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DISTRIBUTION OF POLYNUCLEAR AROMATIC RING CLASSES IN THE  
ALBERTA BASIN BITUMENS AND CRUDE OILS

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MARCH 1981

ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
Report ERP/ERL 81-09(OP)

ERP/ERL 81-09(OP) c.2

01-0003455 c.2

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by

A.E. George\* and J.E. Beshai\*\*

ABSTRACT

The total polynuclear aromatic hydrocarbon (PAH) content and relative distribution of the fused aromatic ring classes have been studied in four Cretaceous bitumens and crude oils of varying degree of geothermal maturation. A high performance liquid chromatographic (HPLC) separation, selective for the number of fused aromatic rings up to four, was used to separate the PAH ring systems. The effect of geothermal maturation was simulated by reductive treatment of the heavy Athabasca bitumen. The treatment produced PAH ring distribution similar to that in the light Medicine River oil, and diminished PAH content considerably. The 3- and 4-fused ring systems increased while hydrocarbons containing more than four fused rings decreased. Alkyl substitution was also reduced as a result of both the natural and simulated maturations. Separation efficiency was monitored by using refractive index and ultraviolet detectors, gas chromatography, mass spectrometry,  $^{13}\text{C}$  NMR and spectrofluorometry.

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## INTRODUCTION

For many years petroleum exploration relied largely on the recognition of suitable structures, the selection of which is based mainly on intuition and general experience. A systematic study of hydrocarbon formation and conversion under the effects of maturation, especially geothermal maturation, can improve the reliability of exploration predictions and hence reduce the financial risk of drilling.

It is generally believed that the heavy oils in the lower Cretaceous reservoir rocks extending from west central Alberta through the Athabasca tar sands area into western Saskatchewan belong to a single oil system, which implies similar modes of origin (1). The process of petroleum formation and maturation depends on the thermal conversion of organic material due to temperature and pressure increase caused by burial depth (2-5). Study of the increasing geothermal maturation effects on the chemical structure of various component types is useful for assessment of their potential as "maturity index" for improved predictions of major oil occurrence. In a previous publication, geothermal maturation of the Athabasca bitumen has been simulated in our laboratory (6) and the resulting chemical effects were compared to those in heavy and light oils from the Alberta Basin at different burial depths. The gross composition and distribution of light fractions relative to residual fractions and asphaltenes have been investigated. Only the saturated, monoaromatic and diaromatic hydrocarbons have been analyzed in detail, and interesting analogies indicating chemical maturation patterns were drawn.

In this study we looked into the effects of simulated and natural geothermal maturation on the total content of polynuclear aromatic hydrocarbons and their ring number distribution. Response of the alkyl substitution on these PAHs to maturation effects has also been monitored. High performance liquid chromatography with refractive index and ultraviolet detectors, gas chromatography, mass spectrometry,  $^{13}\text{C}$  NMR and spectrofluorometry were used in the study.

## EXPERIMENTAL

### Samples

The following five samples were investigated:

1. Athabasca bitumen separated by the hot water process at the Great Canadian Oil Sands (GCOS) plant.
2. Athabasca bitumen sample thermally processed at 470°C, under reducing conditions involving pressure, to simulate maturation.
3. Cold Lake bitumen obtained by steam injection at 1500' (457 m) from the Manville Pool by Imperial Oil Co.
4. Lloydminster oil produced by Husky Oil Co. from the Sparky Formation at 9A-3-50-1W4M, depth 1893' (577 m).
5. Medicine River oil produced by Hudson Bay Oil and Gas Co. from the Glauconite zone, location 2-17-39-4W5M, depth 7326' (2233 m).

The separation-characterization schematic diagram is shown in Fig. 1.

### Distillation and Deasphalting

All the samples were distilled up to 200°C and deasphalted by precipitation in 20 volumes of pentane. The deasphalted residues were vacuum distilled to 350°C, and the fraction boiling above 350°C was used for compound-type separation.

### Compound-Type Separation

The deasphalted distillation residues boiling above 350°C were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar compounds and basic compounds on a dual-packed silica-alumina gel chromatographic column (7) and the polyaromatic concentrate was taken for further HPLC separation.

### High Performance Liquid Chromatography (HPLC)

The silica-R(NH<sub>2</sub>)<sub>2</sub> (10 μm) column (250 x 4.6 mm) was slurry packed at 6000 p.s.i. using heptane with a Haskel DST-150A air-driven liquid pump. HPLC grade methylene chloride, acetonitrile and n-hexane solvents, dried by activated molecular sieves, were used. The HPLC system consisted of a Valco Sample injection valve, a Water's Model 6000 pump, Water's Model 401 RI Detector, and a Schoeffel SF 770 UV spectroflow monitor with 8 μL cell.

Chromatographic separations were performed at a flow rate of 2 mL/min at 24°C. HPLC systems were studied using a 7- $\mu$ L home made loop. A 100- $\mu$ L loop was used for collecting the aromatic sub-fractions and for aromatic type quantitation. The refractive index detector was thermostated at 24°C to monitor the eluent from the R(NH<sub>2</sub>)<sub>2</sub> column. Quantitation was accomplished by using model compounds (phenanthrene and chrysene), as well as standards isolated from fractions of both oils (8).

#### Collection of Aromatic Sub-fractions

The polynuclear aromatic hydrocarbon fractions in hexane (10 mg/mL) were injected in 100- $\mu$ L portions on the silica-R(NH<sub>2</sub>)<sub>2</sub> column. Effluent cuts of 2 ml corresponding to the retention range of the standards of choice and their alkyl derivatives were collected and evaporated down to 10  $\mu$ L with nitrogen. The cuts from four successive collections were combined and studied by means of gas chromatography and mass spectrometry to identify the main components (Fig. 2).

#### Gas Chromatography and Gas Chromatography-Mass Spectrometry

A Tracor model MT-220 gas chromatograph fitted with a FID (350°C) was used for this work. Mixtures were separated on a stainless steel column (3 m x 3.1 mm) packed with 3% OV-1 on (100-120 mesh) Chromosorb W, A.W., DMCS, HP. The injector temperature was held at 240°C and hydrogen at 40 cm<sup>3</sup>/min was used as the carrier gas. Temperature was programmed from 100°C to 300°C at a rate of 10°C/min.

A Finnegan Model 4000 GC-MS system employing electron impact at 70 eV (scan time 0.3 sec/1000 a.m.u.), direct inlet to mass spectrometer and a data acquisition Ingos Nova I computer was used for HPLC cut characterization. Concentrated aromatic sub-fractions were separated on a glass column (1.8 m x 6.3 mm o.d., 2 mm i.d.) packed with 2.5% Dexil 300 on (80-100 mesh) Chromosorb W, A.W. and helium was used as carrier gas (25 cm<sup>3</sup>/min). Samples were injected at 220°C and a temperature program of 10°C/min was used from 100 to 300°C.

#### Nuclear Magnetic Resonance Spectrometry

Samples for <sup>13</sup>C NMR analyses were weighed directly into 5-mm NMR tubes. Deuteriochloroform (CDCl<sub>3</sub>) was added as solvent reference and internal lock. Chromium (tris) acetylacetonate (Cr(ACAC)<sub>3</sub>) was added to the sample so that a rapid pulse repetition rate could be used without severe line broadening or shifting. The analysis was performed on a Varian CFT-20 Fourier transform

### Spectrofluorimetry

Fluorescence excitation and emission spectra, uncorrected for variation of source and photomultiplier response, were recorded in HPLC grade hexane dried with activated molecular sieves. A Varian SF330 spectrofluorimeter was used. The spectra were recorded in dilute solutions to avoid excimer formation. Appropriate cut-off filters were used in the emission beam.

The fluorescence intensity of standard compounds was recorded as a function of the emission wavelength with the excitation wavelength held at a constant long wavelength of relatively high intensity. Similarly, the excitation spectra were recorded by varying the excitation wavelength at a constant emission wavelength.

Seven fractions representing different polyaromatic ring systems were collected from a HPLC separation on the diamine column. The retention times of model compounds were used as an aid in the selection of optimal excitation and emission wavelengths. Each sample was irradiated at several different wavelengths to obtain optimum emission spectra. Similarly, excitation spectra were recorded with the emission monochromator set at different wavelengths.

### Elemental Analysis

Elemental analysis of the PAH fractions of both oils, obtained from the silica-alumina chromatographic separation, was performed on a Perkin Elmer 240 analyzer.

## RESULTS AND DISCUSSION

### Separation of PAH Sub-Fractions

Our previous work proved that the silica-R(NH<sub>2</sub>)<sub>2</sub> based HPLC system is useful for the analysis of PAH mixtures in hydrocarbon materials. It permits the quantitation of meaningful aromatic sub-fractions on the basis of the number of fused rings with insignificant dependence on alkyl substitution (8,9). The scale of separation achieved on the analytical size column is sufficient for hydrocarbon material collection of the predominant aromatic components, and more detailed characterization by gas chromatography-mass spectrometry and spectrofluorometry.

#### PAH Total Content and Burial Depth

The total PAH content in the deasphalted residues boiling higher than 350°C decreases considerably (23.2% to 7.6%) with increasing burial depth of the hydrocarbon pool, Table 1. The liquid chromatographic dual-packed column used in this analysis separates PAH concentrates composed of aromatic nuclei with varying degrees of aliphatic alkyl substitution. The apparent PAH diminution under increasing severity of thermal conditions is due to increasing loss of aliphatic substitution, while aromaticity actually increases, as will be seen later.

#### PAH Ring Distribution and Burial Depth

Separation and characterization of PAH ring classes from these bitumens and oils show that the 3-ring components, phenanthrenes and anthracenes increase gradually with increasing burial depth. The 4-ring aromatics, pyrenes and chrysenes also show the same trend, but to a lesser degree. These increases seem to take place at the expense of PAHs containing more than 4 fused rings per molecule, i.e. benzo[a] pyrenes, perylenes and dibenzo[a,h] anthracenes, which decrease from 25% to 15% with increasing depth. These results have been qualitatively verified by the fluorescence excitation and emission spectra (Table 2), and quantitated using the refractive index detector (Table 3). The strong retention of some of the PAH material on the diamine column so that they could not be recovered by the mobile phase does not lessen the validity of the above observations.

Increase of the 3- and 4-ring molecules at the expense of the higher ring number aromatics resembles hydrocracking effects that cause ring rupture, usually preceded by a saturation step. These results are consistent with the general pattern of thermal maturation of hydrocarbons (10,11).

#### PAH Alkyl Substitution and Burial Depth

The diminution of the alkyl substitution on the aromatic rings, with increasing burial depth, is shown by the <sup>13</sup>C nuclear magnetic resonance and elemental analyses of the total PAH fractions. As the thermal conditions become more severe, the aromatic molecules become increasingly aromatic in character through depletion of the number and length of the aliphatic substituents and possible increased dehydrogenation of the cycloalkyl substituents on the aromatics (see C/H and aromatic/aliphatic ratios in Table 4).

PAH Conversion by Simulated Maturation

The reductive thermal treatment of Athabasca bitumen converted its PAH fraction to resemble the same trend exemplified by polynuclear aromatics of the Medicine River oil. The total PAH content was reduced from 23.2% to 16.2% (Table 1). 3- and 4-ring structures increased, while molecules containing more than 4 fused rings decreased (Table 3). Alkyl substitution diminished and aromaticity became more pronounced as the thermal conditions became more severe by increasing burial depth (Table 4).



REFERENCES

1. Vigrass, L.W. "Geology of Canadian Heavy Oil Sands", Amer. Assoc. Petrol. Geologists Bull., 52, 1984 (1968).
2. Tissot, B. and Welte, D.H. "Petroleum Formation and Occurrence", Springer, Berlin, p. 538 (1978).
3. Hunt, J.M. "Petroleum Geochemistry and Geology", W.H. Freeman, San Francisco, California, p. 617 (1979).
4. Philippi, G.T. Geochimica et Cosmochimica Acta, 29, 1021-1049 (1965).
5. Cordell, R.J. The Amer. Assoc. Petrol. Geologists Bull. 56, 2029-2067 (1972).
6. George, A.E., Banerjee, R.C., Smiley, G.T. and Sawatzky, H. "Simulated Geothermal Maturation of Athabasca Bitumen", Bull. of Can. Petrol. Geology, 25, No. 5, 1085-1096 (1977).
7. Sawatzky, H., George, A.E., Smiley, G.T. and Montgomery, D.S. Fuel, 55, 16 (1976).
8. Chmielowiec, J., Beshai, J.E. and George, A.E. Fuel, 59, 838-844 (1980).
9. Chmielowiec, J. and George, A.E. Anal. Chem., 52, 1154-1157 (1980).
10. Albrecht, P., Vandenbroucke, M. and Mandengue, M. Geochim. Cosmochim. Acta, 40, 791-799 (1976).
11. Alexander, R., Gray, M.D., Kagi, R.I. and Woodhouse, G.W. Chem. Geol., 30, 1-14 (1980).

TABLE 1

Compound-Type Distribution (wt %) in the  
Deasphalted Residues Boiling Higher Than 350°

| Sample                 | Burial<br>Depth<br>(m) | Compound-Type |               |             |               |                    |                   |
|------------------------|------------------------|---------------|---------------|-------------|---------------|--------------------|-------------------|
|                        |                        | Saturates     | Monoaromatics | Diaromatics | Polyaromatics | Polar<br>Compounds | Basic<br>Material |
| Athabasca              | surface                | 19.4          | 12.9          | 8.1         | 23.2          | 21.7               | 6.5               |
| Cold Lake              | 457                    | 20.0          | 11.9          | 8.9         | 25.1          | 23.5               | 6.9               |
| Lloydminster           | 577                    | 20.3          | 6.9           | 9.6         | 13.4          | 37.7               | 8.2               |
| Medicine River         | 2233                   | 56.0          | 14.7          | 8.3         | 7.6           | 11.1               | 2.1               |
| Processed<br>Athabasca | -                      | 34.1          | 16.3          | 9.9         | 16.2          | 15.2               | 4.3               |

TABLE 2

Fluorescence Excitation and Emission Spectra (wavelength, nm) of Bitumens, Oils  
and Simulated Maturation Product of Athabasca Bitumen  
(Solvent: Hexane, Temperature Thermostated at 25°C)

| Fraction                      | Athabasca Bitumen                         |                                      | Cold Lake Bitumen                         |   | Lloydminster Oil                          |                                      | Medicine River                            |  | Processed Athabasca Bitumen               |                                      |
|-------------------------------|---|--------------------------------------|---|---|---|--------------------------------------|---|--|---|--------------------------------------|
|                               | Excitation                                | Emission                             | Excitation                                | Emission                                  | Excitation                                | Emission                             | Excitation                                | Emission                               | Excitation                                | Emission                             |
| 1. Anthracene                 | 252* 310<br>326 353<br>371                | 373 397*<br>413(S)<br>444(S)         | 254* 310<br>327 340<br>356 380            | 366 399*<br>422<br>464(S)                 | 251* 310<br>324 336<br>354 370            | 375* 399<br>415(S)<br>446(S)         | 252* 310<br>325 340<br>356 375            | 377* 399<br>415(S)<br>447(S)           | 251* 310<br>324 355<br>355 373            | 375 399*<br>415(S)<br>446(S)         |
| 2. Phenanthrene               | 240 250*<br>279 282<br>303                | 331 362*<br>371 417(S)               | 240 252*<br>263 283<br>300 307(S)         | 300(S)<br>337 363*<br>377(S)<br>439(S)    | 241* 252<br>280 300<br>300 304            | 335 360*<br>370 426(S)               | 241* 252<br>282 302                       | 335 360*<br>370<br>419(S)              | 241* 252<br>278 280<br>303                | 333 360*<br>370 419(S)               |
| 3. Pyrene                     | 240 252<br>262 270<br>312 320<br>333*     | 374 381<br>390*                      | 240 250*<br>262(S)<br>270 308<br>314 323  | 354 374*<br>380(S)<br>395(S)              | 241 252<br>262 270<br>306 318<br>354*     | 376 382<br>392*                      | 241 252<br>261 272<br>318 334*            | 374 383<br>393*                        | 241 252<br>260 270<br>312 318<br>334*     | 375 382<br>392*                      |
| 4. Chrysene                   | 258 267*<br>296 304                       | 340 361<br>366(S)<br>382* 397<br>424 | 257 266*<br>298 306                       | 359<br>360(S)<br>382*<br>402(S)<br>426(S) | 260 268*<br>294 306                       | 340 362<br>369(S)<br>381* 399<br>426 | 260 277*<br>305 319                       | 340 362<br>369(S)<br>380 402<br>426(S) | 260 268*<br>298 306                       | 340 362<br>367(S)<br>380* 399<br>426 |
| 5. Benzo[a]pyrenes            | 204 252<br>266 286<br>293 345<br>364 385* | 401*<br>405(S)<br>423 450(S)         | 242 262*<br>288 344<br>362 376<br>384 400 | 402* 428<br>455                           | 240 251<br>266 284<br>294 345<br>360 384* | 402*<br>407(S)<br>424 452(S)         | 251 262<br>285 295<br>330 348<br>364 386* | 402*<br>407(S)<br>424 450              | 240 251<br>264 284<br>295 345<br>364 386* | 402*<br>405(S)<br>424 452(S)         |
| 6. Perylene                   | 365 382<br>407* 487                       | 434* 462<br>533(S)                   | 365 382<br>406* 428<br>433                | 432* 460<br>498<br>535(S)                 | 406* 437<br>487                           | 434* 469<br>533(S)                   | 366 386<br>409* 435                       | 435* 464<br>492<br>535(S)              | 366 384<br>409* 487                       | 434* 464<br>533(S)                   |
| 7. Dibenzo[a,h]<br>anthracene | 277* 286<br>293                           | 393 411*<br>441(S)                   | 277* 286<br>296 322<br>330 350(S)         | 380* 408<br>440(S)                        | 276 286*<br>296                           | 393* 410<br>440                      | 275 286*<br>296                           | 395* 412<br>440(S)                     | 276 286*<br>294                           | 395 412*<br>440(S)                   |

\* most intense peak

(S) shoulder

TABLE 3

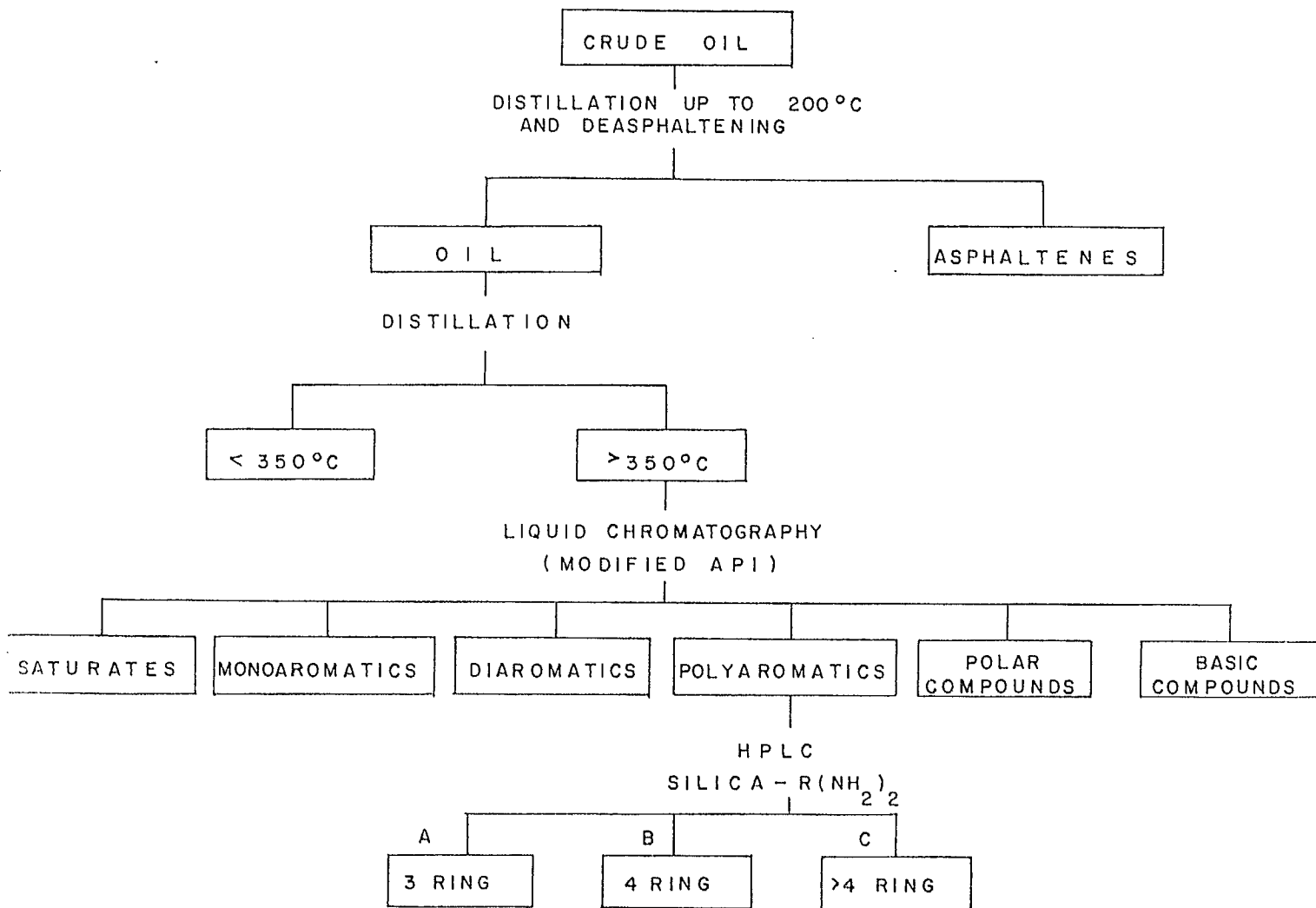
Quantitative Distribution of Aromatic Ring Classes Using Refractive Index Detector  
(wt % of the total PAH fraction in deasphalted residue boiling above 350°C)

|  | Athabasca | Cold Lake                | Lloydminster | Medicine River | Processed Athabasca |
|--|-----------|--------------------------|--------------|----------------|---------------------|
| 3-ring   | 37        | 40                       | 48           | 49             | 52                  |
| 4-ring   | 21        | 23                       | 23           | 25             | 27                  |
| >4-ring  | 25        | 21                       | 19           | 15             | 13                  |
| retained on column                                     | 17        | 16                       | 10           | 11             | 8                   |
| Model compounds used to determine calibration factors: |           |                          |              |                |                     |
| 3-ring   | -         | phenanthrene, anthracene |              |                |                     |
| 4-ring   | -         | pyrene, chrysene         |              |                |                     |
| >4-ring  | -         | dibenzo[a,c]anthracene   |              |                |                     |

TABLE 4

Elemental and  $^{13}\text{C}$  n.m.r. Analysis of PAH Concentrates

|  | Athabasca | Cold Lake | Lloydminster | Medicine River | Processed Athabasca |
|--|-----------|-----------|--------------|----------------|---------------------|
| <u>Elemental Analysis (wt %)</u>             |           |           |              |                |                     |
| C  | 82.01     | 83.18     | 82.52        | 87.31          | 86.29               |
| H  | 9.47      | 9.29      | 9.16         | 8.92           | 7.32                |
| C/H  | 8.65      | 8.95      | 9.0          | 9.8            | 11.80               |
| <u><math>^{13}\text{C}</math> NMR (wt %)</u> |           |           |              |                |                     |
| Aromatic C                                   | 42.03     | 48.56     | 40.91        | 60.53          | 71.83               |
| Aliphatic C                                  | 57.97     | 51.44     | 59.09        | 39.42          | 28.17               |
| Aromatic/Aliphatic                           | 0.73      | 0.94      | 0.69         | 1.53           | 2.54                |



- SPECTROFLUORESCENCE CHARACTERIZATION OF A, B AND C.

- GC - MS IDENTIFICATION OF A, B.

FIGURE 1: Separation and Characterization Schematic

A - Athabasca Polynuclear Aromatic Hydrocarbon Fraction

B - Cold Lake Polynuclear Aromatic Hydrocarbon Fraction

C - Lloydminster Polynuclear Aromatic Hydrocarbon Fraction

D - Medicine River Polynuclear Aromatic Hydrocarbon Fraction (Simulated Maturation)

E - Athabasca Polynuclear Aromatic Hydrocarbon Fraction

F - Mixture of PAH Standards

- 1: naphthalene; 2: anthracene;
- 3: phenanthrene; 4: pyrene;
- 5: benzo[b]fluorene;
- 6: benzo[a]anthracene;
- 7: chrysene; 8: benzo[a]pyrene;
- 9: perylene; 10: anthanthrene;
- 11: benzo[ghi]perylene

ABSORBANCE (254 NM)

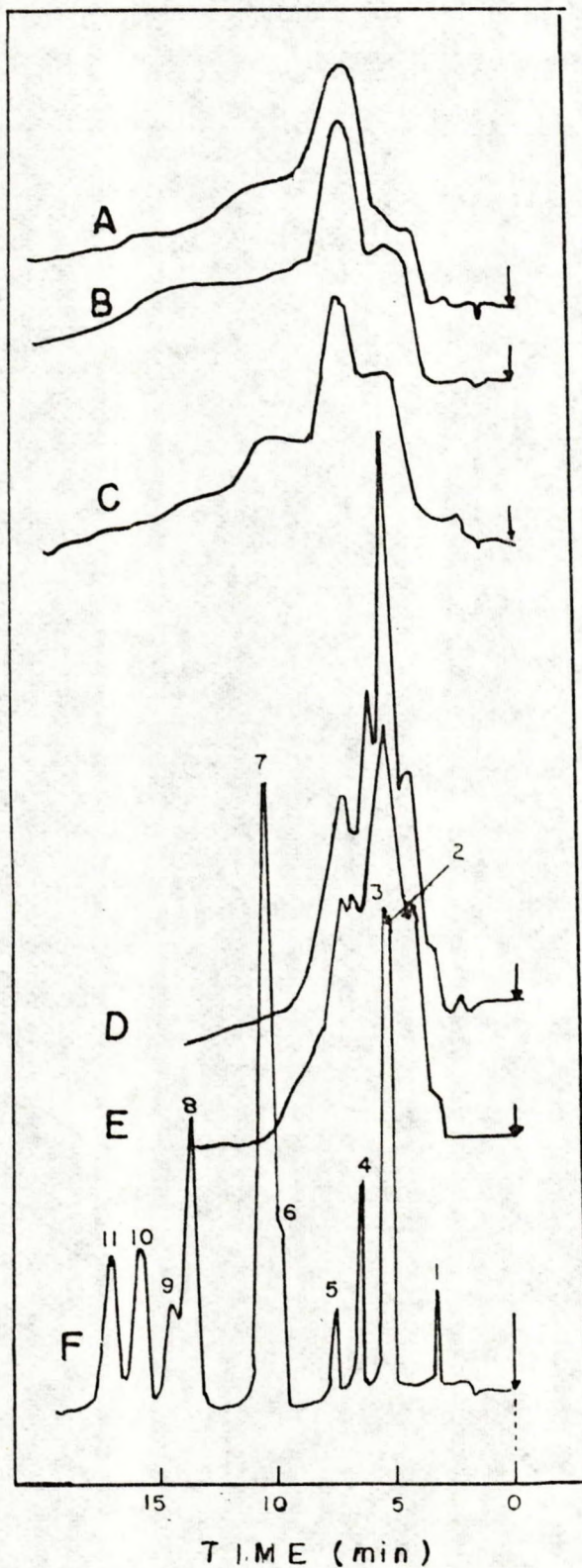


FIGURE 2: Chromatograms Obtained on the Silica-Diamine Column with Mobile Phase of Methylene Chloride-Hexane (4:96)