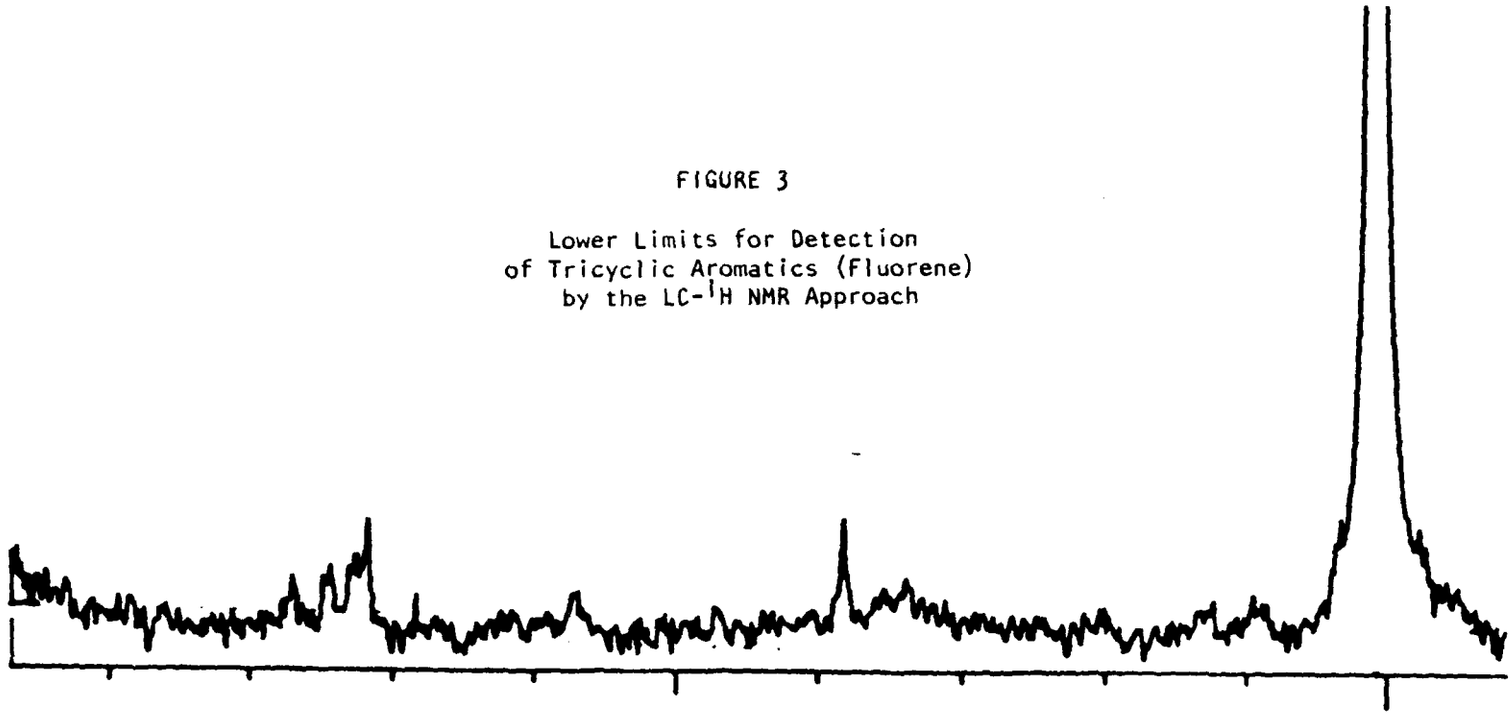
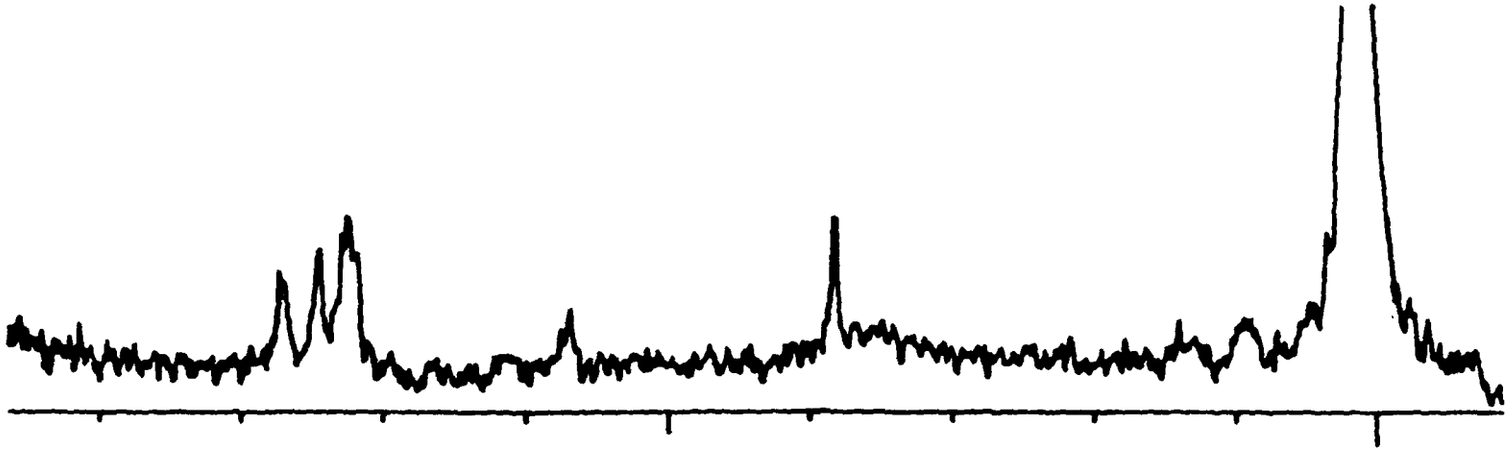


FIGURE 3

Lower Limits for Detection
of Tricyclic Aromatics (Fluorene)
by the LC-^{1}H NMR Approach



(a) Fluorene at 0.5% level (4.5 min. observation time)



(b) Fluorene at 1% level (4.5 min. observation time)

FIGURE 4

TRICYCLIC AROMATICS

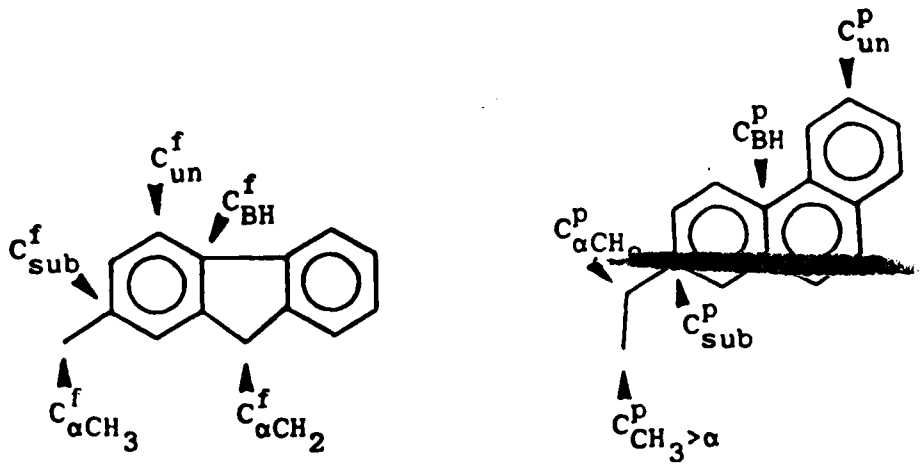
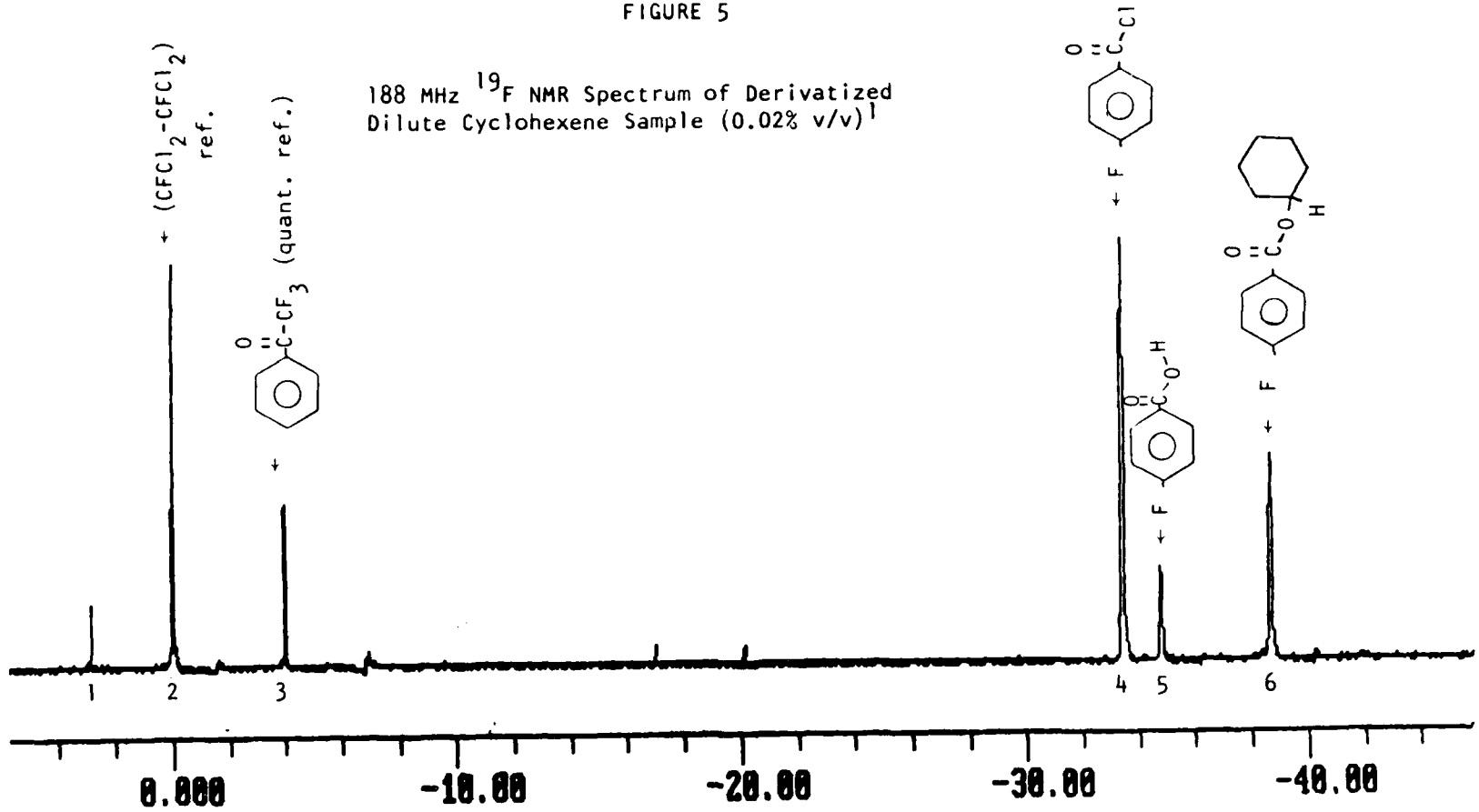


FIGURE 5

188 MHz ^{19}F NMR Spectrum of Derivatized Dilute Cyclohexene Sample (0.02% v/v)[1]



1) A yield of 55.9% can be estimated for the overall conversion of yclohexene → cyclohexanol → p-fluorobenzoate ester based on the quantitative ^{19}F NMR reference ααα-trifluoroacetophenone. For other details see the text and reference 14.

Expansion of Figure 5

(-32 to -42 ppm)

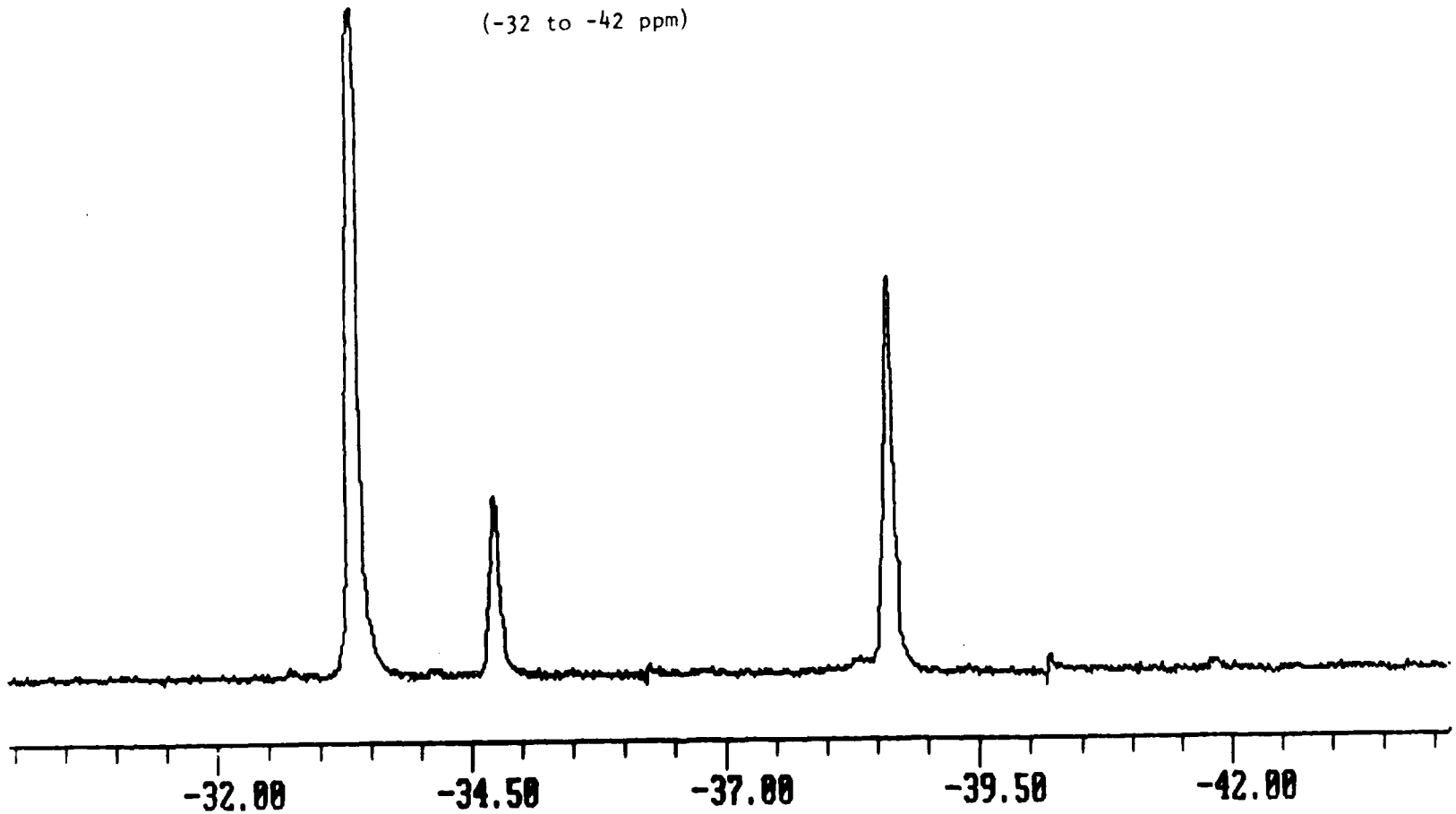
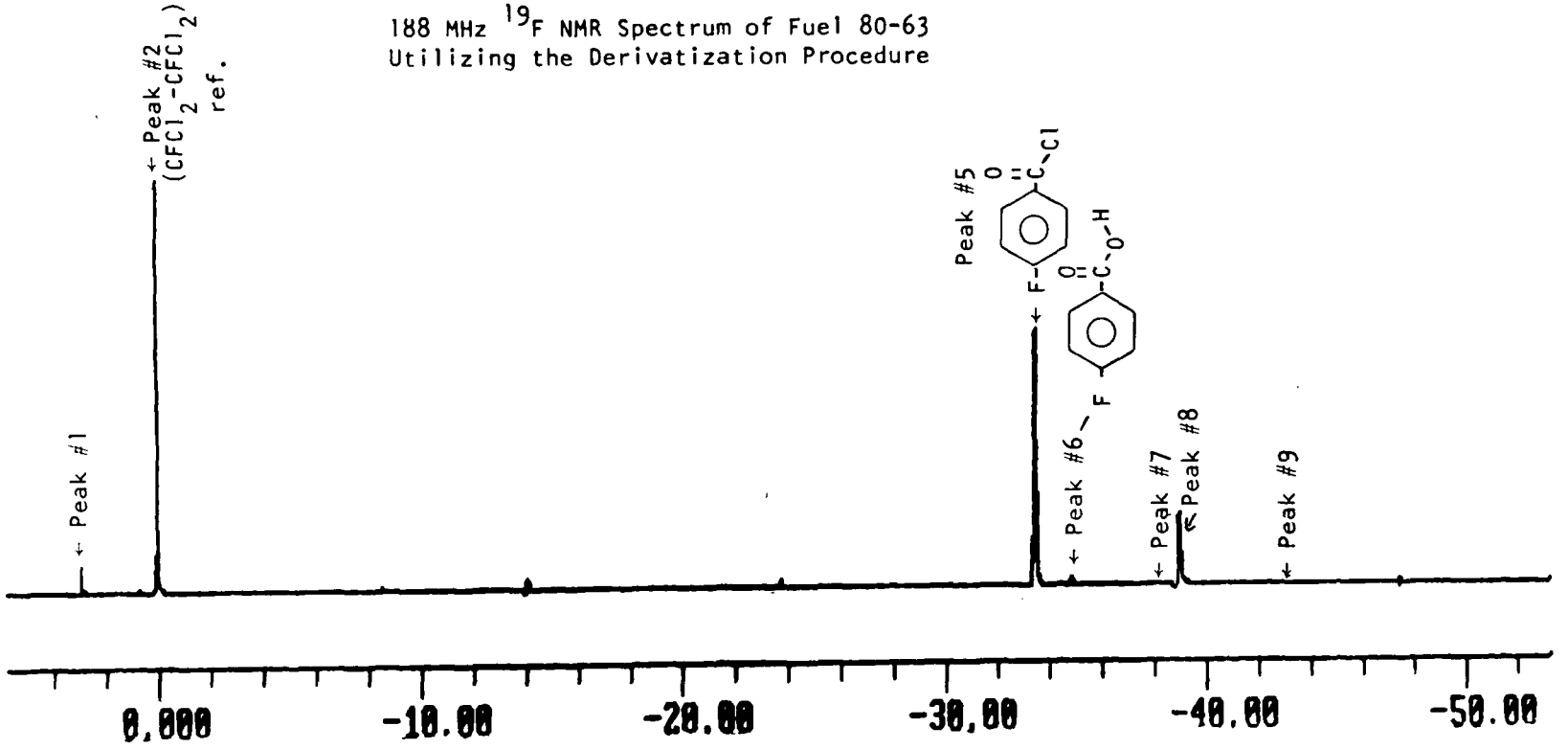
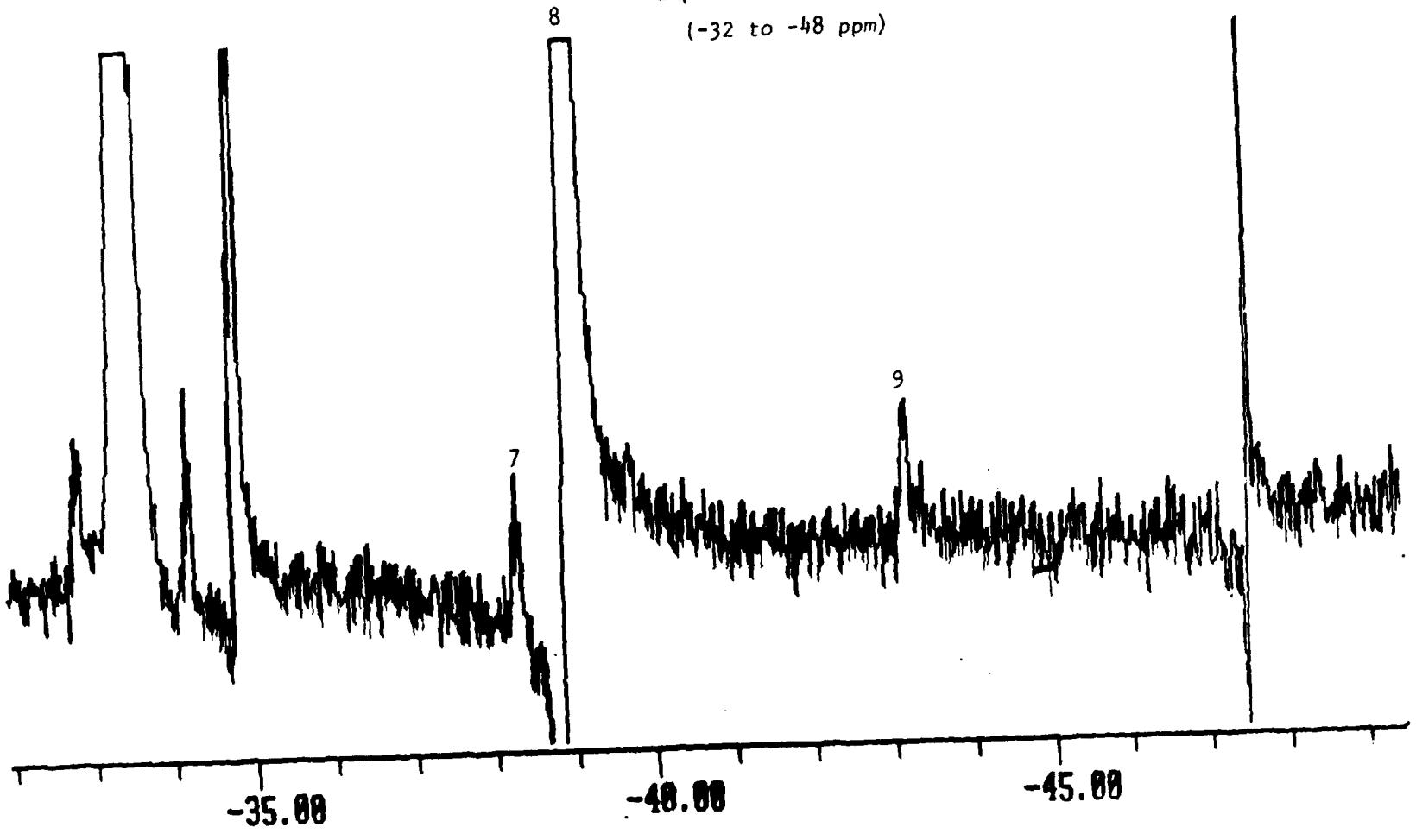


FIGURE 6

188 MHz ^{19}F NMR Spectrum of Fuel 80-63
Utilizing the Derivatization Procedure



Expansion of Figure 6
(-32 to -48 ppm)



```
10 REM              This is the LC-NMR program revised 1984
20 REM    This is essentially the original LCNMR program.  It has been modified
26 REM    to handle putting the data into and out of a disk file.  It also
27 REM    prints out the wt %'s  for 2 different methods of calcualtion.
30 REM
40 REM
50 REM
60 REM              The first section is a general input section to get the
70 REM              softkeys defined and determine how you wish to enter the
80 REM              data.  It also gets the file name
90 REM
100 CLS
110 GOSUB 6510                                          ! Sets up blanks for subtrn
120 TEXT (25,225,"Please press the first softkey to begin.",2)
130 INPUT "",A$ : LOCATE 0,0 : PRINT SPACE$(10)   CLS
140 IF A$="EDIT" THEN GOSUB 6420 ELSE GOSUB 6170
150 LOCATE 12,14:PRINT"Do you wish to use the parameters stored in a file (F),"
160 PRINT TAB (12)"enter them manually (M), or stored from manual entry (S) ? "
170 LOCATE 14,40 : INPUT "";PARAM$
180 LOCATE 18,17 : PRINT "Do you wish to use blank #1 or #2? (1)/(2): ";
190 INPUT "";BLANK
200 LOCATE 12,10 : PRINT SPACE$(620)
210 OPEN "#PR" AS FILE #1
220 X9=0
230 LOCATE 12,25 : INPUT "Please enter the sample name: ";N$
240 IF N$="" THEN 230
250 LOCATE 12,20 : PRINT SPACE$(100);
260 IF PARAM$="F" OR PARAM$="f" OR PARAM$="S" OR PARAM$="s" THEN GOSUB 5800
270 D$=DATE$
280 TEXT (0,450,N$,2) : TEXT (620,450,D$,2)
290 REM
300 REM
310 REM                 The first section gets the Monocyclic inputs.
320 REM
330 REM
340 LOCATE 3,4
350 PRINT "THE FOLLOWING INPUTS ARE FROM THE MONOCYCLIC AROMATIC ";
360 PRINT "CHROMATOGRAPHIC PEAK"
370 ASD=1                                               ! Screen number for editing
380 RECNUM=1
390 IF PARAM$="F" OR PARAM$="f" THEN GOSUB 5910
400 GOSUB 3570
410 IF PARAM$="F" OR PARAM$="f" OR PARAM$="S" OR PARAM$="s" THEN GOSUB 5980
420 GOSUB 6660                                          ! Subrtn to sub out blank
430 REM       Will calculate volume from # of scans.
440 REM    To change the variables in the calculation, edit the following line
450 FLOWRATE=1.02 : SCANTIME=2.912 : CONVERT=60000
460 V=(V*SCANTIME*FLOWRATE)/CONVERT
470 R2=R\M1=A\M2=A3\M3=A2\M4=A1\M5=T\V2=V\M6=G
475 R=0 : A=0 : A3=0 : A2=0 : A1=0 : T=0 : V=0 : G=0
480 REM
490 REM
500 REM                 This is the section to get the Napthelene data.
510 REM
520 REM
530 GOSUB 6080                                          ! Sub to clear 'tween inputs
540 LOCATE 3,8 : PRINT "THE FOLLOWING INPUTS ARE FROM THE ";
550 PRINT "NAPTHALENE CHROMATOGRAPHIC PEAK"
560 RECNUM=3
```

```
570 IF PARAM$="F" OR PARAM$="f" THEN GOSUB 5910
580 GOSUB 3570
585 IF PARAM$="F" OR PARAM$="f" OR PARAM$="S" OR PARAM$="s" THEN GOSUB 5980
590 GOSUB 6750                                          ' Subrtn to sub out blank
600 V=(V*SCANTIME*FLOWRATE)/CONVERT
620 R3=R\N1=A\N2=A3\N3=A2\N4=A1\N5=T\V3=V\N6=G
625 R=0 : A=0   A3=0   A2=0   A1=0   T=0 : V=0   G=0
630 REM
640 REM
650 REM              This is the section to get the Flourene data
660 REM
670 REM
680 GOSUB 6080
690 LOCATE 3,12 : PRINT "THE FOLLOWING ",
700 PRINT "INPUTS ARE FROM THE FLUORENE CHROMATOGRAPHIC PEAK"
710 RECNUM=5
720 IF PARAM$="F" OR PARAM$="f" THEN GOSUB 5910
730 GOSUB 3570
735 IF PARAM$="F" OR PARAM$="f" OR PARAM$="S" OR PARAM$="s" THEN GOSUB 5980
740 GOSUB 6750                                          ' Subrtn to sub out blank
750 V=(V*SCANTIME*FLOWRATE)/CONVERT
770 R4=R\J1=A\J2=A3\J3=A2\J4=A1\J5=T\V4=V\J6=G
775 R=0 : A=0 : A3=0 : A2=0 : A1=0 : T=0 : V=0 : G=0
780 REM
790 REM
800 REM              This is the section to get the Phenanthrene input.
810 REM
820 REM
830 GOSUB 6080
840 LOCATE 3,32 : PRINT "PHENANTHRENE INPUT"
850 RECNUM=7 : IF PARAM$="F" OR PARAM$="f" THEN GOSUB 5910
860 GOSUB 3570
865 IF PARAM$="F" OR PARAM$="f" OR PARAM$="S" OR PARAM$="s" THEN GOSUB 5980
870 GOSUB 6750                                          ' Subrtn to sub out blank
880 V=(V*SCANTIME*FLOWRATE)/CONVERT
900 RR3=R\NN1=A\NN2=A3\NN3=A2\NN4=A1\NN5=T\VV3=V\NN6=G
905 R=0 : A=0 : A3=0 : A2=0 : A1=0 : T=0 : V=0 : G=0
910 REM
920 REM
930 REM              This is the section to get the Conc of HMDS and the C-13
940 REM              aromaticity.  Will also edit screens for inputs.
950 REM
960 REM
970 LOCATE 3,2 : PRINT SPACE$(1670)
980 LOCATE 11,15 : PRINT "Molar Concentration of HMDS: "
990 LOCATE 13,15 : PRINT "            C-13 Aromaticity: "
1000 ASD-2                                              ' Screen 2 for editing
1010 IF PARAM$="F" OR PARAM$="f" THEN 1070
1020 LOCATE 11,45 : INPUT "",M
1030 LOCATE 13,45 : INPUT "",F1
1040 GOSUB 3840
1050 IF PARAM$="S" OR PARAM$="s" THEN 1110
1060 GOTO 1170
1070 GET #2, RECORD 9 : M=CVT$F(N1$) : F1=CVT$F(N2$)
1080 LOCATE 11,45 : PRINT M;
1090 LOCATE 13,45 : PRINT F1;
1100 GOSUB 3840
1110 LSET N1$=CVTF$(M) : LSET N2$=CVTF$(F1) : PUT #2, RECORD 9
1120 REM
1130 REM
```

```
1140 REM                This is the section to do most of the calculations
1150 REM
1160 REM
1170 K2=M*V2*18/R2
1180 K3=M*V3*18/R3
1190 K4=M*V4*18/R4
1200 K5=M*VV3*18/RR3
1210 S2=(M2/3+M3/2+M4+M5/2)/(M1+M2/3+M3/2+M4+M5/2)
1220 S3=(N2/3+N3/2+N4+N5/2)/(N1+N2/3+N3/2+N4+N5/2)
1230 S4=(J2/3+J3/2+J4+J5/2)/(J1+J2/3+J3/2+J4+J5/2)
1240 S5=(NN2/3+NN3/2+NN4+NN5/2)/(NN1+NN2/3+NN3/2+NN4+NN5/2)
1250 D2=6*S2
1260 D3=8*S3
1270 D4=8*S4
1280 DD3=10*S5
1290 Z2=(M1+M2/3+M3/2+M4+M5/2)/6
1300 P1=K2*M1
1310 P2=K2*(M2/3+M3/2+M4+M5/2)
1320 P3=P2-K2*M5/2
1330 I3=K2*(M2/3)\I2=K2*(M3/2)
1340 I1=K2*M4
1350 Q5=D2-M2/(3*Z2)-M5/(2*Z2)
1360 Q4=M6/(2*Z2)-1.5*Q5
1365 IF Q4<=0 THEN Q4=0
1370 P5=K2*Z2*Q5
1380 P4=K2*Z2*Q4
1390 P6=K2*M5/2
1400 Q1=P1/(Z2*K2)
1410 Q2=P2/(Z2*K2)
1420 Q3=P3/(Z2*K2)
1430 Q6=P6/(Z2*K2)
1440 I6=I3/(Z2*K2)
1450 I5=I2/(Z2*K2)
1460 I4=I1/(Z2*K2)
1470 P7=P1+P2
1480 P8=P7+P3+P4+P5+P6
1490 W2=13*Q1+12*Q2+12*Q3+(M2+M3+M4)/Z2+14*Q4+15*Q5+14*Q6
1500 W2=W2+.011*(6+I6+I5+I4+Q6+Q5+Q3)
1510 Z3=(N1+N2/3+N3/2+N4)/8
1520 T1=K3*N1
1530 T2=K3*(N2/3+N3/2+N4)
1540 T3=(T1+T2)/4
1550 T4=T2
1560 X3=K3*N2/3\X2=K3*N3/2
1570 X1=K3*N4
1580 X6=X3/(Z3*K3)
1590 X5=X2/(Z3*K3)
1600 X4=X1/(Z3*K3)
1610 U6=D3-N2/(3*Z3)
1620 U5=N6/(2*Z3)-1.5*U6
1625 IF U5<=0 THEN U5=0
1630 U1=T1/(Z3*K3)
1640 U2=T2/(Z3*K3)
1650 U3=T3/(Z3*K3)
1660 U4=T4/(Z3*K3)
1670 T5=K3*Z3*U5
1680 T6=K3*Z3*U6
1690 W3=13*U1+24*U2+12*U3+(N2+N3+N4)/Z3+14*U5+15*U6
1700 W3=W3+.011*(10+U6+U5+X6+X5+X4)
1710 Z4=(J1+J2/3+J3/2+J4)/8
```

```
1720 L1=K4*J1
1730 L2=K4*(J2/3+J3/2+J4)
1740 L3=(L1+L2)/2
1750 L4=(L1+L2)/8
1760 H3=K4*J2/3\H2=K4*J3/2
1770 H1=K4*J4
1780 H6=H3/(Z4*K4)
1790 H5=H2/(Z4*K4)
1800 H4=H1/(Z4*K4)\U8=D4-J2/(3*Z4)
1810 U7=J6/(2*Z4)-1.5*H5
1815 IF U7<=0 THEN U7=0
1820 H7=L1/(Z4*K4)\H8=L2/(Z4*K4)
1830 H9=L3/(Z4*K4)\R7=L4/(Z4*K4)
1840 R8=K4*Z4*U7\R9=K4*Z4*U8\RR7=K4*Z4*R7
1850 W4=13*H7+24*H8+12*H9+14*R7+(J2+J3+J4)/Z4+14*U7+15*U8
1860 W4=W4+.011*(13+U8+U7+R6+R5+R4)
1870 ZZ3=(NN1+NN2/3+NN3/2+NN4)/10
1880 TT1=K5*NN1
1890 TT2=K5*(NN2/3+NN3/2+NN4)
1900 TT3=(TT1+TT2)/2.5
1910 XX3=K5*NN2/3\XX2=K5*NN3/2
1920 XX1=K5*NN4
1930 XX6=XX3/(ZZ3*K5)
1940 XX5=XX2/(ZZ3*K5)
1950 XX4=XX1/(ZZ3*K5)
1960 UU6=DD3-NN2/(3*ZZ3)
1970 UU5=NN6/(2*ZZ3)-1.5*UU6
1975 IF UU5<=0 THEN UU5=0
1980 UU1=TT1/(ZZ3*K5)
1990 UU2=TT2/(ZZ3*K5)\UU3=TT3/(ZZ3*K5)\UU4=TT4/(ZZ3*K5)
2000 TT5=K5*ZZ3*UU5\TT6=K5*ZZ3*UU6
2010 WW3=13*UU1+24*UU2+12*UU3+(NN2+NN3+NN4)/ZZ3+14*UU5+15*UU6
2020 WW3=WW3+.0011*(14+UU6+UU5+XX6+XX5+XX4)
2030 T7=T1+T2+T3
2040 T8=T7+T4+T5+T6
2050 TT7=TT1+TT2+TT3
2060 TT8=TT7+TT4+TT5+TT6
2070 W6=L1+L2+L3
2080 W7=L1+L2+L3+R8+R9+L2+L4
2090 W8=F1*W6/(P7+T7+W6+TT7)
2100 W9=W8*W7/W6
2110 F2=F1*P7/(P7+T7+W6+TT7)
2120 F3=F1*T7/(P7+T7+W6+TT7)
2130 FF3=F1*TT7/(P7+T7+W6+TT7)
2140 FF5=FF3*TT8/TT7
2150 F4=F2*P8/P7
2160 F5=F3*T8/T7
2170 F6=1-F4-F5-W9-FF5
2180 A8=F/*(P8+T8+W7+TT8)/(1-F6)
2190 REM
2200 REM
2210 REM              This is the section to start the printout
2220 REM
2230 REM
2240 PRINT #1,"*****************************************************************"
2250 PRINT #1,"*****************************************************************"
2260 PRINT #1,"******************LC-NMR ANALYSIS*****************************"
2270 PRINT #1,"****************REPORT OF FUEL SAMPLE*****************************"
2280 PRINT #1,"*****************",N$,"************************"
2290 PRINT #1,"*******T  E. GLASS, H. C. DORN, AND K.A. CASWELL****************"
```

```
2300 PRINT #1,"***********V. P. I. DEPT. OF CHEMISTRY***************************"
2310 PRINT #1,"***************BLACKSBURG, VIRGINIA*********************************"
2320 LOCATE 3,2 : PRINT SPACE$(1670);
2330 LOCATE 11,18
2340 PRINT "Do you wish to skip the full printout? (Y/N) "; \ INPUT "";AS$
2350 PRINT #1, D$
2360 PRINT #1," "
2370 PRINT #1," "
2380 PRINT #1,"****************MONOCYCLIC PEAK DATA****************************"
2390 O1=Q1\O2=Q2\O3=Q3\O4=Q4\O5=Q5\O6=Q6\O7=W2\O8=S2\O9=D2
2400 Y1=F1\Y2=F2\Y3=F3\Y4=F4\Y5=F5\Y6=F6\Y7=F7\Y8=F8\Y9=0
2410 E1=F2\E2=F4\Y=0\C1=I1\C2=I2\C3=I3\C4=I4\C5=I5\C6=I6
2420 GOSUB 3910
2430 PRINT #1," "
2440 PRINT #1," "
2450 PRINT #1,"***************NAPTHALENES PEAK DATA****************************"
2460 O1=U1\O2=U2\Y9=U3\O3=U4\O4=U5\O5=U6\O6=0\Y1=T1\Y2=T2
2470 Y=T3\Y3=T4\Y4=T5\Y5=T6\Y6=0\O7=W3\O8=S3\O9=D3\Y7=T7
2480 Y8=T8\E1=F3\E2=F5\C1=X1\C2=X2\C3=X3\C4=X4\C5=X5\C6=X6
2490 GOSUB 3910
2500 PRINT #1," "
2510 PRINT #1," "
2520 PRINT #1,"****************FLUORENE PEAK DATA*******************************"
2530 O1=H7\O2=H8\Y9=H9\O3=R7\O4=U7\O5=U8\O6=R7\Y1=L1\Y2=L2
2540 Y=L3\Y3=L4\Y4=R8\Y5=R9\Y6=RR7\O7=W4\O8=S4\O9=D4\Y7=W6
2550 Y8=W7\E1=W8\E2=W9\C1=H1\C2=H2\C3=H3\C4=H4\C5=H5\C6=H6
2560 GOSUB 3910
2570 PRINT #1,"******************PHENANTHRENE PEAK DATA*****************"
2580 O1=UU1\O2=UU2\Y9=UU3\O3=UU4\O4=UU5\O5=UU6\O6=0\Y1=TT1\Y2=TT2
2590 Y=TT3\Y3=TT4\Y4=TT5\Y5=TT6\Y6=0\O7=WW3\O8=S5\O9=DD3\Y7=TT7
2600 Y8=TT8\E1=FF3\E2=FF5\C1=XX1\C2=XX2\C3=XX3\C4=XX4\C5=XX5\C6=XX6
2610 GOSUB 3910
2620 LOCATE 12,18
2630 PRINT "Do you wish an aliphatic analysis? (Y/N) "; \ INPUT "";A$
2640 IF A$="N" OR A$="n" THEN 3560
2650 ASD=3                                          ! Screen 3 for editing
2660 REM
2670 REM
2680 REM            This is the section to get the inputs and edit screens.
2690 REM
2700 REM
2705 DUM1=0 : DUM2=0
2710 LOCATE 11,1 : PRINT SPACE$(400)
2720 LOCATE 6,35 : PRINT "      HMDS Integral: "
2730 LOCATE 8,35 : PRINT "       CH3 Integral: "
2740 LOCATE 10,35 : PRINT "       CH2 Integral: "
2750 LOCATE 12,35 : PRINT "        CH Integral: "
2760 LOCATE 14,1 PRINT "Estimated quarternary carbon relative to CH integral."
2770 LOCATE 16,35 : PRINT "   Number of Scans: "
2780 LOCATE 19,8 : PRINT "Do you wish to assume linear alkanes for",
2790 PRINT " normalization? (Y/N) "
2800 IF PARAM$="F" OR PARAM$="f" THEN 2890
2810 LOCATE 6,60 : INPUT "",R
2820 LOCATE 8,60 : INPUT "";A3
2830 LOCATE 10,60 : INPUT "";A2
2840 LOCATE 12,60 : INPUT "";A1
2850 LOCATE 14,60 : INPUT "";A4
2860 LOCATE 16,60 : INPUT "";V
2870 LOCATE 19,75 : INPUT "";L$
2880 GOTO 2980
```

```
2890 GET #2, RECORD 9 : R=CVT$F(N3$) : A3=CVT$F(N4$) : A2=CVT$F(N5$)
2895 DUM1=CVT$F(N1$) : DUM2=CVT$F(N2$)
2900 GET #2, RECORD 10 : A1=CVT$F(N1$)   A4=CVT$F(N2$) : V=CVT$F(N3$)   L$=" "
2910 LOCATE 6,60   : PRINT R;
2920 LOCATE 8,60   : PRINT A3;
2930 LOCATE 10,60  : PRINT A2;
2940 LOCATE 12,60  : PRINT A1;
2950 LOCATE 14,60  : PRINT A4;
2960 LOCATE 16,60  : PRINT V;
2970 LOCATE 19,75  : PRINT L$
2980 LOCATE 23,18  : PRINT "Press the appropriate softkey to continue.";
2990 INPUT "";A$
3000 IF A$="SCRN" THEN 3030
3010 IF A$="EDIT" THEN GOSUB 5460                    ! Editing routine
3020 GOTO 2980
3030 IF PARAM$="F"OR PARAM$="f"OR PARAM$="S" OR PARAM$="s" THEN 3040 ELSE 3090
3040 LSET N3$=CVTF$(R) : LSET N4$=CVTF$(A3) : LSET N5$=CVTF$(A2)
3045 LSET N1$=CVTF$(DUM1) : LSET N2$=CVTF$(DUM2)
3050 PUT #2, RECORD 9
3060 LSET N1$=CVTF$(A1) : LSET N2$=CVTF$(A4) : LSET N3$=CVTF$(V) : LSET N4$=L$
3070 LSET N5$=" "
3080 PUT #2, RECORD 10
3090 V=(V*SCANTIME*FLOWRATE)/CONVERT
3100 V1=V\LL3=A3\LL2=A2\LL1=A1\LL4=A4*A1\LR1=R\K1=M*V1*18/LR1 : R1=R
3110 B3=K1*LL3/3\B2=K1*LL2/2\B1=K1*LL1\B4=K1*LL4\B5=B3+B2+B1
3115 BB5=B5/(B5+P8+T8+W7+TT8)
3120 IF L$<>"Y" THEN 3150
3130 NNN1=LL3/6
3140 GOTO 3160
3150 NNN1=(LL3-3*LL1)/6-A4*LL1
3160 LX3=B3/(K1*NNN1)\LX2=B2/(K1*NNN1)\LX1=B1/(K1*NNN1)\LX4=A4*LX1
3170 W1=15.011*LX3+14.011*LX2+13.011*LX1+12.011*LX4
3180 IF AS$="Y" GOTO 4250
3190 PRINT #1, " "
3200 PRINT #1, " "
3210 PRINT #1, "*****************ALKANE PEAK DATA****************************"
3220 PRINT #1, " "
3230 PRINT #1, " "
3240 PRINT #1, "AVERAGE STRUCTURE DATA AND TOTAL # OF MOLES OF EACH CARBON"
3250 PRINT #1, "*************TYPE IN AN INJECTION****************************"
3260 PRINT #1, " "
3270 IF L$<> "Y" THEN 3290
3280 PRINT #1, "***********LINEAR ALKANE ASSUMPTION*************************"
3290 PRINT #1, "CARBON TYPE","AVERAGE #","ABS MOLES"
3300 PRINT #1, " "
3310 PRINT #1, "#CH3", : PRINT #1 USING "###.##          ####.##";LX3;B3
3320 PRINT #1, "#CH2", : PRINT #1 USING "### ##          ####.##";LX2;B2
3330 PRINT #1, "#CH",  : PRINT #1 USING "###.##          ####.##";LX1,B1
3340 PRINT #1, "QUATERNARY", PRINT #1 USING "### ##          ####.##",LX4;B4
3350 LX5=LX1+2*LX4
3360 PRINT #1, " "
3370 PRINT #1, "AVERAGE MOLECULAR WEIGHT= "; : PRINT #1 USING "#####.###",W1
3380 PRINT #1, "AVERAGE DEGREE OF BRANCHING= ", PRINT #1 USING "#####.###";LX5
3390 PRINT #1, "TOTAL #MOLES OF CARBON IN THIS FILE(METHOD 1)= ";
3400 PRINT #1 USING "######.###";A8
3410 PRINT #1, "TOTAL #MOLES OF CARBON IN THIS FILE(METHOD 2)= ";
3420 PRINT #1 USING "######.###",B5
3430 PRINT #1, "FRACTION OF TOTAL CARBON IN THIS LS PEAK(METHOD 1)= ";
3440 PRINT #1 USING "######.###";F6
3450 B6=B5+T8+P8\B7=B5/B6\B8=P8/B6\B9=T8/B6
```

```
3460 PRINT #1, "FRACTION OF TOTAL CARBON BY METHOD 2  ";BB5
3470 PRINT #1, " "
3480 PRINT #1, " "
3490 PRINT #1, "ALKANE PEAK",, : PRINT #1 USING "## #####";B7
3500 PRINT #1, "MONOCYCLIC PEAK", : PRINT #1 USING "## #####";B8
3510 PRINT #1, "NAPTHALENES PEAK",: PRINT #1 USING "## #####";B9
3520 PRINT #1, "FLUORENE PEAK", : PRINT #1 USING "## #####";FF1
3530 LOCATE 3,2  PRINT SPACE$(1670)
3540 LOCATE 11,15 : PRINT "Do you wish to redo the alkanes? (Y/N) ",
3550 INPUT "";Q$    IF Q$="Y" OR Q$="y" THEN 2710
3560 GOTO 4250
3570 REM INPUT SUBROUTINE
3580 LOCATE 6,15 : PRINT "                HMDS Integral  "
3590 LOCATE 8,15 : PRINT "           Aromatic Integral: "
3600 LOCATE 10,15 :PRINT "          Alpha CH3 Integral  "
3610 LOCATE 12,15 :PRINT "          Alpha CH2 Integral: "
3620 LOCATE 14,15 :PRINT "           Alpha CH Integral: "
3630 LOCATE 16,15 :PRINT "    Alpha Tetralin Integral: "
3640 LOCATE 18,15 :PRINT "Greater Than Alpha Integral: "
3650 LOCATE 20,13 :PRINT "Number of Scans for this file: "
3660 IF PARAM$="F" OR PARAM$="f" THEN 3760        ! If using file just print
3670 LOCATE 6,45  : INPUT "";R
3680 LOCATE 8,45  : INPUT "";A
3690 LOCATE 10,45 : INPUT "";A3
3700 LOCATE 12,45 : INPUT "";A2
3710 LOCATE 14,45 : INPUT "";A1
3720 LOCATE 16,45 : INPUT "";T
3730 LOCATE 18,45 : INPUT "";G
3740 LOCATE 20,45 : INPUT "";V
3750 GOTO 3840
3760 LOCATE 6,45  : PRINT R;
3770 LOCATE 8,45  : PRINT A;
3780 LOCATE 10,45 : PRINT A3;
3790 LOCATE 12,45 : PRINT A2;
3800 LOCATE 14,45 : PRINT A1;
3810 LOCATE 16,45 : PRINT T;
3820 LOCATE 18,45 : PRINT G;
3830 LOCATE 20,45 : PRINT V;
3840 LOCATE 23,18 : PRINT "Press the appropriate softkey to continue.";
3850 INPUT "";A$
3860 IF A$="SCRN" THEN RETURN
3870 IF A$="EDIT" THEN 3890                       ! Editing routine
3880 GOTO 3840
3890 ON ASD GOSUB 5020, 5270, 5460
3900 GOTO 3840
3910 REM OUTPUT SUBROUTINE
3920 IF AS$="Y" THEN RETURN
3930 PRINT #1, " "
3940 PRINT #1, " "
3950 PRINT #1, "AVERAGE STRUCTURE DATA AND TOTAL # OF MOLES OF EACH CARBON"
3960 PRINT #1, "                    TYPE IN AN INJECTION                  "
3970 PRINT #1, " "
3980 PRINT #1, "CARBON TYPE", "AVERAGE #", "ABSOLUTE MOLES"
3990 PRINT #1, " "
4000 PRINT #1,"UNSUBSTITUTED",:PRINT #1 USING "## #####        # ######";O1,Y1
4010 PRINT #1, "SUBSTITUTED",  PRINT #1 USING "## #####        # ######";O2,Y2
4020 IF X9)=1 THEN 4040
4030 PRINT #1, "BRIDGEHEAD",  PRINT #1 USING "## #####        # ######",Y9,Y
4040 PRINT #1, "ALPHA CH3",   PRINT #1 USING "## #####        # ######";C6,C3
4050 PRINT #1, "ALPHA CH2",   PRINT #1 USING "## #####        # ######";C5,C2
```

```
4060 PRINT #1, "ALPHA CH",     : PRINT #1 USING "##.#####          #.######";C4,C1
4070 PRINT #1, "CH2 > ALPHA",: PRINT #1 USING "##.#####          #.######",O4,Y4
4080 PRINT #1, "CH3 > ALPHA",  PRINT #1 USING "##.#####          #.######",O5,Y5
4090 IF X9=2 THEN 4110
4100 PRINT #1, "ALPHA TET",     PRINT #1 USING "##.#####          #.######",O6,Y6

4110 PRINT #1, " "
4120 PRINT #1, "AVERAGE MOLECULAR WEIGHT= ",  PRINT #1 USING "#####.###";O7
4130 PRINT #1,"FRACTION OF SUBSTITUTED SITES= ";PRINT #1 USING "#####.###",O8
4140 PRINT #1, "AVERAGE DEGREE OF SUBSTITUTION= ",
4150 PRINT #1 USING "#####.###";O9
4160 PRINT #1, "TOTAL # MOLES OF AROMATIC CARBON IN THIS FILE= ";
4170 PRINT #1 USING "# #######";Y7
4180 PRINT #1, "TOTAL # MOLES OF CARBON (AROMATIC + ALKYL) IN THIS FILE= ",
4190 PRINT #1 USING "# #######";Y8
4200 PRINT #1, "FRACTIONAL AROMATICITY= "
4210 PRINT #1 USING "#####.###";E1
4220 PRINT #1, "FRACTION OF TOTAL CARBON IN THIS LC PEAK= ";
4230 PRINT #1 USING "#####.###";E2
4240 RETURN
4250 PRINT #1
4260 PRINT #1
4270 PRINT #1, "MONOCYCLIC INPUT DATA"
4280 PRINT #1, "HMDS INTEGRAL",: PRINT #1 USING "###.####";R2
4290 PRINT #1, "AROMATIC INT", : PRINT #1 USING "###.####";M1
4300 PRINT #1, "ALPHA CH3 INT",: PRINT #1 USING "###.####";M2
4310 PRINT #1, "ALPHA CH2 INT",: PRINT #1 USING "###.####";M3
4320 PRINT #1, "ALPHA CH INT", : PRINT #1 USING "###.####";M4
4330 PRINT #1, "ALPHA TET INT",: PRINT #1 USING "###.####";M5
4340 PRINT #1, "> ALPHA INT",  : PRINT #1 USING "###.####";M6
4350 PRINT #1, "VOL OF FILE",  : PRINT #1 USING "###.#####";V2
4360 PRINT #1\PRINT #1
4370 PRINT #1, "NAPHTHALENE DATA INPUT"
4380 PRINT #1, "HMDS INTEGRAL",: PRINT #1 USING "###.####";R3
4390 PRINT #1, "AROMATIC INT", : PRINT #1 USING "###.####";N1
4400 PRINT #1, "ALPHA CH3 INT",: PRINT #1 USING "###.####";N2
4410 PRINT #1, "ALPHA CH2 INT",: PRINT #1 USING "###.####";N3
4420 PRINT #1, "ALPHA CH INT", : PRINT #1 USING "###.####";N4
4430 PRINT #1, "ALPHA TET INT",: PRINT #1 USING "###.####";N5
4440 PRINT #1, "> ALPHA INT",  : PRINT #1 USING "###.####";N6
4450 PRINT #1, "VOL OF FILE",  : PRINT #1 USING "###.#####";V3
4460 PRINT #1\PRINT #1
4470 PRINT #1, "FLUORENE DATA INPUT"
4480 PRINT #1, "HMDS INTEGRAL",: PRINT #1 USING "###.####",R4
4490 PRINT #1, "AROMATIC INT", : PRINT #1 USING "###.####",J1
4500 PRINT #1, "ALPHA CH3 INT",: PRINT #1 USING "###.####",J2
4510 PRINT #1, "ALPHA CH2 INT",: PRINT #1 USING "###.####",J3
4520 PRINT #1, "ALPHA CH INT", : PRINT #1 USING "###.####",J4
4530 PRINT #1, "ALPHA TET INT",: PRINT #1 USING "###.####";J5
4540 PRINT #1, "> ALPHA INT",  : PRINT #1 USING "###.####",J6
4550 PRINT #1, "VOL OF FILE",  : PRINT #1 USING "###.#####";V4
4560 PRINT #1\PRINT #1
4570 PRINT #1, "PHENANTHRENE DATA INPUT"
4580 PRINT #1, "HMDS INTEGRAL",: PRINT #1 USING "###.####",RR3
4590 PRINT #1, "AROMATIC INT",  : PRINT #1 USING "###.####",NN1
4600 PRINT #1, "ALPHA CH3 INT",: PRINT #1 USING "###.####",NN2
4610 PRINT #1, "ALPHA CH2 INT",: PRINT #1 USING "###.####";NN3
4620 PRINT #1, "ALPHA CH INT", : PRINT #1 USING "###.####",NN4
4630 PRINT #1, "ALPHA TET INT",: PRINT #1 USING "###.####",NN5
4640 PRINT #1, "> ALPHA INT",  : PRINT #1 USING "###.####",NN6
```

```
650 PRINT #1, "VOL OF FILE",    PRINT #1 USING "### #####";VV3
660 PRINT #1, "MOLAR CONC OF HMDS",: PRINT #1 USING "# ######";M
670 PRINT #1, "C-13 AROMATICITY",  PRINT #1 USING "# ####";F1
680 IF A$="N" THEN 4960
690 PRINT #1\PRINT #1
700 PRINT #1, "ALKANE INPUT DATA"
710 PRINT #1, "HMDS INTEGRAL",  : PRINT #1 USING "### ######";R1
720 PRINT #1, "CH3 INT",        : PRINT #1 USING "### ######";L3
730 PRINT #1, "CH2 INT",        : PRINT #1 USING "### ######";L2
740 PRINT #1, "CH INT",         : PRINT #1 USING "### ######";L1
750 PRINT #1, "EST  QUARTERNARY CARBON INT. RELATIVE TO CH INT : ",
760 PRINT #1 USING "### ######";A4
770 PRINT #1, "VOL OF FILE: "; : PRINT #1 USING "### ######";V1
780 PRINT #1, "LINEAR ALKANES ASSUMED FOR NORMALIZATION: ";L$
790 CH0=12.011\CH1=13.01179\CH2=14.0268\CH3=15.0347
800 MONO=F1*CH1+F2*CH0+I3*CH3+I2*CH2+I1*CH1+P4*CH2+P5*CH3+P6*CH2
810 DI=T1*CH1+T2*CH0+T3*CH0+X3*CH3+X2*CH2+X1*CH1+T5*CH2+T6*CH3
820 FL=L1*CH1+L2*CH0+L3*CH0+H3*CH3+H2*CH2+R8*CH2+R9*CH3+RR7*CH2
830 PH=TT1*CH1+TT2*CH0+TT3*CH0+XX3*CH3+XX2*CH2+TT5*CH2+TT6*CH3
840 AL=A8*CH2
850 TOTAL=MONO+DI+FL+PH+AL
855 ALBB=B1*CH3+B2*CH2+B3*CH1
856 TOTAL2=MONO+DI+FL+PH+ALBB
860 MONOPC=MONO/TOTAL*100
870 DIPC=DI/TOTAL*100
880 FLPC=FL/TOTAL*100
890 PHPC=PH/TOTAL*100
900 ALPC=AL/TOTAL*100
905 ALBBPC=ALBB/TOTAL2*100
910 PRINT #1, "ALKANE WT. % = "; : PRINT #1 USING "### #####";ALPC
920 PRINT #1, "MONOCYCLIC WT. % = "; : PRINT #1 USING "### #####";MONOPC
930 PRINT #1, "DICYCLIC WT. % = "; : PRINT #1 USING "### #####";DIPC
940 PRINT #1, "FLUORENE WT. % = "; : PRINT #1 USING "### #####";FLPC
950 PRINT #1, "PHENAN. WT. % = "; : PRINT #1 USING "### ####";PHPC
955 PRINT #1, "ALKANE WT. % (METHOD 2)= "; : PRINT #1 USING "### ####";ALBBPC
960 REM
970 REM      Routine to end the pgm and sign off.
980 REM
990 CLOSE #1 : CLOSE #2 : CLOSE #5
1000 TEXT (200,100,"Have a glorious day!!!",2)
1010 END
5020 REM
5030 REM        This is the subroutine to edit the input screens.
5040 REM
5050 A$=""
5060 COLU=6
5070 IF COLU<6 THEN COLU=6
5080 IF COLU>20 THEN COLU=20
5090 LOCATE COLU,55   INPUT "";A$
5100 LOCATE COLU,55  : PRINT SPACE$(10);
5110 IF A$="NEXT" THEN COLU=COLU+2  : GOTO 5070
5120 IF A$="PREV" THEN COLU=COLU-2  : GOTO 5070
5130 IF A$="SCRN" THEN RETURN
5140 IF A$="CHANGE" THEN 5150 ELSE 5070
5150 REM          Section to replace the number.
5160 LOCATE COLU,45   PRINT SPACE$(30);
5170 LOCATE COLU,45   INPUT "";DUMMY
5180 IF COLU=6  THEN R=DUMMY    GOTO 5070
5190 IF COLU=8  THEN A=DUMMY    GOTO 5070
5200 IF COLU=10 THEN A3=DUMMY   GOTO 5070
```

```
5210 IF COLU=12 THEN A2=DUMMY : GOTO 5070
5220 IF COLU=14 THEN A1=DUMMY : GOTO 5070
5230 IF COLU=16 THEN T=DUMMY : GOTO 5070
5240 IF COLU=18 THEN G=DUMMY : GOTO 5070
5250 IF COLU=20 THEN V=DUMMY : GOTO 5070
5260 GOTO 5070
5270 REM
5280 REM      This is the subroutine to edit the second type of input screen.
5290 REM
5300 A$=""
5310 COLU=11
5320 IF COLU<11 THEN COLU=11
5330 IF COLU>13 THEN COLU=13
5340 LOCATE COLU,55 : INPUT "";A$
5350 LOCATE COLU,55 : PRINT SPACE$(10);
5360 IF A$="NEXT" THEN COLU=COLU+2   GOTO 5320
5370 IF A$="PREV" THEN COLU=COLU-2 : GOTO 5320
5380 IF A$="SCRN" THEN RETURN
5390 IF A$="CHANGE" THEN 5400 ELSE 5320
5400 REM    Section to replace the number.
5410 LOCATE COLU,45 : PRINT SPACE$(30);
5420 LOCATE COLU,45 : INPUT "";DUMMY
5430 IF COLU=11 THEN M=DUMMY : GOTO 5320
5440 IF COLU=13 THEN F1=DUMMY : GOTO 5320
5450 GOTO 5320
5460 REM
5470 REM        This is the subroutine to edit the third screen.
5480 REM
5490 A$=""
5500 COLU=6 : RROOWW=70
5510 IF COLU<6 THEN COLU=6
5520 IF COLU>16 THEN 5710
5530 LOCATE COLU,RROOWW : INPUT "";A$
5540 LOCATE COLU,RROOWW : PRINT SPACE$(15);
5550 IF A$="NEXT" THEN COLU=COLU+2 : GOTO 5510
5560 IF A$="PREV" THEN COLU=COLU-2 : GOTO 5510
5570 IF A$="SCRN" THEN RETURN
5580 IF A$="CHANGE" THEN 5590 ELSE 5510
5590 REM    Section to replace the number.
5600 RROOWW=60
5610 LOCATE COLU,RROOWW : PRINT SPACE$(15);
5620 LOCATE COLU,RROOWW : INPUT "";DUMMY
5630 RROOWW=70
5640 IF COLU=6  THEN  R=DUMMY : GOTO 5510
5650 IF COLU=8  THEN A3=DUMMY   GOTO 5510
5660 IF COLU=10 THEN A2=DUMMY : GOTO 5510
5670 IF COLU=12 THEN A1=DUMMY   GOTO 5510
5680 IF COLU=14 THEN A4=DUMMY : GOTO 5510
5690 IF COLU=16 THEN  V=DUMMY : GOTO 5510
5700 GOTO 5510
5710 REM    If got to here must want to edit the string variable
5720 LOCATE 19,77   INPUT "",A$
5730 LOCATE 19,77   PRINT SPACE$(10),
5740 IF A$="PREV" THEN COLU=16 : GOTO 5510
5750 IF A$="SCRN" THEN RETURN
5760 IF A$="CHANGE" THEN 5770 ELSE 5720
5770 LOCATE 19,75 : PRINT SPACE$(10);
5780 LOCATE 19,75   INPUT "",L$
5790 GOTO 5510
5800 REM
```

```
5810 REM      This is the subroutine to get the parameters from a file.
5820 REM
5830 LOCATE 12,14
5840 PRINT "What is the name of the file that you wish to use?"
5850 LOCATE 13,38 : INPUT "";FLNAM$
5860 IF FLNAM$="" THEN FLNAM$=N$+".DAT"
5870 LOCATE 12,10 : PRINT SPACE$(320);
5880 OPEN FLNAM$ AS FILE #2
5890 FIELD #2, 12 AS N1$, 12 AS N2$, 12 AS N3$, 12 AS N4$, 12 AS N5$
5900 RETURN
5910 REM
5920 REM     Subroutine to get the inputs from the disk
5930 REM
5940 GET #2, RECORD RECNUM : R=CVTSF(N1$)   A=CVTSF(N2$) : A3=CVTSF(N3$)
5950 A2=CVTSF(N4$) : A1=CVTSF(N5$)
5960 GET #2, RECORD RECNUM+1 : T=CVTSF(N1$)   G=CVTSF(N2$) : V=CVTSF(N3$)
5970 RETURN
5980 REM
5990 REM     Subroutine to place the parameters back in the file.
6000 REM
6010 LSET N1$=CVTF$(R) : LSET N2$=CVTF$(A) : LSET N3$=CVTF$(A3)
6020 LSET N4$=CVTF$(A2): LSET N5$=CVTF$(A1)
6030 PUT #2, RECORD RECNUM
6040 LSET N1$=CVTF$(T) : LSET N2$=CVTF$(G) : LSET N3$=CVTF$(V)
6050 LSET N4$=" "      : LSET N5$=" "
6060 PUT #2, RECORD RECNUM+1
6070 RETURN
6080 REM
6090 REM      This is the subroutine to clear the screen between input pages.
6100 REM
6110 LOCATE 3,0 : PRINT SPACE$(79)
6120 FOR KKI=6 TO 23 STEP 2
6130    LOCATE KKI,44 : PRINT SPACE$(30);
6140 NEXT KKI
6150 LOCATE 23,17 : PRINT SPACE$(60);
6160 RETURN
6170 REM
6180 REM         This is the subroutine to assign the softkeys.
6190 REM              It is executed on the first run of the pgm only!!!
6200 REM
6210 DIM FPK%(30)
6220 OPEN "*KPD" AS FILE #5
6230 CLS
6240 DATA "EDIT"," "," ","NEXT","PREV","CHANGE"," "," "," ","SCRN"
6250 READ NAME$(I) FOR I=1 TO 10
6260 FPK%(1)=12
6270 FPK%(3)=0
6280 FPK%(4)=2
6290 FOR I=1 TO 10
6300 FPK%(2)=189+I
6310 FPK%(5)=LEN(NAME$(I))
6320 FOR J=1 TO FPK%(5)
6330 FPK%(J+5)=ASCII(MID(NAME$(I),J,1))
6340 NEXT J
6350 FPK%(J+5)=13
6360 FPK%(J+6)=0
6370 CALL SYSFUNC(5,FPK%(1))
6380 NEXT I
6390 GOSUB 6420
6400 RETURN
```

```
6410 END
6420 REM
6430 REM      This is the subroutine to lable the softkeys
6440 REM
6450 RESTORE
6460 FOR IIII=1 TO 10
6470 READ NAME$
6480 TEXT ((IIII-1)*72+40,0,NAME$)
6490 NEXT IIII
6500 RETURN
6510 REM
6520 REM          This is the subroutine to subrtact out the blank integrals
6530 REM
6540 NOSC=300                                   ! Number of Scans for file
6550 BNK1GA=0.00651/NOSC                        ! Blank #1  0.60 - 2.00 ppm
6560 BNK1AM=0.00651/NOSC                        ! Blank #1  0.60 - 1.95 ppm
6570 BNK1CH=0.00134/NOSC                        ! Blank #1  2.90 - 3.10 ppm
6580 BNK1MA=0.0104/NOSC                         ! Blank #1  6.30 - 7.50 ppm
6590 BNK1NA=0.0104/NOSC                         ! Blank #1  6.70 - 8.50 ppm
6600 BNK2GA=0.1607/NOSC                         ! Blank #2  0.60 - 2.00 ppm
6610 BNK2AM=0.1493/NOSC                         ! Blank #2  0.60 - 1.95 ppm
6620 BNK2CH=0.0115/NOSC                         ! Blank #2  2.90 - 3.10 ppm
6630 BNK2MA=0.0721/NOSC                         ! Blank #2  6.30 - 7.50 ppm
6640 BNK2NA=0.1122/NOSC                         ! Blank #2  6.70 - 8.50 ppm
6650 RETURN
6660 REM
6670 REM     Section to subtract out the blank from Monocyclics.
6680 REM
6690 IF BLANK<1 OR BLANK>2 THEN PRINT "ERROR IN BLANK SUBROUTINE" : GOTO 4960
6700 IF BLANK=2 THEN 6730
6710 G=G-(V*BNK1AM) : A1=A1-(V*BNK1CH) : A=A-(V*BNK1MA)
6720 RETURN
6730 G=G-(V*BNK2AM) : A1=A1-(V*BNK2CH) : A=A-(V*BNK2MA)
6740 RETURN
6750 REM
6760 REM     Section to subtract out the blank for Napthelenes and higher.
6770 REM
6780 IF BLANK<1 OR BLANK>2 THEN PRINT "ERROR IN NAPTH & HIGHER " : GOTO 4960
6790 IF BLANK=2 THEN 6820
6800 G=G-(V*BNK1GA) : A=A-(V*BNK1NA)
6810 RETURN
6820 G=G-(V*BNK2GA) : A=A-(V*BNK2NA)
6830 RETURN
```

END
FILMED
4-86
DTIC