Analysis of Polycyclic Aromatic Hydrocarbon Derivatives by On-Line Coupled Packed-Capillary High-Performance Liquid Chromatography–High-Temperature Gas Chromatography

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Abstract

A packed-capillary high-performance liquid chromatograph (μ-HPLC) is coupled on-line to a high-temperature capillary gas chromatograph (HTGC) through a multiloop, nonsplit, in-column interface. Polycyclic aromatics and aliphatics of oils of residuum and extracts of residue in the petrochemical industry are analyzed using μ-HPLC–HTGC. Quantitative results are obtained and discussed with respect to frame structure and carbon number distribution.

Introduction

Polycyclic aromatic hydrocarbon (PAH) derivatives present in the oils of extracts of residue and oils of residuum in the petrochemical industry are a class of compounds that can be further utilized to produce high-profit products. Investigation of the content of the PAH derivatives according to their frame structure and carbon number distribution is vitally important for their utilization. The PAHs are also widely distributed in the environment and are toxic and potential carcinogens. Determination of their levels and ring structure is necessary for environmental protection.

Analysis of these compounds requires 2 chromatographic stages. Liquid chromatography (LC) is used to separate the sample on the basis of chemical class; thus, fractions containing aliphatics, aromatics of different ring structure, and polars can be obtained. HPLC in normal-phase mode (1–4) using silica or amino-bonded phases is used to provide class separation. The collected fractions are then further analyzed using capillary gas chromatography (GC) with mass spectrometric detection (1,5,6).

On-line coupled microbore LC–GC (2–9) allows the fractions from the LC separation to be introduced into the capillary GC column, improving the sensitivity, reproducibility, and detection limits. However, early solvent exit has been employed in most cases because of the rather large injection volume produced by microbore LC. This will affect the accuracy of the quantitation of light compounds and the reproducibility of the analysis. The flow rate of packed capillary HPLC (μ-HPLC) is in the range of a few microliters per minute (10), resulting

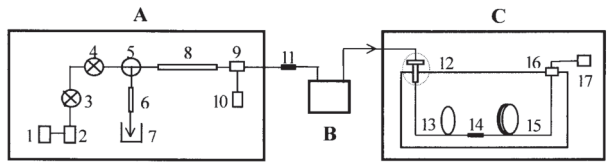

Figure 1. Schematic diagram of μ-HPLC–HTGC: μ-HPLC (A), interface (B), and HTGC (C). 1, solvent reservoir; 2, pump; 3, gradient valve; 4, injector valve; 5, three way split; 6, split resistor; 7, waste collector; 8, μ-HPLC analytical column; 9, UV detector; 10, LC recorder; 11, micro-connector; 12, GC injector; 13, retention gap; 14, butt connector; 15, GC analytical column; 16, FID detector; 17, GC recorder.

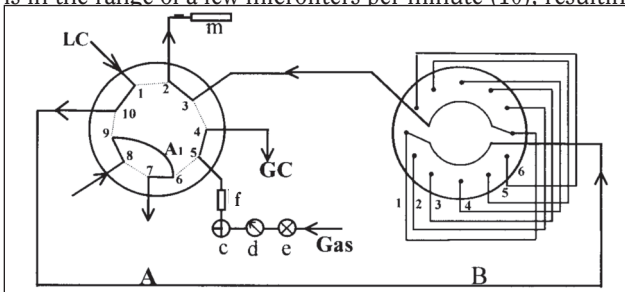

Figure 2. The structure of the multiloop interface. Valve A (10-port valve): 1, from LC; 2, to microflow meter; 3, from valve B; 4, to GC; 5, auxiliary gas for injection; 7, outlet of wash solvent; 8, inlet of wash solvent; f, filter; c, switch valve; d, pressure gauge; e, flow control valve; m, microflow meter. Valve B is a multiposition multiloop valve. There are six loops for collecting LC fractions. The volumes of the loops are 25 μL for the wash loop on valve A (between ports 6 and 9), 60 μL for loop 1, and 30 μL for loops 2–6 on valve B.

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Table I. Standards of Aromatics Used in This Study

Code	Name	*m* + *n**
1	Benzene	C_6
2	1,4-Dimethylbenzene	C_{6+2}
3	1,2,4,5-Tetramethylbenzene	C_{6+4}
4	Naphthalene	C_{10}
5	2,3-Dimethylnaphthalene	C_{10+2}
6	Acenaphthylene	C_{10+2}
7	Acenaphthene	C_{10+2}
8	Diphenyl	C_{12}
9	Fluorene	C_{13}
10	Anthracene	C_{14}
11	Phenanthrene	C_{14}
12	9,10-Dimethylanthracene	C_{14+2}
13	Pyrene	C_{16}
14	Fluoranthene	C_{16}
15	*p*-Terphenyl	C_{18}
16	7,12-Dimethyl benzo[*a*]anthracene	C_{18+2}
17	Chrysene	C_{18}
18	Benzo[*a*]anthracene	C_{18}
19	Triphylene	C_{18}
20	3-Methylcholanthrene	C_{18+3}
21	Benzo[*e*]pyrene	C_{20}
22	Benzo[*b*]fluoranthene	C_{20}
23	Dibenzo[*a*,*h*]anthracene	C_{22}

* *m*, carbon number on the ring; *n*, carbon number of substituted hydrocarbons.

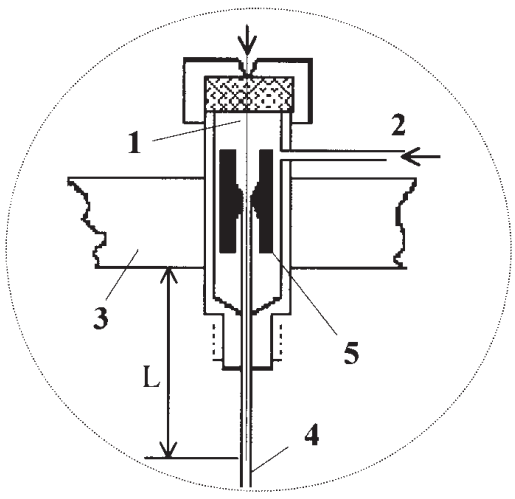

Figure 3. The structure of the GC injector. 1, silica capillary tubing from interface; 2, carrier gas; 3, oven wall; 4, retention gap; 5, liner. *L* is the distance between the oven wall and the location of injection, and it is set at 10 cm.

Table II. Carbon Number Distribution of Aliphatics and Tri- and Tetra-Nuclear Aromatics of Sample A1 (% Weight)*

Carbon number	Fraction 1st	3rd	4th⁄	5th"
C_{13}	0.07	–	–	–
C_{14}	0.17	0.62	–	–
C_{15}	0.19	1.61	–	–
C_{16}	0.19	3.90	0.35	–
C_{17}	0.23	5.94	1.91	–
C_{18}	0.30	9.39	6.96	3.12
C_{19}	0.38	15.03	15.03	12.40
C_{20}	0.52	19.76	22.53	21.04
C_{21}	0.71	15.13	20.99	20.89
C_{22}	0.97	11.88	14.78	17.13
C_{23}	1.45	7.44	9.73	13.26
C_{24}	1.96	4.67	4.75	7.71
C_{25}	2.70	2.45	2.06	3.03
C_{26}	3.65	1.43	0.71	1.10
C_{27}	5.96	0.54	0.2	0.63
C_{28}	7.94	0.22	–	–
C_{29}	11.35			
C_{30}	11.38			
C_{31}	8.32			
C_{32}	10.89			
C_{33}	5.9			
C_{34}	4.35			
C_{35}	3.95			
C_{36}	3.98			
C_{37}	3.17			
C_{38}	2.19			
C_{39}	1.71			
C_{40}	1.35			
C_{41}	1.06			
C_{42}	0.78			
C_{43}	0.69			
C_{44}	0.47			
C_{45}	0.34			
C_{46}	0.34			
C_{47}	0.21			
C_{48}	0.14			
C_{49}	0.04			

* The integer in the first row indicates the fraction number.
† Aliphatics (solutes).
‡ Tri-nuclear aromatics.
§ Tetra-nuclear aromatics (pyrene, fluoranthene).
" Tetra-nuclear aromatics (chrysene, benzo[*a*]anthracene).

All samples were high-aromatic-content oil from 3 different origins: sample A was oil of residuum, sample B was an extract of distillation residue of diesel fuel, and sample C was an extract of distillation residue of lubricating oil. One gram of sample was dissolved in 40 mL of iso-octane or *n*-hexane, sonicated for 10 min, then allowed to stand overnight. The asphaltene contained in sample A was removed according to the method described by Speight et al. (11) and weighed. The sample solution was evaporated under slow nitrogen at 18°C to concentrate it and then added to *n*-hexane to a final volume of 5 mL. The boiling point of the samples was in the range of 250–550°C.

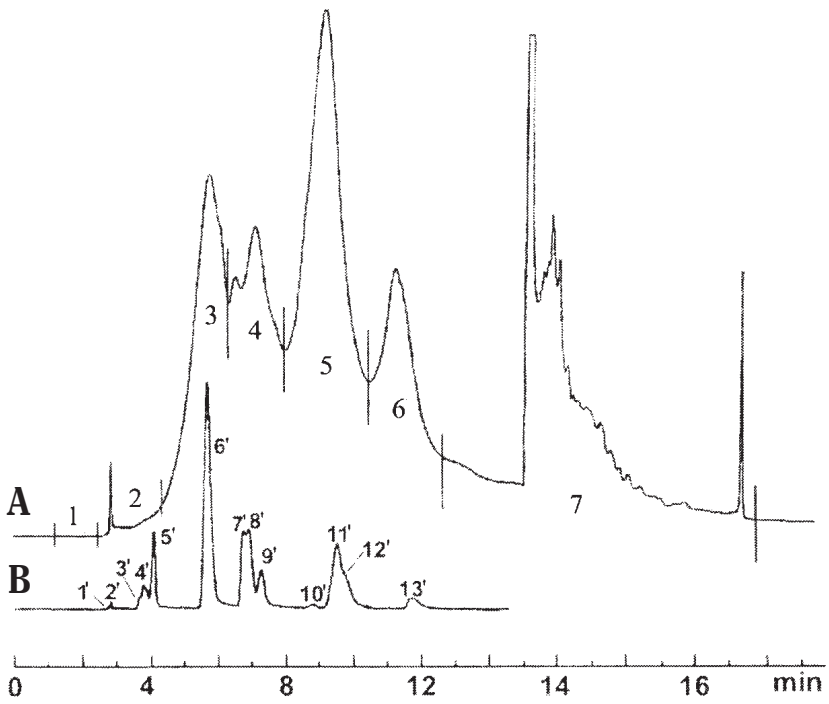

Figure 4. µ-HPLC chromatogram. Sample A1 (A): 1, aliphatics; 2, mono- and binuclear aromatics; 3, tri-nuclear aromatics; 4, tetra-nuclear aromatics of pyrene and fluoranthene (similar frame); 5, tetra-nuclear aromatics of chrysene (similar frame); 6, penta-nuclear aromatics (except pentacene frame); 7, resin. Standard samples (B): 1', 1,2,5-trimethylbenzene; 2', 1,2,4,3-tetramethylbenzene; 3', 2,6-dimethylnaphthalene; 4', naphthalene; 5', biphenyl; 6', phenanthrene, anthracene, and 9,10-dimethylanthracene; 7', pyrene; 8', fluoranthene; 9', *p*-terphenyl; 10', 9,10-dimethylbenz[*a*]anthracene, 11', benzo[*a*]anthracene; 12', chrysene; 13', perylene, benzo[*e*]pyrene, and benzo[*b*]fluoranthene. Conditions: packed-capillary HPLC column (30 cm × 0.32-mm i.d., 5-µm aminobonded phase); mobile phase, *n*-hexane; flow rate, 3.5 µL/min; step gradient, 100% chloroform at *t* = 13 min.

HPLC

A Jasco (Tokyo, Japan) 980 pump was used to deliver 14 µL/min mobile phase to the LC column (Figure 1). The injection volume was 0.5 µL using an internal loop valve (Valco, Houston, TX). The split ratio was 1:3 using a "T" piece and a restrictor after the injection valve. The mobile phase through the column was 3.5 µL/min. To reduce the extra-column volume, a Jasco CE-975 on-column ultraviolet (UV) detector using a wavelength of 254 nm was used to monitor the fractions and locate the time of cutting. A 6-port timer-controlled valve (Valco) with a 500-µL loop filled with chloroform was connected in front of the injection valve to facilitate a step gradient.

A fused-silica capillary column (30 cm × 0.32-mm i.d.) packed with 5-µm Spherisorb NH_2 (Phase Separations, U.K.) was used for the µ-HPLC separation (10), and a 10-cm µ-HPLC column was used as the split restrictor.

The sample was injected into the mobile phase of *n*-hexane under isocratic conditions. At 13 min, the step gradient was started, and the remaining polar compounds and PAHs with ring numbers greater than 5 were coeluted as the last fraction. The pump was stopped at 30 min or after all fractions were transferred to the GC.

Cutting and transfer

Fractions were cut and stored in a multiloop interface and then transferred to the GC using the in-column interface (12) shown in Figure 2. The 10-port cutting valve (valve A) guided the eluent into a

Table III. Contents of Each Fraction (% Weight) of Samples A1 and A2

Sample	Asphaltene	1	2	3	4	5	6	7
A1	4.9	25.0	2.5	9.3	10.6	17.0	11.0	19.7
(RSD, %)*		(0.89)	(1.89)	(1.37)	(1.22)	(1.55)	(1.04)	(1.43)
A2	6.3	25.3	3.4	9.4	10.5	15.2	10.9	19.1

* RSD, relative standard deviation.

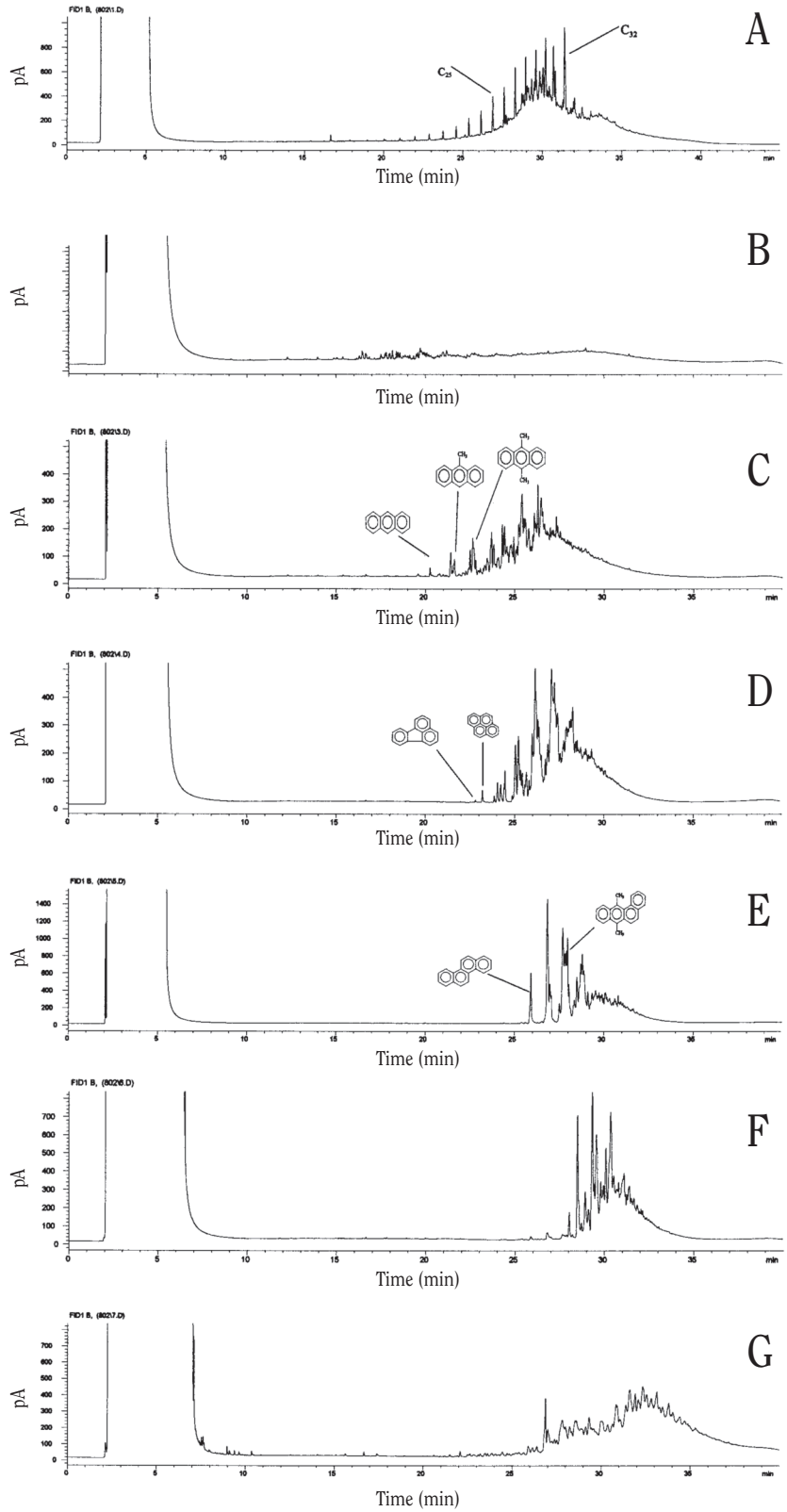

Figure 5. GC chromatograms of LC fractions of sample A1: aliphatics (A), mononuclear and binuclear aromatics (B), tri-nuclear aromatics (C), tetra-nuclear aromatics of pyrene and fluoranthene of similar frame (D), tetra-nuclear aromatics of chrysene and benzo[*a*]anthracene of similar frame (E), penta-nuclear aromatics (except compounds of pentacene structure) (F), and resin (G). Conditions: carrier gas, H_2; constant flow controlled at 8 mL/min; auxiliary gas for injection, H_2; constant flow controlled at 1 mL/min; detector, FID at 380°C.

multiloop, multiposition valve (valve B) for the collection of different fractions. When the pump stopped, valve B was switched to loop 1, and valve A was switched to the dotted line position. The auxiliary carrier gas drove the wash solvent in loop A1 together with the mobile phase remaining in the connection tubing between the two valves, and the stored fraction was driven through the GC injector to the retention gap in the oven. The initial oven temperature was kept at 50°C for 10 min, programmed to 360°C at 10°C/min, and held for 5 min. Valve A was switched back, valve B was switched to loop 2, and the wash loop was filled again for a second transfer.

An HP 6890-Plus GC (Hewlett-Packard, Wilmington, DE) with a cold on-column injector was used. The temperature control of the injector was turned off in the experiments. An uncoated retention gap (20 m × 0.53 mm) was connected to an analytical column (30 m × 0.53 mm) with MXT-1 phase (Restek, Bellelfonte, PA) using a zero-volume butt connector (SGE, Ringwood, Australia). This configuration allowed a maximum of 100 µL of *n*-hexane or iso-octane to be injected without early solvent vapor exit. The initial oven temperature was kept 20°C lower than the boiling point of the solvent until elution from the analytical column. The temperature programming was then started to quantitate the compounds with boiling point values 30°C higher than that of the solvent. Detection was made using a flame ionization detector (FID).

Calibration

The system was calibrated using a range of PAHs (listed in Table I) to determine the location of fraction cutting (t_c) on the LC chromatogram. The delay time (τ) caused by the dead volume (V_d, where $V_d = \tau$/flow rate) between the UV detection point and the entrance of each loop on valve B was measured using naphthalene. The actual cutting time of fraction number i is $t(i) = t_c(i) + \tau(i)$. The FID detector response factors (R_f) were determined using internal standards loaded into the wash loop on valve A, and it was found that they are rather uniform regardless of the ring structure and the chain length. The R_f value of a polar fraction is approximately 0.8 relative to PAHs.

The carbon number range of PAHs was determined using a series of *n*-alkanes and PAHs standards. The method is similar to that used in simulated distillation. The error is less than one carbon number and is acceptable by industry standards.

Results and Discussion

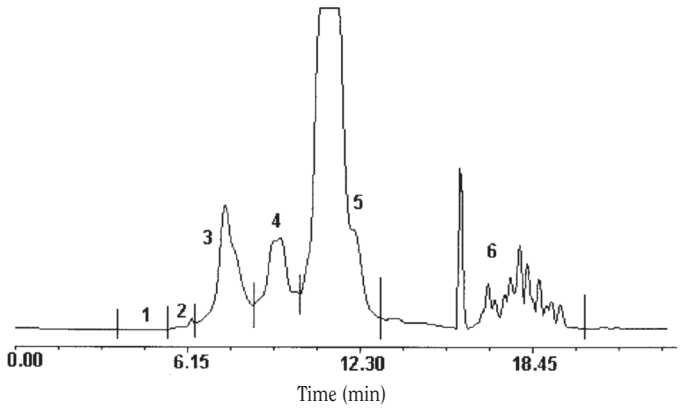

Figure 6. Packed-column HPLC chromatogram of sample B: 1, aliphatics; 2, mononuclear aromatics; 3, binuclear aromatics; 4, aromatics of flourine-like frame; 5, trinuclear aromatics; 6, resin. Conditions were the same as in Figure 4.

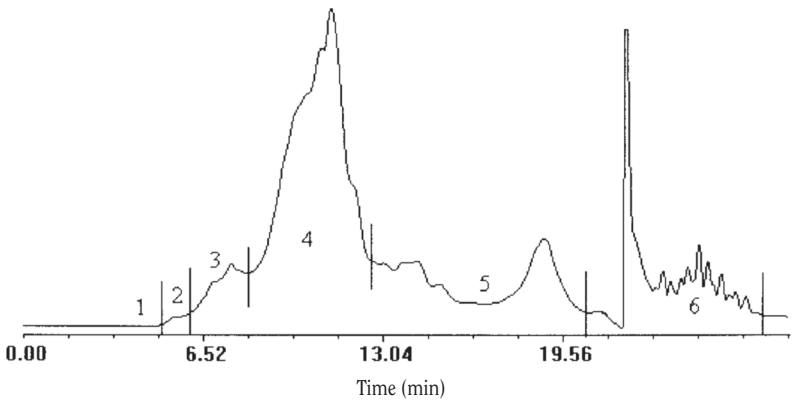

Figure 7. Packed-column HPLC chromatogram of sample C: 1, aliphatics; 2, mononuclear; 3, dinuclear aromatics; 4, trinuclear aromatics; 5, tetranuclear aromatics; 6, resin. Conditions were the same as in Figure 4.

Table IV. Contents of Each Fraction (% Weight) of Samples B and C

Sample	1	2	3	4	5	6
B	7.20	5.10	57.25	7.71	16.12	6.63
		86.17				
C	37.85	10.86	20.44	15.75	6.14	8.97
		53.19				

The purpose of this work was to quantitate and compare the class composition of PAHs and their derivatives in high-aromatic-content oil of residuum and extracts from different process conditions and sources in the petrochemical industry and to develop an automated μ-HPLC–HTGC for their analysis and for the samples from environmental sources.

Because all of the fractions (*n* in total) eluted from μ-HPLC are collected and transferred sequentially into the GC without splitting, quantitation is relatively simple. The content (C) of fraction number i is then $C(i) = \text{Area}(i)/\Sigma\text{Area}(j) \cdot R_f(j)$, where $j = 1 \sim n$, $1 \le i \le n$, and Area(i) is the total peak area of fraction number i.

The samples used in this study contain tens of thousands of compounds yielded from cracking and polymerization processes; therefore, both LC and GC were optimized for separation. The industry requires the identification of the contents of PAHs according to their ring number and the carbon number range of each class to at least 4 ring compounds. Two samples (A1 and A2) of oil of residuum from different sources were analyzed and quantitated. The LC separated the sample into 7 fractions: aliphatics, mononuclear and binuclear aromatics, tri-nuclear aromatics, tetra-nuclear aromatics of pyrene and fluoranthene of similar frame, tetra-nuclear aromatics of chrysene and benzo[*a*]anthracene of similar frame, penta-nuclear aromatics (except compounds of pentacene structure), and resin. Because there were only 6 loops on valve B, the last fraction was collected in loop 1 after the first fraction was transferred into the GC. LC stop flow was applied during this transfer period. Figure 3 shows the LC chromatograms of standards and sample A1, and the vertical lines in the chromatogram mark the time windows of fraction cutting. The GC chromatograms of the 7 fractions are shown in Figure 4. Some of the compounds were identified based on retention data using standards. The 7 chromatograms show the complexity of the sample, even with class separation. The carbon number ranges of aliphatics and tri- and tetra-nuclear aromatics are listed in Table II. Five repeated analyses were performed, and the relative standard deviation of the peak areas was less than 2%. The contents of each fraction of the 2 samples are listed in Table III. The data show that the content of PAHs exceeds 35% for both samples, and that

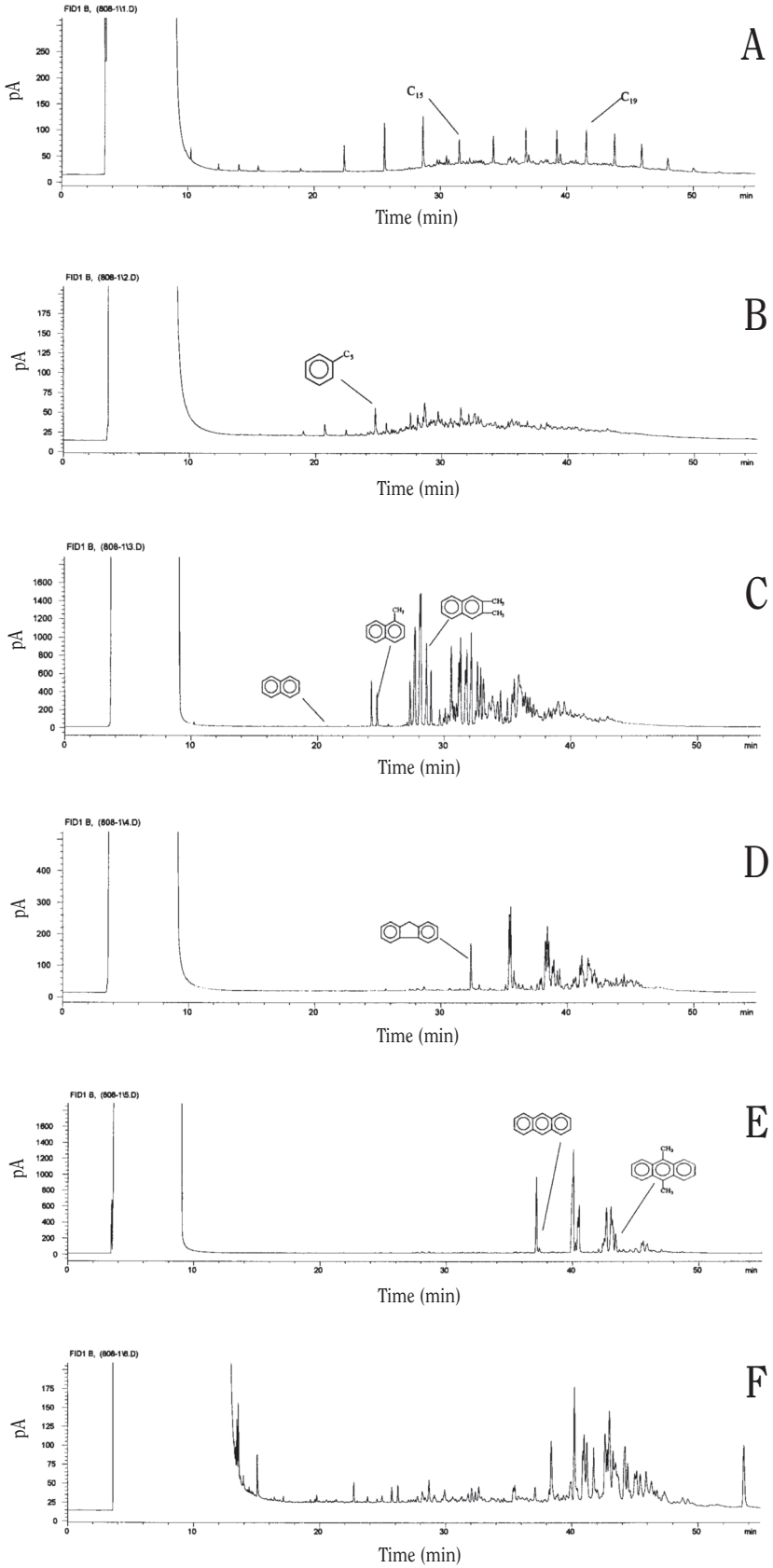

Figure 8. GC chromatograms of transferred fractions of sample B: aliphatics (A), mononuclear aromatics (B), binuclear aromatics (C), aromatics of fluorene-like frame (D), trinuclear aromatics (E), and resin (F). Conditions: oven temperature, 50°C (10 min) to 360°C at 4°C/min, held 5 min; carrier gas, H_2 at 5 mL/min; auxiliary gas for injection, H2 at 0.6 mL/min; detector, FID at 380°C.

meets the basic requirement of needle tar production. It also shows that the content of asphaltine and resin is rather high in the samples, indicating that further treatment of the oil is necessary.

Samples B and C are much lighter than sample A and require separation into 6 fractions. The LC chromatograms of samples B and C are demonstrated in Figures 5 and 6; GC chromatograms of the 6 fractions of the samples are shown in Figures 7 and Figure 8. The results of the analysis are shown in Table IV. The carbon number distributions of aliphatic fractions of samples B and C were determined to be in the range of C12 ~ C23 and C18 ~ C32, respectively. Because of the complexity of sample C, little improvement in the GC separation can be obtained by using higher efficiency or polar phase columns even after the class separation. Nevertheless, the information provided is sufficient for industry uses (i.e., the content of each class, the boiling range and content of each $\Delta_{\text{boiling point}}$ or carbon number distribution of each class, and the paraffin content in aliphatics).

Conclusion

The on-line coupled µ-HPLC–HTGC method proved to be a powerful separation technique for the analysis of PAHs and their derivatives in oil samples from the petrochemical industry and spilled oil in the ocean. The advantages of the technique include the versatility of the multiloop interface, nonsplit on-line interfacing, high-efficiency µ-HPLC, and HTGC.

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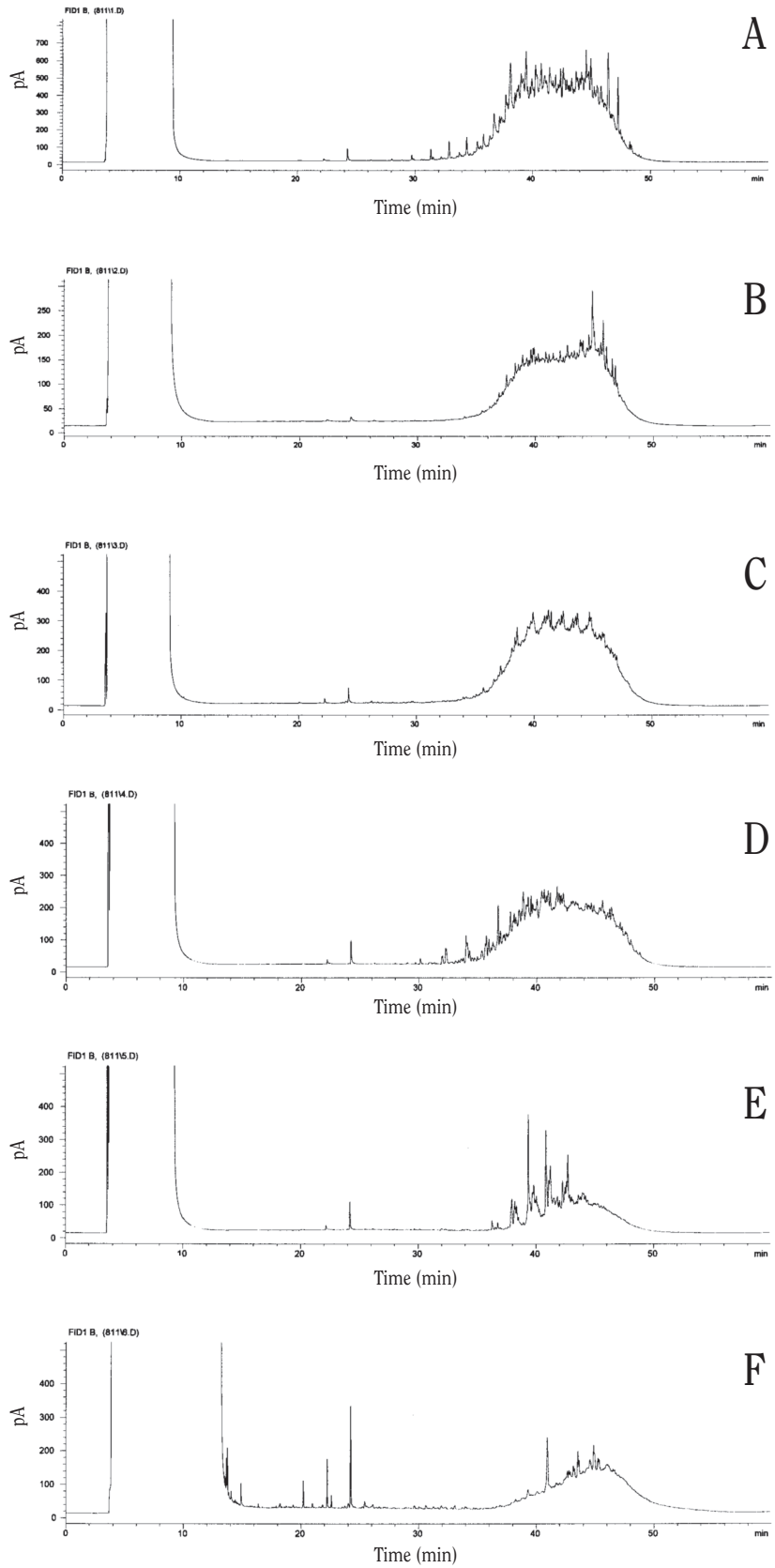

Figure 9. GC chromatograms of transferred fractions of sample C: aliphatics (A), mononuclear aromatics (B), binuclear aromatics (C), trinuclear aromatics (D), tetranuclear aromatics (E), and resin (F). Conditions: oven temperature, 50°C (10 min) to 360°C at 6°C/min, held 5 min; carrier gas, H_2 at 5 mL/min; auxiliary gas for injection, H_2 at 0.6 mL/min; detector, FID at 380°C.

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