Table III. Results of Determination of Gold in Geochemical Reference Samples

Sample	Sample size, grams	Results,[a] ppm	Reported value, ppm
Kennecott Exploration Inc. Geochemical Standards			
GRLD 102	5	1.44 ± 0.09	1.42[b]
GRLD 105	10	0.44 ± 0.04	0.46[b]
GRLD 115	20	0.04 ± 0.01	0.04[b]
GRLD 116	20	0.08 ± 0.02	0.11[b]
U.S. Bur. of Mines Reference Ores			
USBM Reference Ore C16	5	6.3 ± 0.1	7.06–7.78[c]
College Park High Reference Ore	5	10.4 ± 0.1	12.7 ± 0.37[c]
College Park Low Reference Ore	5	1.77 ± 0.07	1.82 ± 0.04[c]
South African Reference Ores			
Blyvooruitzicht	5	0.75 ± 0.1	0.69–0.84[c]
Harmony Mines	5	0.60 ± 0.08	.40[c]

[a] Precision estimated (based on duplicate analyses). [b] Kennecott Exploration Inc. values determined by Atomic Absorption. [c] Reference 19.

these ions are just outside the limits of conventional methods such as X-ray fluorescence. After preconcentration of these ions on ion exchange resins, less than 0.01 micromole can be determined for many elements using X-ray fluoresence and, in some cases, lower amounts could possibly be determined using neutron activation analysis. By careful selection of the resin and extraction conditions, selectivity can be obtained. However, it is also possible to analyze for several elements on one ion exchange resin pellet. The major disadvantage of the technique is that it is not particularly fast and does not lend itself to automation. However, the fact that after preconcentration of ions several conventional analytical techniques may be used is of considerable value.

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Polyaromatic Hydrocarbons in High-Boiling Petroleum Distillates

Isolation by Gel Permeation Chromatography and Identification by Fluorescence Spectrometry

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The identification of seven polyaromatic ring systems in petroleum is reported. The ring systems are 1,12,2,3-dibenzoperylene; 1,12-o-phenyleneperylene, pyreno[1.3:10′.2′]pyrene; 2.3,10.11-dibenzoperylene; 1,2,4,5-dibenzopyrene, benzo[*e*]pyrene, and benzo[*g*]chrysene. These polyaromatic hydrocarbons were isolated by a separation scheme involving ion exchange chromatography, gel permeation chromatography, and thin-layer chromatography and were identified by fluorescence spectroscopy. Gel permeation chromatography separated pericondensed aromatic ring systems from catacondensed ring systems and the other components of an acid concentrate.

Polyaromatic hydrocarbons have been studied extensively in recent years as a result of their occurrence in such diverse sources as automobile exhaust, coal tars, cigarette smoke, sediments, shale oil, and crude oil. Many investigations have been conducted to examine the carcinogenicity of the polycyclic hydrocarbons. The high-molecular weight polyaromatics are of special interest to the petroleum industry because these compounds have chemical and physical properties that interfere with commercial refining processes.

The polyaromatic ring systems previously identified in petroleum have generally contained up to five aromatic rings. Investigations conducted in conjunction with American Petroleum Institute Project 6 (*1–5*) resulted in the

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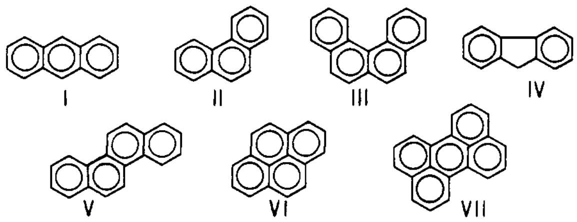
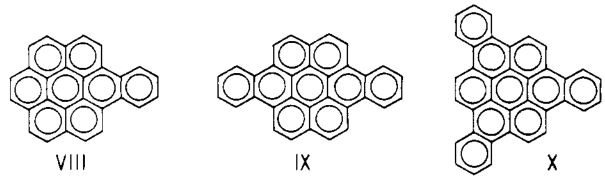
identification of many monoaromatic, diaromatic, and triaromatic hydrocarbons; but hydrocarbons having more than four aromatic rings were not found. Typical of the petroleum polyaromatic hydrocarbons that have been isolated or observed spectroscopically by various research groups are anthracenes, I (*6*); phenanthrenes, III (*5, 7*); benzophenanthrenes, IV (*8*); fluorenes, (*5, 9*); chrysenes, V (*8, 10, 11*); pyrenes, VI (*5, 7*); and perylenes, VII (*11*). Recently, larger ring systems such as 1,12-benzoperylene (six rings) and coronene (seven rings) have been identified in virgin petroleum (*12*).



Polyaromatic hydrocarbons with very large ring systems have been identified in cracked petroleum distillates (*13*). Ring systems such as benzocoronenes (VIII), dibenzocorones (IX), and tribenzocoronenes (X) were generated during the high-temperature hydroconversion of high-boiling distillates and caused serious problems with the commercial processing of the feedstock.



This paper reports the identification of seven polyaromatic hydrocarbons not previously found in virgin petroleum. These polyaromatic hydrocarbons and six additional polyaromatic ring systems known to be constituents of petroleum were separated by gel permeation and thin-layer chromatography and were identified by fluorescence spectroscopy. The compounds are present in trace amounts in the acid concentrate studied but may be present in substantial amounts in the total crude oil.

EXPERIMENTAL

Apparatus. Fluorescence emission and fluorescence excitation spectra were recorded using a Perkin-Elmer MPF-2A fluorescence spectrophotometer.

Reagents. The polyaromatic hydrocarbons were found in trace amounts in a concentrate of petroleum acids that was obtained from a Recluse, Wyo., crude oil distillate that had a corrected boiling range of 335–530 °C. While being distilled on a Rota-Film molecular still, the distillate was actually subjected to a temperature of about 175 °C for 1 or 2 sec. No evidence has been obtained that chemical artifacts were formed during the distillation.

Model compounds were obtained from various chemical supply houses. The desired model compounds were separated from impurities using thin-layer chromatography on silica gel G or aluminum oxide G.

Procedure. The separation scheme is shown in Figure 1. The 335–530 °C distillate was passed over anion exchange resin, and

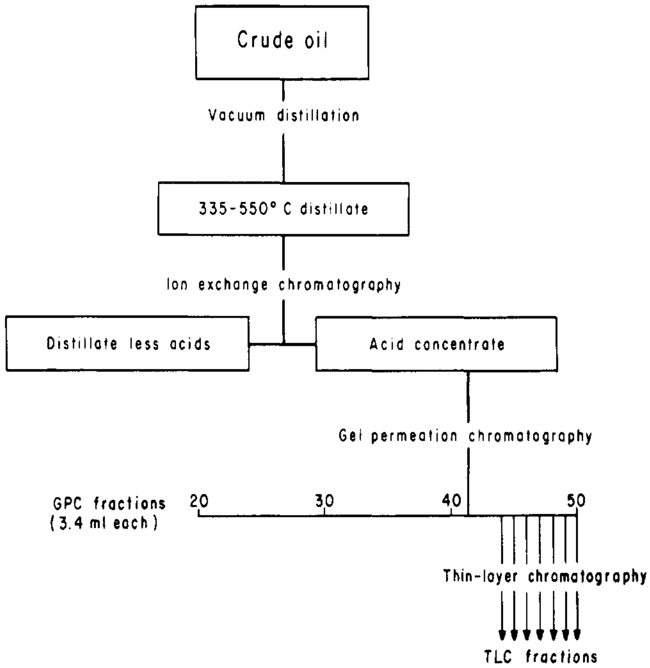


Figure 1. Separation scheme

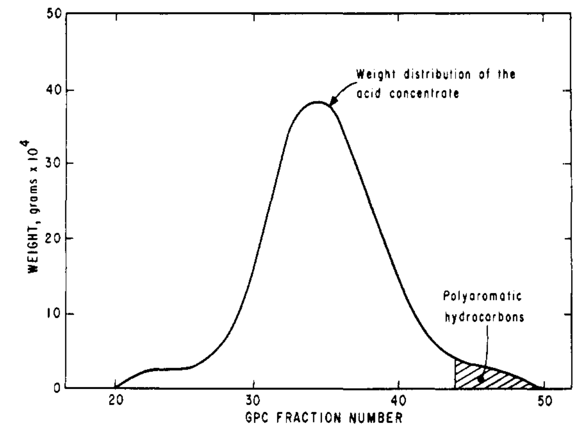


Figure 2. The GPC weight distribution of the acid concentrate

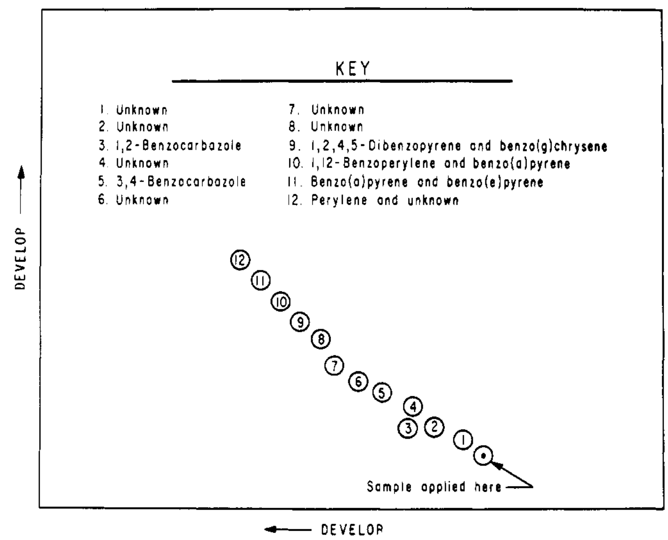


Figure 3. Thin layer chromatogram of GPC fraction 44

the materials retained by the resin were defined as the acid concentrate. The acids were removed from the resin and passed through a gel permeation chromatographic (GPC) column. The weight distribution of the acid concentrate as it was eluted from the GPC column is shown in Figure 2. Details of the isolation and

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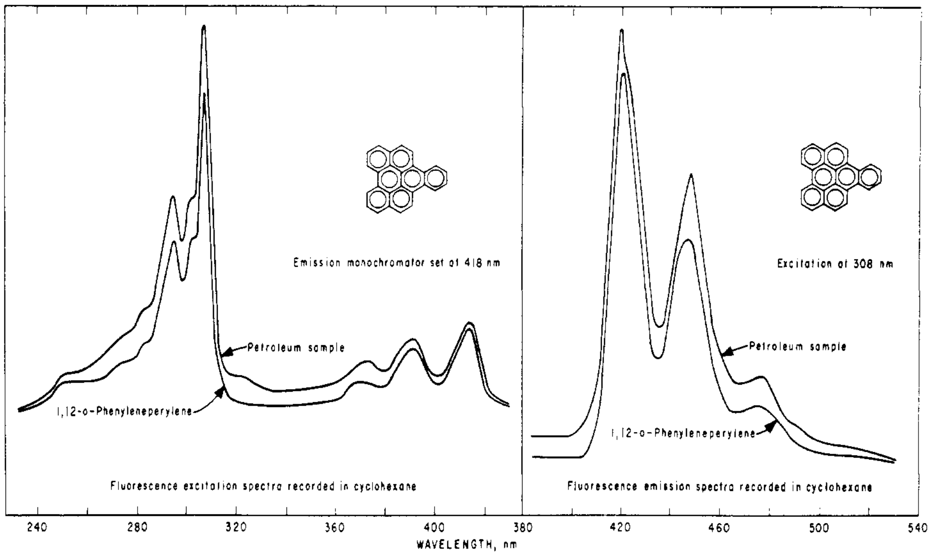

Figure 4. Fluorescence emission and fluorescence excitation spectra of 1,12-*o*-phenyleneper

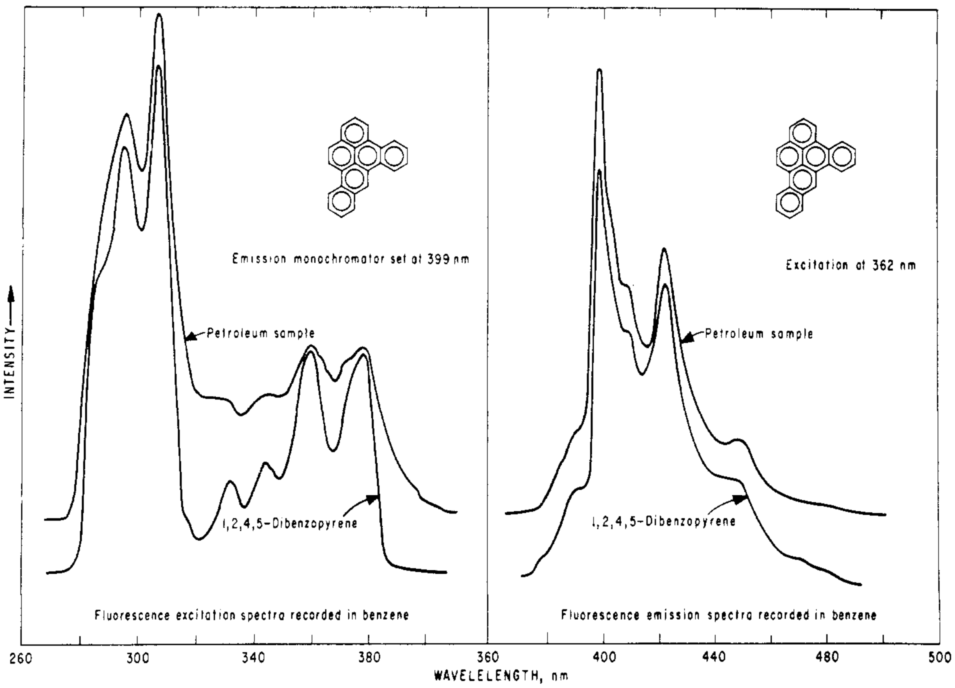

Figure 5. Fluorescence emission and fluorescence excitation spectra of 1,2,4,5-dibenzopyrene

separation of a high-boiling acid concentrate by ion exchange chromatography and GPC and examination of the acids have been previously described (*14*).

Visual examination of the individual GPC fractions with ultraviolet light showed that fractions 35–50 contained fluorescent compounds. A preliminary survey of these GPC fractions was then made using fluorescence spectroscopy. Although GPC fractions 35–43 contained fluorescent materials, they were too complex to be effectively separated by thin-layer chromatography (TLC) for fluorescence analysis and were not studied in detail. GPC fractions 44–50 were further separated by TLC to obtain a more complete analysis of a given GPC fraction and to obtain improved fluorescence spectra. Thin-layer plates 20 × 20 cm were prepared using a 2:1 mixture of aluminum oxide type E (E. Merck) and 20% acetylated cellulose (MN 300 AC, Macherey, Nagel and Co.) suspended in ethanol. The plates were developed in two directions with a mixture of diethyl ether, toluene, and cyclohexane, 2:1:7 by volume. The TLC fractions were removed from the plates by vacuuming the adsorbent into disposable pipets packed with glass wool. The polyaromatic hydrocarbons were then eluted with benzene and fluorescence emission and fluorescence excitation spectra recorded in solution. Figure 3 shows the TLC chromatogram of GPC fraction 44. The fractions eluting later than fraction 44 were observed to be progressively less complex.

All spectra were recorded in dilute solutions (10^{-4} to $10^{-6}M$) of spectra-grade cyclohexane, benzene, or ethanol. Significant solvent shifts were observed for several spectra. Fluorescence emission and fluorescence excitation spectra of model compounds were available to aid in the identification of the 1,12-phenyleneperylene and 1,2,4,5-dibenzopyrene ring systems. The other ring systems were identified by comparison of the fluorescence excitation spectra with published ultraviolet absorption spectra (*15*).

RESULTS AND DISCUSSION

The polyaromatic hydrocarbons found in the Recluse, Wyo., high-boiling distillate contained as many as eight aromatic rings. The ring systems identified were 1.12,2.3-dibenzoperylene (XI); 1,12-*o*-phenyleneperylene (XII); pyreno[1.3:10′2′]pyrene (XIII); 2.3,10.11-dibenzoperylene (XIV); 1,2,4,5-dibenzopyrene (XV); benzo[*e*]pyrene

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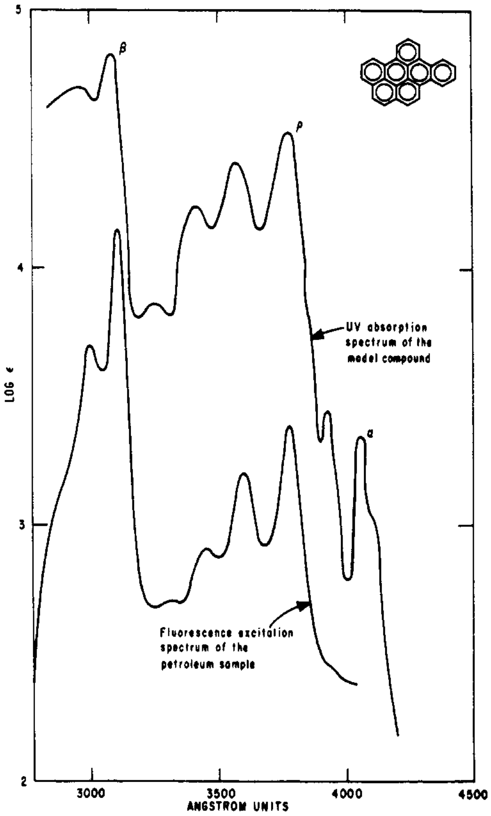
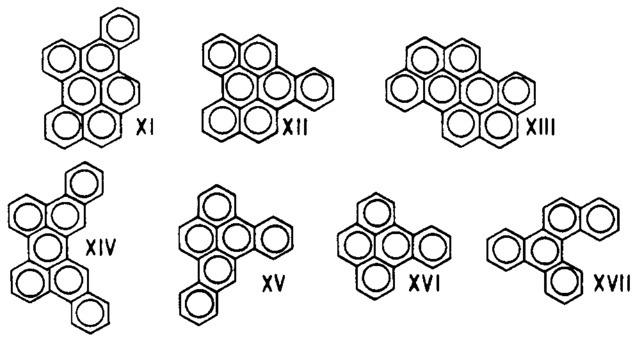


Figure 6. UV absorption and fluorescence excitation spectra of 1.12,2.3-dibenzoperylene

(XVI); and benzo[*g*]chrysene (XVII).



Figures 4 and 5 show the fluorescence emission and fluorescence excitation spectra of the model compounds 1,12-*o*-phenyleneperylene and 1,2,4,5-dibenzopyrene together with the corresponding spectra recorded from the petroleum samples. The model compound spectra are essentially superimposable on the spectra of the petroleum samples. The fluorescence emission and fluorescence excitation data obtained from these samples are shown in Table I. The peak of maximum intensity in each spectrum is underlined.

Figures 6–10 show the ultraviolet absorption spectra of model compounds reported by Clar (*15*) together with the fluorescence excitation spectra of petroleum samples. The units of log ε in these spectra refer only to the ultraviolet absorption spectra.

Table II is a compilation of the peak maxima, reported in angstrom units, obtained from these spectra. In general, the fluorescence excitation spectra of the petroleum samples compare favorably with the ultraviolet absorption spectra of the model compounds. The differences in intensity of fluorescence excitation peak maxima and ultraviolet absorption peak maxima result from the differences in

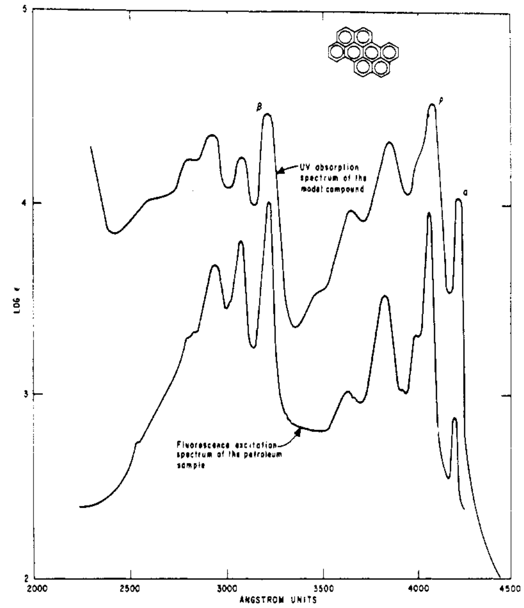


Figure 7. UV absorption and fluorescence excitation spectra of pyreno [1.3:10′.2′]pyrene

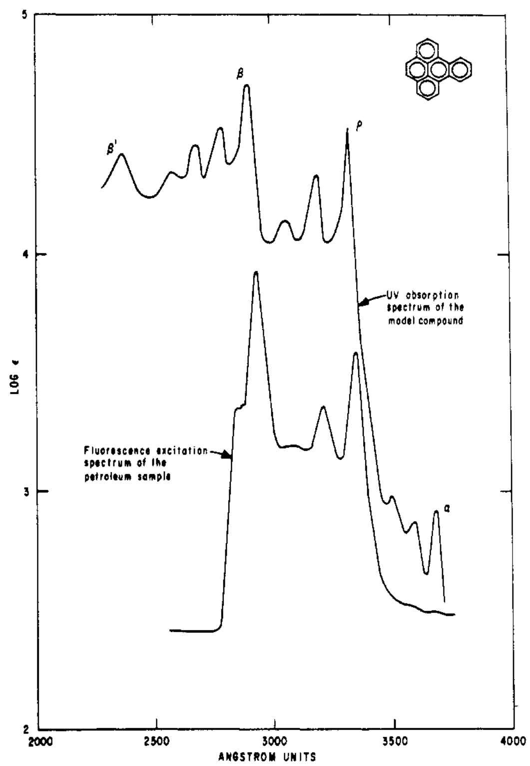


Figure 8. UV absorption and fluorescence excitation spectra of benzo[*e*]pyrene

instrumental methods by which the two spectra are recorded. For example, the longest wavelength ultraviolet absorption bands were less difficult to observe than were the corresponding longest wavelength fluorescence excitation bands. In the case of recording ultraviolet spectra, the problem of observing the longest wavelength absorption band is mainly one of sample concentration. In the case of the fluorescence excitation spectra, the problem of observing the longest wavelength band may depend on a number of factors including sample concentration, the intensity of the fluorescence emission band maxima, or the amount of overlap of excitation and emission bands. Significant solvent shifts were noted when the fluorescence

Table I. Fluorescence Emission and Fluorescence Excitation Data for 1,12-o-Phenyleneperylene and 1,2,4,5-Dibenzopyrene Model Compounds and Petroleum Samples

	Excitation spectra, nm	Emission spectra, nm
1,12-o-Phenyleneperylene[a]	296, 304, 309, 372, 392, 415	418, 445, 473
Petroleum sample[a]	296, 304, 309, 372, 392, 415	418, 445, 473
1,2,4,5-Dibenzopyrene[b]	287, 296, 308, 333, 345, 361, 380	399, 422, 449
Petroleum sample[b]	287, 296, 308, 333, 345, 361, 380	399, 422, 449

[a] Cyclohexane used as solvent. [b] Benzene used as solvent.

Table II. Ultraviolet Absorption Data of Model Compounds and Fluorescence Excitation Data of Petroleum Samples (Angstrom Units)

1.12,2.3-Dibenzoperylene (absorption spectrum[a])	2970, 3095, 3270, 3430, 3585, 3775, 3920, 4040
Petroleum sample (excitation spectrum[a])	2990, 3100, 3250, 3450, 3590, 3770, 3930
Pyreno(1.3:10′.2′)pyrene (absorption spectrum[b])	2930, 3080, 3220, 3640, 3850, 4060, 4200
Petroleum sample (excitation spectrum[c])	2859; 3090, 3230, 3660, 3840, 3070, 4200
Benzo[e]pyrene (absorption spectrum[d])	2780, 2890, 3040, 3165, 3315, 3480, 3570, 3660
Petroleum sample (excitation spectrum[a])	2860, 2940, 3090, 3210, 3360, ----, 3600, 3680
Benzo[g]chrysene (absorption spectrum[d])	2765, 2860, 3080, 3210, 3340, 3520, 3710
Petroleum sample (excitation spectrum[d])	2770, 2880, 3020, 3150, 3270
2.3,10.11-Dibenzoperylene (absorption spectrum[a])	3920, 4140, 4400
Petroleum sample (excitation spectrum[a])	2880, 3080, 3200, 3960, 4160, 4400
2.3,10.11-Dibenzoperylene (absorption spectrum[d])	2881, 3020
Petroleum sample (excitation spectrum[d])	2880, 3020, 4130, 4370

[a] Benzene used as solvent. [b] Dioxane used as solvent. [c] Cyclohexane used as solvent. [d] Ethanol used as solvent.

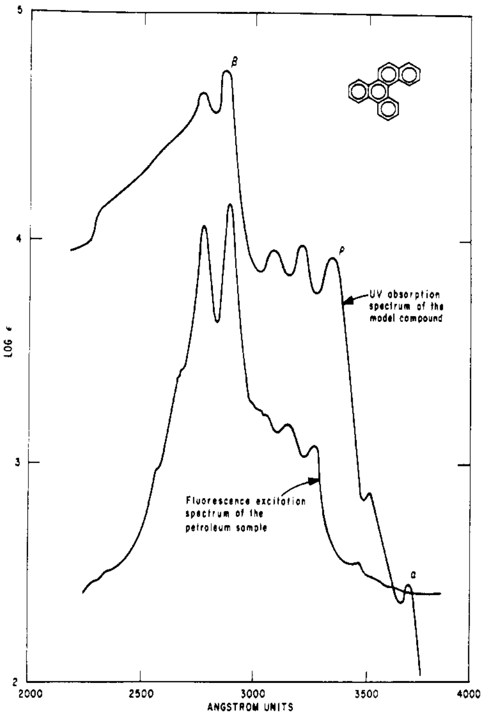


Figure 9. UV absorption and fluorescence excitation spectra of benzo[g]chrysene

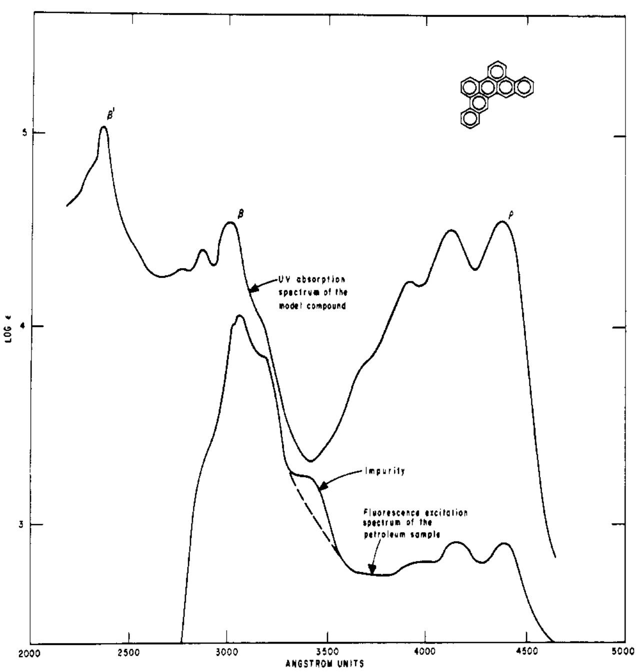


Figure 10. UV absorption and fluorescence excitation spectra of 2.3, 10.11-dibenzoperylene

excitation spectra of the polyaromatic hydrocarbons were recorded in various solvents. For example, in order to compare the ultraviolet absorption spectra of the model compound 2.3,10.11-dibenzoperylene recorded by Clar in two different solvents with the fluorescence excitation spectra of the petroleum sample, it was necessary to record the fluorescence excitation spectra of the petroleum sample in the same two solvents. These data are shown in Table II. The identification of benzo[g]chrysene should be considered tentative. The excitation spectrum of the petroleum sample is not superimposeable on the ultraviolet absorption spectrum of the model compound. The differences in the two spectra may be due to substituent groups on the aromatic ring system of the petroleum sample.

The mass spectra of these polyaromatic hydrocarbons have not yet been recorded. As a result, the degree of substitution, if any, is uncertain. However, some indirect evidence of the degree of substitution has been obtained. The pericondensed polyaromatic hydrocarbons in the petroleum distillates show GPC distributions which are very similar to those of the unsubstituted model compounds. The GPC elution volumes are similar to those of model compounds, and, like model compounds, the ring systems are eluted from the column in a relatively small number of GPC fractions. This behavior, together with the TLC separation characteristics, suggests that the polyaromatic hydrocarbons are unsubstituted or have very little substitution. (The perylene observed in this petroleum sample, see Figure 11, and in earlier work *(12)*, has been shown by mass spectroscopy to be unsubstituted.)

Gel permeation chromatography has an important role in the separation and identification of the polyaromatic hydrocarbons. Most of the polyaromatic hydrocarbons identified in the late-eluting GPC fractions are pericondensed aromatics. The pericondensed ring systems in the acid concentrate were separated from the other components due to a gel permeation chromatographic effect which we call a "pericondensation effect." This effect was first observed in model compounds by Oelert, Latham, and Haines *(16)* and was examined further by Bergmann, Duffy, and Stevenson *(17)*. Because of this effect, high-molecular weight pericondensed ring systems are eluted from a GPC column later than low-molecular weight pericondensed ring systems—a reversal of the usual GPC distribution. As an additional general rule, pericondensed aromatics are eluted later than catacondensed aromatics of similar molecular weight. The cause of the pericondensation effect is not known but may be related to sorption on the gel and/or solubility.

The distribution of the polyaromatic ring systems identified in GPC fractions 44–50 is shown in Figure 11. GPC fraction 44, the most complex fraction, contained aromatic hydrocarbons having five and six aromatic rings. As the GPC fraction number increased, the fractions became less complex and the number of rings in the aromatic hydrocarbons increased to seven and eight. Catacondensed aromatics, such as phenanthrene and anthracene, and the four-ring pericondensed aromatic, pyrene, were not identified in GPC fractions 44–50 but if present would elute in earlier GPC fractions. Studies of other distillate fractions have shown that four-ring catacondensed aromatics such as chrysene and 1,2-benzoanthracene elute before five-ring pericondensed aromatics. The GPC fractions of high-boiling distillates eluting later than fraction 50 are currently being investigated because these fractions would be expected to contain polyaromatic hydrocarbons in the C_{30}–C_{40} range. Polyaromatic hydrocarbons in this carbon-number range probably have more than eight aromatic rings.

Although the polyaromatic hydrocarbons discussed here represent only a small fraction of the acid concentrate being investigated, they may be present in much larger quantities in the aromatic concentrate of the same distillate. Furthermore, since our investigations of a Recluse 500–650 ≃C distillate indicate that these compound types are even more prevalent in the higher boiling distillate, it is not unreasonable to assume that these large aromatic ring systems, and even larger ring systems, could represent a substantial portion of the very high-boiling petroleum distillates and residuals. A definitive study as to why these polyaromatic hydrocarbons are found in an acid concentrate has not been made. Perhaps these materials are adsorbed on the anion exchange resin or precipitate on the resin due to very low solubility.

CONCLUSIONS

Seven polyaromatic ring systems not previously found in virgin petroleum have been identified in a 335–550 °C petroleum distillate: 1.12,2.3-dibenzoperylene; 1,12-*o*-phenyleneperylene; pyreno[1.3:10′.2′]pyrene; 2.3,10.11-dibenzoperylene; 1,2,4,5-dibenzopyrene; benzo[*e*]pyrene; and benzo[*g*]chrysene. These and other pericondensed aromatic hydrocarbons were separated from the other components of an acid concentrate because of a gel permeation chromatographic effect which separates large pericondensed aromatic hydrocarbons from smaller pericondensed aromatic hydrocarbons and catacondensed aromatic hydrocarbons. The polyaromatic hydrocarbons are thought to be unsubstituted or have very little substitution. These ring systems, and even larger ring systems, may represent a significant percentage of a total crude oil.

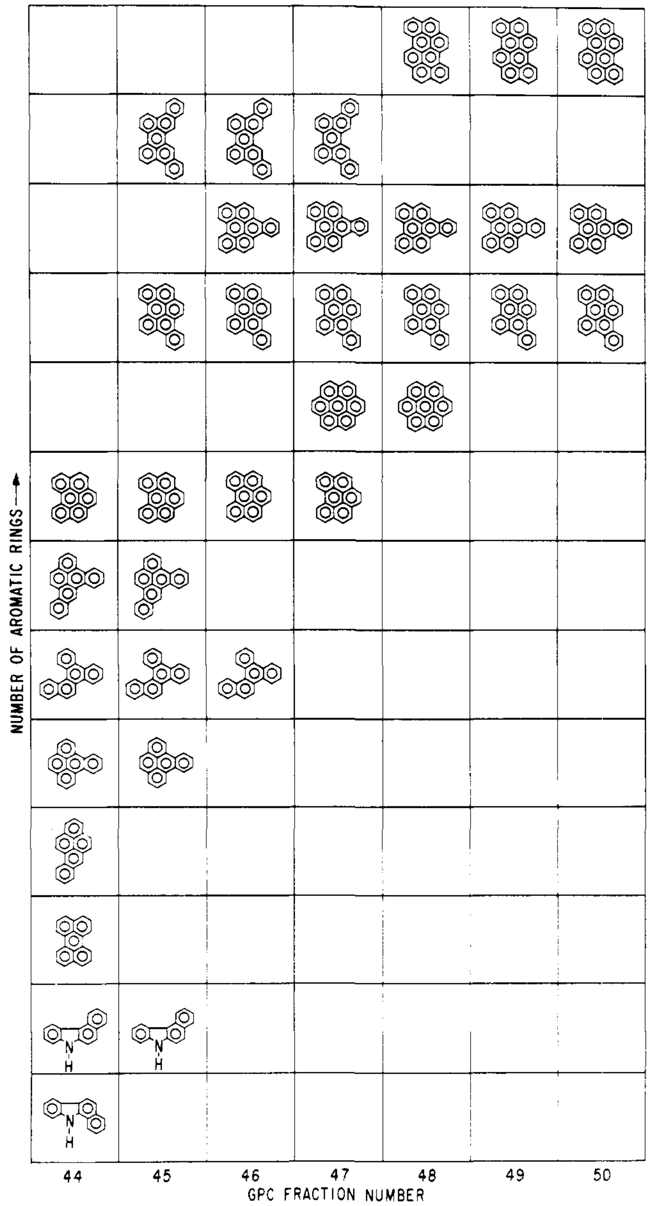


Figure 11. GPC distribution of polyaromatic ring systems

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