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CHARACTERIZATION OF PETROLEUM RESIDUES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

The ability of different high-performance liquid chromatographic (HPLC) columns to separate hydrocarbons according to the number of aromatic rings is tested, as this is an important parameter in separation of petroleum residues. A fluorescence method is used to evaluate the homogeneity of the HPLC-fractions. To illustrate the possibility for off-line combination of HPLC and ^{1}H NMR, the NMR spectra of some of the HPLC fractions are presented.

INTRODUCTION

High-performance liquid chromatography (HPLC) is one of the few efficient separation techniques that can be used to separate components with boiling points (b.p.s) above 500°C. Since petroleum residues consist to a large extent of components with such b.p.s, HPLC is one of the most powerful separation techniques for these residues.

Another analytical challenge in petroleum characterization is the extreme complexity of the samples. Consequently, a separation into single components is undesirable, because of the enormous difficulties with interpretation of the data. The problem is merely to separate the fuel into a few groups that are as homogeneous as possible. One way to achieve this could be to separate the residue into fractions such as aliphatic, mono-, di-, triaromatic, etc. This demands a column that separates the components according to the number of rings in the molecules, independent of alkylation, *i.e.*, a highly alkylated species must have almost the same retention time as its non-alkylated analogue. In the present work, a petroleum residue was used to test the ability of three different columns to perform this separation.

It is well known[1,2] that the NH_2 column is best suited for unsubstituted and slightly alkylated aromatic hydrocarbons, but little work has been done on highly alkylated aromatic hydrocarbons, as found in petroleum residues.

Lloyd[3,4] has shown by a synchronous scanning fluorescence method that the wavelength of maximum emission is a function of the number of fused rings in a molecule. Hence, this method can be used to determine the distribution of aromatic hydrocarbons, *i.e.*, from alkylated benzene to large fused-ring systems.

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EXPERIMENTAL

Apparatus

The liquid chromatograph consisted of a M6000A pump, U6K sample valve, M440 UV-detector, M720 System Controller, M730 Data Module (all from Waters Assoc., Milford, MA, U.S.A.) and a Rheodyne M7000 six-port switching valve, operated manually. The fluorescence spectrophotometer was a Perkin-Elmer Model 650-10S (Perkin-Elmer, Norwalk, CT, U.S.A.). The NMR instrument was a Bruker Model WM 400.

Materials

Columns used were Rad Pak silica (5 μm, 100 × 8 mm I.D.), Rad Pak CN (10 μm, 100 × 8 mm I.D.) and μBondapak-NH_2 (8 μm, 300 × 4 mm I.D.), all from Waters Assoc. Hexane, HPLC grade, from Rathburn was used both as the mobile phase and as solvent for fluorescence. The sample was an Arabian Light residue.

Chromatographic procedures

The silica and CN columns were eluted with 100% hexane at 1 ml/min, whereas the NH_2 column was eluted at 2 ml/min. The columns were backflushed at an elution volume of 11.5 ml for the silica column, 5.9 ml for the CN column and 23 ml for the NH_2 column.

Fluorescence procedure

In the synchronous scanning fluorescence method the excitation scanning starts at 220 nm and ends at 400 or 450 nm, depending on the fraction. The emission is measured at a wavelength 25 nm higher than that of excitation. The volume of each HPLC fraction was adjusted to 4 ml before the fluorescence spectra were recorded.

NMR procedure

The samples for ^1H NMR were dissolved in carbon tetrachloride with [$^2H_8$]dioxane and tetramethylsilane (TMS) as internal standards[5].

RESULTS AND DISCUSSION

The goal was to collect all the di-, tri- and tetraaromatic hydrocarbons of the petroleum residue each in one fraction. For the diaromatic fraction this means that the highly alkylated naphthalenes and naphthalene itself should be eluted at approximately the same time or at least after the last monoaromatic hydrocarbon and before the first triaromatic hydrocarbon. Hence, non-alkylated and slightly alkylated aromatic hydrocarbons should be used to determine the limits for each of the collected fractions. The elution volumes of these models species are shown in Table I.

Because of the small percentage of large ring systems in petroleum residues, a back-flush technique[6] is used to collect all species with five or more condensed rings in one fraction, here called the polar fraction. On he basis of the elution volumes in Table I, the limits for the fractions were chosen as shown in Table II.

As is seen from Table I, the alkylated aromatic hydrocarbons have a larger

TABLE I

RETENTION VOLUMES (ml) FOR THE DIFFERENT STANDARDS

n.e. = not eluted.

Sample	*Columns*		
	Silica	*CN*	*NH_2*
Benzene	4.48	3.85	3.93
Ethylbenzene	4.60	3.76	3.88
Naphthalene	5.23	4.24	5.55
1-Methylnaphthalene	5.36	4.18	5.50
2,3,5-Trimethylnaphthalene	5.85	4.16	5.90
Anthracene	6.86	4.76	9.41
Phenanthrene	7.15	4.78	9.95
1-Methylphenanthrene	7.51	4.75	10.17
3,6-Dimethylphenanthrene	7.80	4.70	10.12
Pyrene	7.71	5.06	12.71
1-Methylpyrene	8.18	5.01	13.20
Chrysene	11.15	5.60	22.16
Benz[*a*]anthracene	11.05	5.62	21.30
Coronene	13.97	6.90	n.e.

elution volume on the silica column than the non-alkylated analogues, whereas the opposite is the case for the CN column. For the NH_2 column no such trend can be found. With the exception of pyrene, which is eluted from the silica column before 3,6-dimethylphenanthrene, the species are eluted according to the number of rings.

The chromatograms of Arabian Light residue are shown in Figs. 1–3. The sample load was 1 mg for the silica and CN columns, and 2.5 mg for the NH_2 column.

Fluorescence

Wakeham[7] has used a synchronous fluorescence method to determine the distribution of hydrocarbons in petroleum. The benzenes give the strongest response when excited in the region of 255–265 nm, naphthenes in the region 285–295 nm, three- and four-ring systems between 315 and 355 nm, whereas five-ring systems and larger hydrocarbons give the highest response with excitation above 375 nm. The naphthalenes give a response 10–50 times higher than that of the benzenes, whereas

TABLE II

FRACTION LIMITS (in ml)) FOR THE DIFFERENT COLUMNS

Group	*Silica*		*CN*		*NH_2*	
	Start	*Stop*	*Start*	*Stop*	*Start*	*Stop*
Aliphatic	3.00	4.30	2.50	3.60	2.50	3.70
Monoaromatic	4.30	5.10	3.60	4.10	3.70	5.20
Diaromatic	5.10	6.50	4.10	4.60	5.20	8.00
Triaromatic	6.50	8.00	4.60	4.95	8.00	12.00
Tetraaromatic	8.00	11.50	4.95	5.90	12.00	23.00
"Polar"	> 11.50		> 5.90		> 23.00	

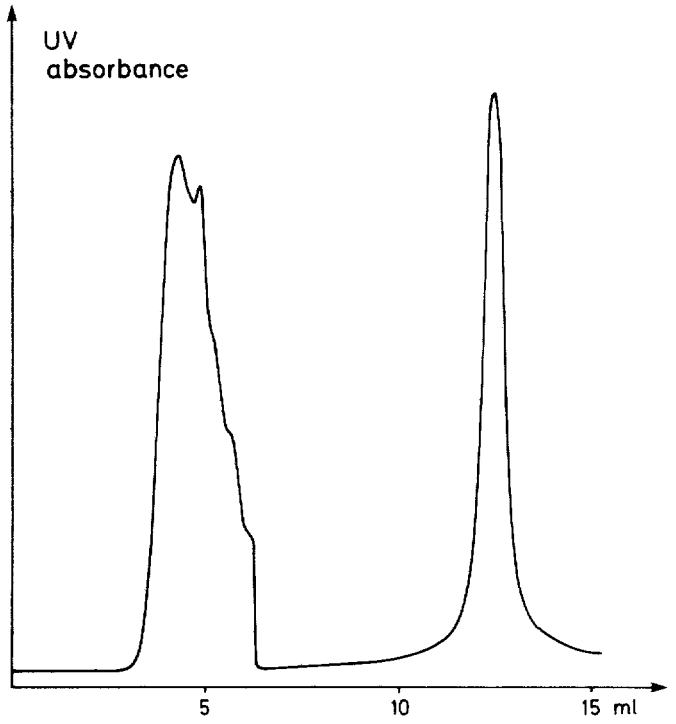

Fig. 1. HPLC of Arabian Light residue on a Waters Rad Pak CN column, eluted with hexane; flow-rate: 1 ml/min. UV detection at 254 nm. Backflushed at 5.9 ml.

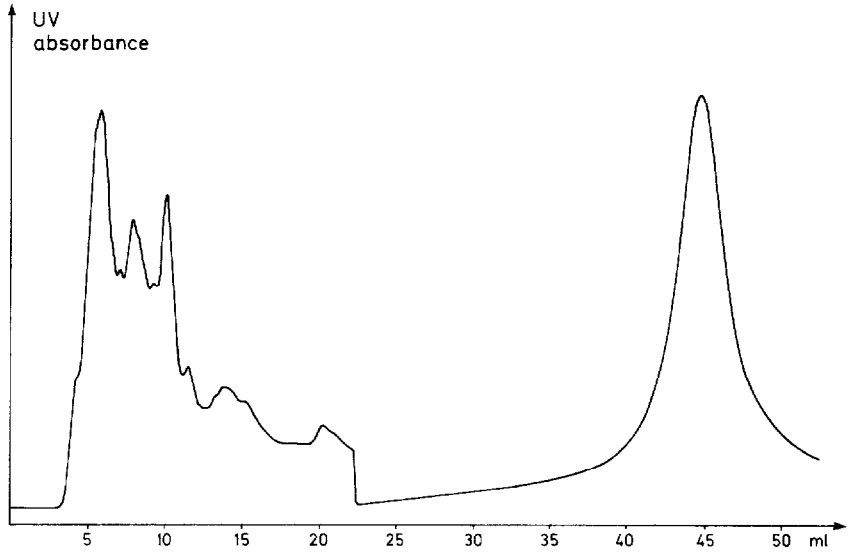

Fig. 2. HPLC of Arabian Light residue on a Waters μBondapak-NH_2 column, eluted with hexane; flow-rate: 2 ml/min. UV detection at 254 nm. Backflushed at 23.0 ml.

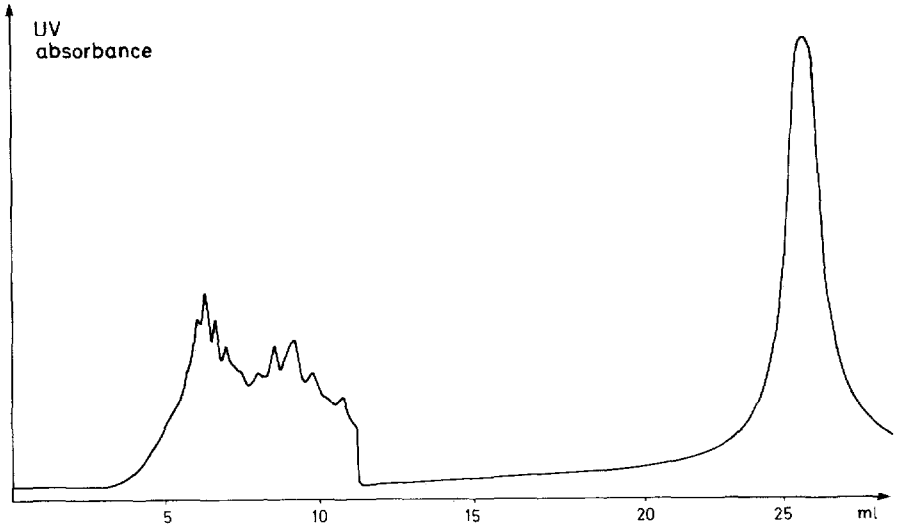

Fig. 3. HPLC of Arabian Light residue on a Waters Rad Pak silica column, eluted with hexane; flow-rate: 1 ml/min. UV detection at 254 nm. Backflushed at 11.5 ml.

the tri- and tetraaromatic hydrocarbons show very large response differences, varying from responses similar to those of naphthalenes to responses at least 100 times higher.

In Fig. 4 the fluorescence spectra of the monoaromatic fractions from the three columns are shown. In spite of the differences in response, it is obvious that the fraction from the CN columns contains large amounts of larger ring systems. Even the silica and NH_2 column fractions contain some (approximately the same) amounts of larger ring systems.

The three diaromatic fractions are shown in Fig. 5. The CN column fraction contains large amounts of tri- and tetraaromatic hydrocarbons as well as considerable amounts of polar hydrocarbons. The fraction from the silica column contains the largest quantity of monoaromatic hydrocarbons, and also a significant amount of tri- and tetraaromatic hydrocarbons. The fraction from the NH_2 column consists mostly of diaromatic hydrocarbons.

The three triaromatic fractions are shown in Fig. 6. The fraction from the CN

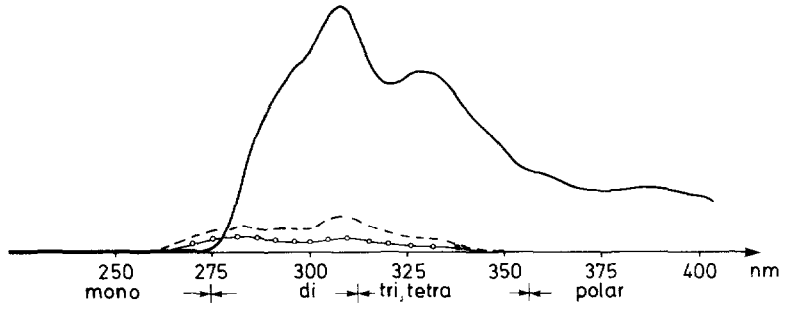

Fig. 4. Synchronous fluorescence spectra with emission wavelength 25 nm higher than that of exitation. Sample: monoaromatic fractions from HPLC. Columns: ——, CN; ----, NH_2; o o, silica.

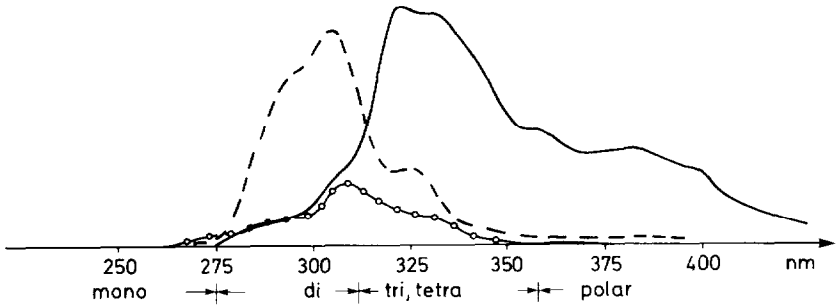

Fig. 5. Conditions as in Fig. 4. Sample: diaromatic fractions.

column mainly contains not only tri- and tetraaromatic hydrocarbons, but also a considerable amount of polar hydrocarbons. From the previous results from this column, it is suspected this triaromatic fraction may contain at least as much of the tetra- as triaromatic hydrocarbons. The silica column fraction consists mostly of diaromatic hydrocarbons, and the fraction from the NH_2 column has an even distribution between di- and tri- or tetraaromatic hydrocarbons.

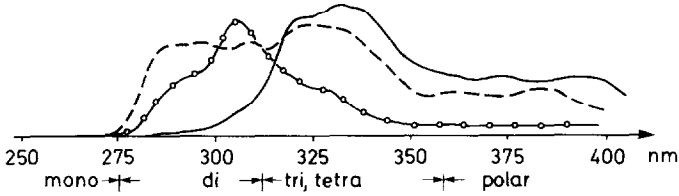

Fig. 6. Conditions as in Fig. 4. Sample: triaromatic fractions.

In Fig. 7 are shown the three tetraaromatic fractions. The CN column fraction consists mainly of polar hydrocarbons. The fraction from the silica column is dominated by the diaromatic hydrocarbons, whereas the NH_2 column fraction consists mainly of tri- or tetraaromatic hydrocarbons.

The fluorescence spectra of the polar fractions are shown in Fig. 8. They all contain the same amount of polar hydrocarbons, but as would be expected from the previous fractions, the fraction from the silica column contains most mono- to tetraaromatic hydrocarbons. The fraction from the CN column shows the lowest content of mono- to tetraaromatic hydrocarbons, also as expected. The fraction from the NH_2 column has a composition intermediate between those from the silica and CN columns.

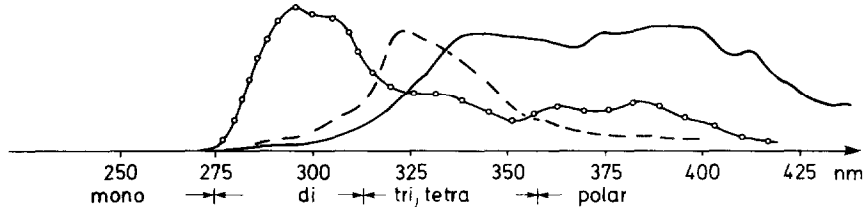

Fig. 7. Conditions as Fig. 4. Sample: tetraaromatic fractions.

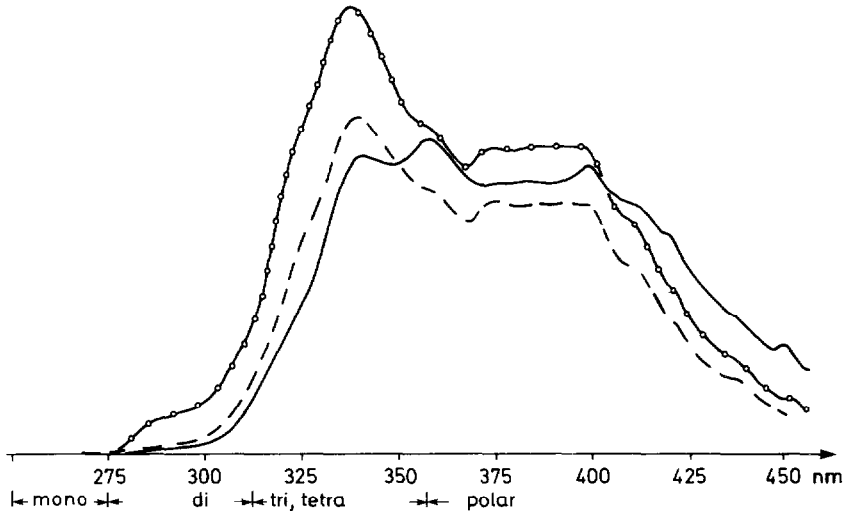

Fig. 8. Conditions as Fig. 4. Sample: polar fractions

The mono- to tetraaromatic fractions from the CN column have one thing in common: they all contain larger amounts of larger-ring systems than expected. On the other hand, all the substituted standards in Table I had a shorter retention time than their unsubstituted analogues. If this applies to all components on this column, it would explain these observations.

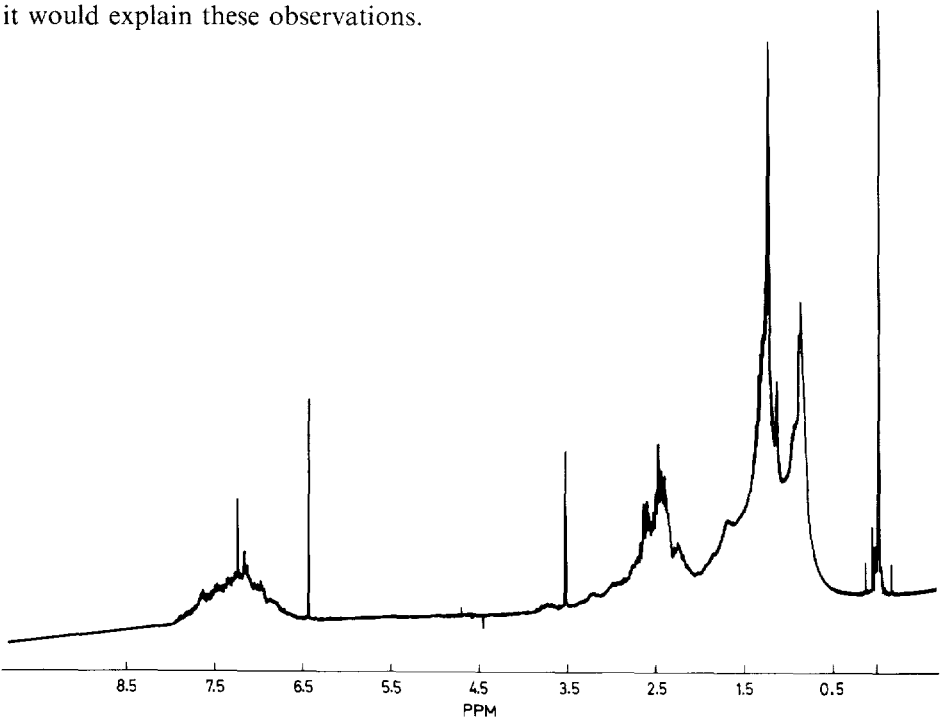

Fig. 9. ^1H NMR spectrum of monoaromatic fraction from NH_2 column.

All the fractions from the silica column contain a greater amount of smaller-ring systems than expected from the unsubstituted standards. If this is consistently true for this column, it can be explained by the fact that all the substituted species shown in Table I had a longer retention time than their unsubstituted analogues.

Comparisons of the mono- to tetraaromatic fractions from the silica and NH_2 columns definitely show that the separations on the NH_2 column are closer to the ideal. This is actually the case for mono-, di-, tri- and tetraaromatic hydrocarbons.

NMR

In Figs. 9–12 the ^1H NMR spectra of the mono- to tetraaromatic fractions from the NH_2 column are shown. Especially in the aromatic region, large differences can be observed. Both the tri- and tetraaromatic fractions contain components with chemical shifts up to 8.5 ppm, whereas the monoaromatic fraction terminates at 8 ppm. Also, the integrals of the aromatic regions relative to the aliphatic regions are different for the different fractions. In addition, significant differences can be observed between 2 and 3 ppm, corresponding to protons belonging to aromatic rings. From the NMR data it may be possible to calculate an average molecular structure for each fraction[5].

CONCLUSIONS

The data presented in this work demonstrate that of the commercially avail-

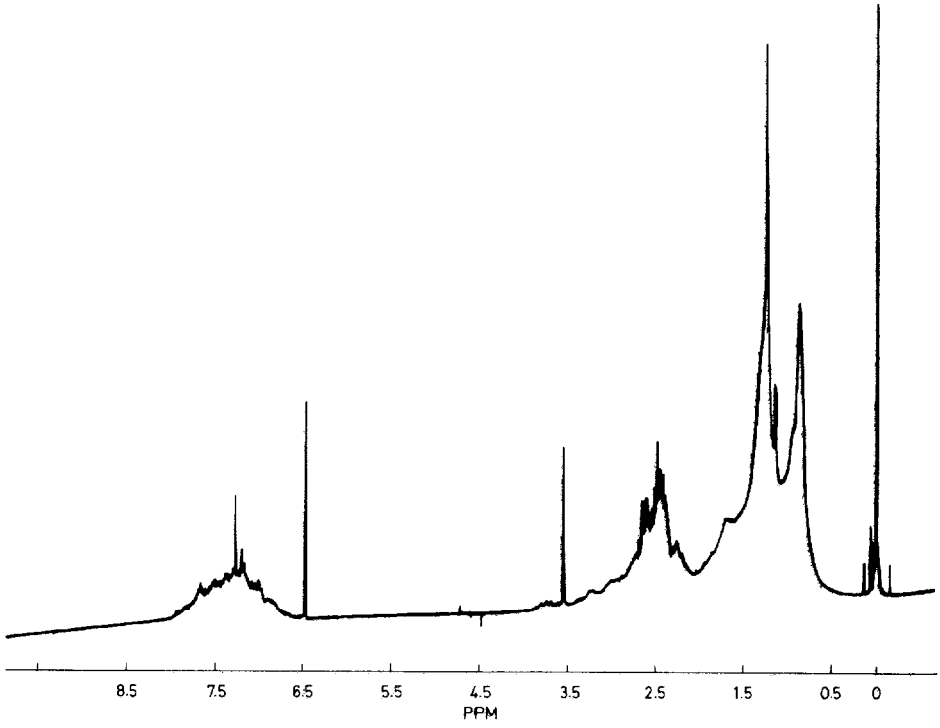

Fig. 10. As Fig. 9. Sample: diaromatic fraction.

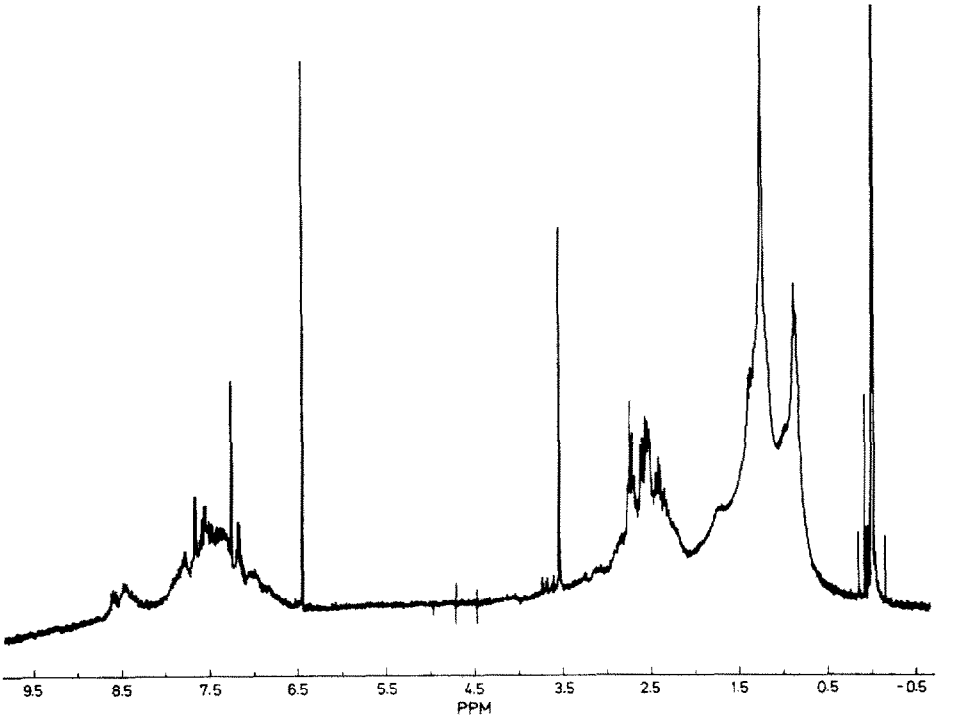

Fig. 11. As Fig. 9. Sample: triaromatic fraction.

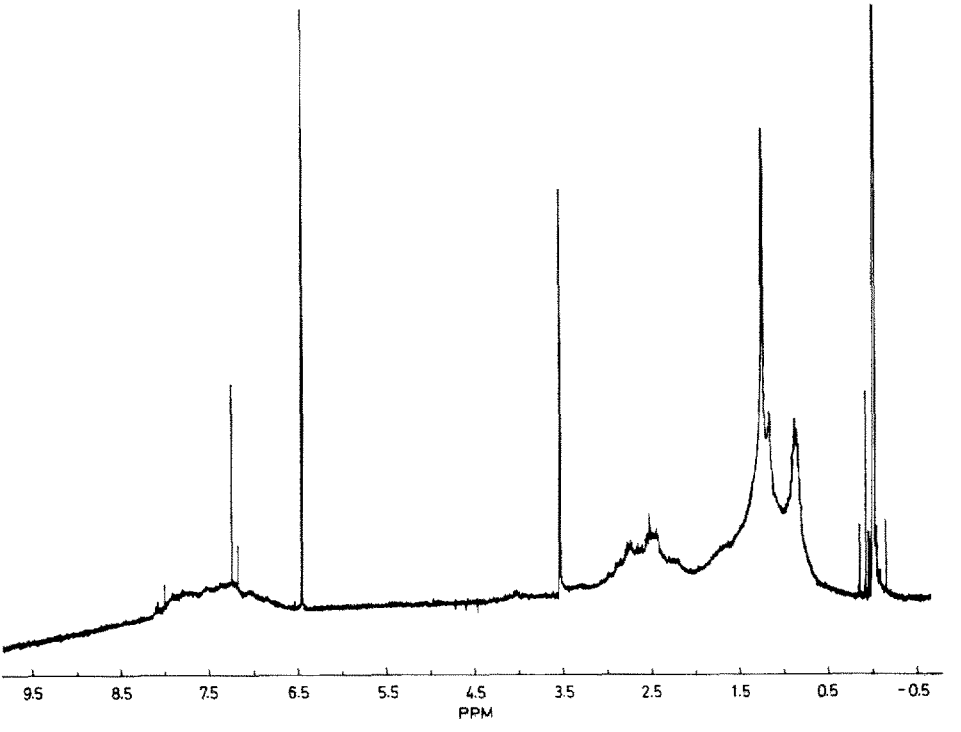

Fig. 12. As Fig. 9. Sample: tetraaromatic fraction.

able column types silica, nitrile and amino, the amino column gives the best separation according to the number of condensed rings. This is not only the case for unsubstituted or slightly substituted hydrocarbons, but also for highly alkylated hydrocarbons in a petroleum residue. The synchronous scanning fluorescence method has proven to be a simple and efficient way to determine the distribution of aromatic systems in complex mixtures. The offline combination of HPLC and ^{1}H NMR is relatively simple to perform, and may give valuable information on the average composition of fractions produced by HPLC.

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