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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN LUBRICATING OIL BASE STOCKS USING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

A high-performance liquid chromatography (HPLC) method has been developed for the separation of aromatic compounds from the saturated hydrocarbons in lubricating oil base stocks and the further separation of polycyclic aromatic hydrocarbons (PAHs) into fractions based on the number of fused rings. Aromatic compounds were separated from the saturated hydrocarbons by HPLC using a silica column. The aromatic compounds were then backflushed onto an amine derivatized silica column using a six-port two-position switching valve. The PAHs were separated according to the differing number of fused rings. Further analysis by high-resolution gas chromatography–low-resolution mass spectrometry with a fused-silica DB-5 capillary column showed the presence of various parent and alkylated PAHs in the lubricating oil base stocks and 10W30 oil at the part per billion (10^9) level.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds with structures based on fused benzene rings. PAHs differ in the number and position of the fused rings and may contain heteroatoms such as oxygen, nitrogen and sulfur[1]. There has been an increased interest in the identification and quantitation of PAHs in the environment and fossil fuels because of their carcinogenic properties[2]. PAHs are present in lubricating oils in the part per billion to part per trillion concentration range with the alkylated PAHs present in greater abundance than their unalkylated parent PAHs[3,4].

Lubricating oils are composed of normal paraffin hydrocarbons, isoparaffins, naphthenes, aromatics, and some oxygen and sulfur compounds. They are divided into two base stock types, one naphthenic (aromatic), the other paraffinic (aromatic with a large number of alkyl side groups). The composition of a base stock depends

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on its origin and the extent of refinement. Base oil stocks are blended together to form specific lubricating oils prior to incorporation of additives. Lubricating oils are treated to remove PAHs because they form sludges and acids in car engines[5].

The analysis of fossil fuels for PAHs is difficult because they are composed of mostly hydrocarbons which interfere with the analysis of the PAHs. Many techniques have been developed to solve this problem. An open column technique was used for the separation of aliphatic and aromatic compounds in diesel fuel[6]. Aliphatic hydrocarbons were eluted from a silica gel column using pentane. The aromatic compounds were eluted using benzene and the effluent was concentrated before analysis by gas chromatography (GC) using an ion trap detector. A number of PAHs in the sample were identified but were not separated into fractions based on the number of fused rings.

HPLC has also been used for the separation of PAHs. Wise *et al.*[4] have studied normal-phase and reversed-phase high-performance liquid chromatography (HPLC) columns for the separation of PAHs. They compared the retention characteristics of the μBondapak NH_2 and μBondapak C_{18} columns against literature values for silica and aluminia columns for the separation of PAHs. The μBondapak NH_2 column separated PAHs into compound classes according to the increasing number of fused rings. All PAHs with three fused rings including alkyl substituted derivatives have similar retention on this column, unlike silica columns where addition of alkyl side groups causes them to elute later than their unalkylated parent-PAHs. The μBondapak C_{18} column separated PAHs in a manner similar to silica and alumina columns, but alkyl-substituted PAHs also have increased retention.

Many HPLC techniques have been developed to separate PAHs from the bulk of the aliphatic hydrocarbons. A 4-port 2-position switching valve was used in a study on the separation of components of various petroleum products[7]. Saturated compounds and olefins eluted together from the column, then the flow was reversed (backflush) to elute the aromatic compounds from the column. This resulted in a fast analysis with a sharper peak for the aromatic compounds which without backflush would have eluted as a broad tailing peak. Polar compounds did not elute from the column.

Dark[8] used an NH_2-derivatized silica column with backflush for the separation and quantitation of crude oil. The NH_2 column gave a better separation of the aromatics than the silica column. The backflush was performed after the aromatic compounds were eluted from the column (rather than after elution of the saturated compounds). This gave a good separation of aromatic from polar compounds, but a poor separation of saturated from aromatic compounds.

Davies *et al.*[9] used an automated on-line HPLC–GC technique for the analysis of PAHs in diesel exhaust particulates. An HPLC system was used to separate the aromatic compounds from the alkanes on a silica column. Then, a 10-port valve interface was used to backflush the aromatic compounds onto a GC column through a retention gap after the alkanes had left the system. The aromatics were transferred to the GC column as a single peak and analyzed by GC using flame ionization detection. PAHs were identified in the aromatic fraction but were not resolved according to the number of fused rings.

An on-line HPLC column-switching technique was used for the separation and quantitation of paraffins, olefins, naphthenes and aromatics (PONA) in gasoline and

kerosene products[10]. Two switching valves and five columns were used to isolate the olefins and aromatics from the saturated compounds. Aromatic compounds and olefins were later eluted separately using the switching valves. Separation and identification of the aromatic compounds was not achieved.

Analysis of commercial lubricating oils for PAHs is very difficult. This paper demonstrates the separation of PAHs from the bulk of the aliphatic compounds using a single injection HPLC technique and the identification of PAHs by using GC–mass spectrometry (MS) and retention indices.

EXPERIMENTAL

Glassware, sample and standard preparation

All glassware was washed with detergent using ultrasonic agitation (30 min) and rinsed three times with tap water, twice with distilled water, and dried overnight at 230°C. Glassware was pre-rinsed with organic solvents. All solvents were distilled in glass, UV-grade from Caledon Labs. (Georgetown, Canada). PAH standards were purchased from Aldrich (Montreal, Canada) or Chem Service (West Chester, PA, U.S.A.) and had a minimum purity of 97%. A PAH standard solution was prepared by weighing 20 mg of each of ten PAHs into a 100-ml volumetric flask. The solution was made to volume with hexane and 2–5 ml of dichloromethane. The spiked oil sample was prepared by weighing 1 mg of each of four PAH standards: naphthalene, phenanthrene, chrysene, and picene into a volumetric flask and the flask made to volume with diluted base oil C4. The solution was sonicated (30 min) and then filtered using a disposable filter disk (Zetapor 25 mm, 0.45 μm porosity, Supelco, Bellefonte, PA, U.S.A.). The base oil samples A1, A2, C3, C4 (Imperial Oil) and 10W30 oil (Canadian Tire, API SFC-CC 28-8213-2) were prepared by weighing 50 mg of the oil into a 100-ml volumetric flask, and making to volume with hexane.

Semi-preparative HPLC

HPLC solvents were filtered and degassed using an aspirator vacuum filtering flask. Hexane was dried with molecular sieves (8–12 mesh, activated type 4A, J. T. Baker) for 24 h prior to filtration.

The instrument used in the HPLC fractionation was a Varian 5000 HPLC system with Vista CDS 402 integrator for recording and manipulating data on floppy disk. Samples were injected using an automated Rheodyne injector with a 100-μl injection loop. A six-port two-position switching valve was used for flow reversal. Semi-preparative μPorasil silica (250 mm × 7.8 mm I.D., 10 μm particle size, Waters Assoc., Milford, MA, U.S.A.) and μBondapak amine (250 mm × 7.8 mm I.D., 10 μm particle size, Waters Assoc.) columns were used. A Hewlett-Packard 1037A refractive index (RI) detector was positioned between an ultra-violet (UV) detector and the waste collection valve (Fig. 1). Solvent gradient and flow-rate changes were used as shown in Table I.

Fractions collected from the HPLC were concentrated by rotary evaporation under reduced pressure to near dryness. The contents were transferred to calibrated "Reacti-vials" (Pierce). Flasks were rinsed three times with benzene and their contents transferred to the vials. Samples were reduced in volume to 10 μl using a gentle stream of high-purity nitrogen gas.

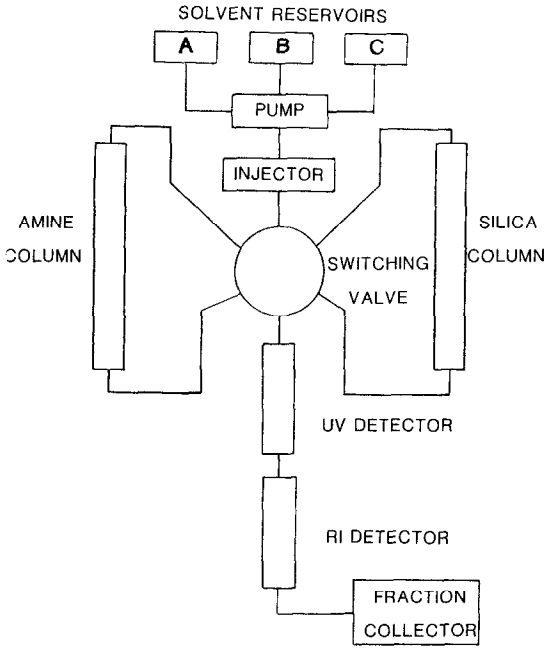

Fig. 1. HPLC block diagram.

TABLE I

SOLVENT GRADIENT AND FLOW-RATES USED IN HPLC FRACTIONATION OF THE OILS

HEX = hexane, DCM = dichloromethane, ACN = acetonitrile.

Time (min)	*Solvent*	*Flow-rate (ml/min)*
0	100% HEX	1
13.5	100% HEX	1
14.0	100% HEX	2.5
35.0	100% HEX	2.5
40.0	50% HEX	2.5
	50% DCM	
45.0	100% DCM	2.5
45.5	95% DCM	2.5
	5% ACN	
46.0	90% DCM	2.5
	10% ACN	
51.0	90% DCM	2.5
	10% ACN	
51.5	95% DCM	2.5
	5% ACN	
52.0	100% DCM	2.5
55.0	50% DCM	2.5
	50% HEX	
58.0	100% HEX	2.5
64.5	100% HEX	2.5
65.0	100% HEX	1.0

GC analysis

Initial fraction analysis was performed on a Hewlett-Packard 5880A GC system using cool on-column injector, flame ionization detector and DB-5 fused-silica capillary column (30 m × 0.32 mm I.D., J&W Scientific, Rancho Cordova, CA, U.S.A.).

GC–MS analysis

A Hewlett-Packard 5987A GC–MS system in the positive ion, electron impact (EI) ionization and linear scanning (50–500 a.m.u.) modes was used for analysis of the HPLC fractions. The system consisted of a 5880A gas chromatograph, 5987A mass spectrometer, HP 1000 data system, cool on-column injector and a DB-5 fused-silica capillary column (30 m × 0.32 mm I.D.). Temperature programming for GC and GC–MS consisted of an initial temperature of 80°C held for 1 min and ramped up at 3.5°C/min to 300°C and held for 10 min. The GC–MS computer system contained a mass spectral library searching system based on Probability Based Matching (PBM) and a reference file of 70 000 EI spectra for the identification of unknowns.

Compound identification was performed by using the PBM search system on the EI mass spectrum and the PAHs retention index system developed by Lee and Vassilaros[11] and Vassilaros *et al.*[12]. A retention window of ±0.2 retention index units was used for provisional identification of PAHs. Positive isomer identification could not be done without standards. Where more than one isomer could be the correct compound, all were listed in the table.

RESULTS AND DISCUSSION

Determination of backflush time

Aromatic compounds were separated from the saturated hydrocarbons in base oil C4 by HPLC using a μPorasil silica column and hexane. The flow-rate was varied until baseline separation of saturated and aromatic compounds was achieved. The optimum flow-rate was found to be 1 ml/min, and the separation was monitored on UV and RI detectors as shown in Fig. 2. An RI detector was used to monitor the separation of aromatic from saturated compounds because both show a response on the RI detector. Only the aromatic compounds show a response on the UV detector.

A silica column was used to separate the aromatic from the saturated compounds, but further resolution of the aromatics from each other using this column was poor. After the aromatics were separated from the saturated hydrocarbons, they were backflushed as a narrow plug onto the μBondapak amine column (using a six-port two-position switching valve) where they were separated according to the differing number of fused rings. The optimum backflush time was found to be 13.3 min. Once the backflush time was determined, the RI detector was removed from the HPLC set-up.

Optimization of HPLC separation of PAHs

Solvent gradient and flow-rate changes were used to further improve and speed up the separation of the PAHs. The components of the PAH standard solution were separated on the HPLC system using the solvent gradient and fractions were collected according to the UV detector signal in Fig. 3. The valleys in the HPLC–UV chromatogram were used as rough fraction cut points.

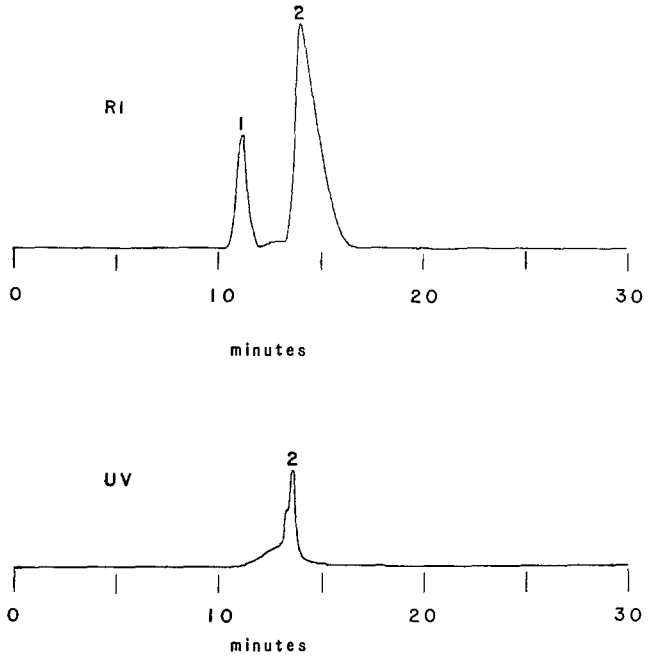

Fig. 2. HPLC separation of aromatic compounds (2) from saturated hydrocarbons (1) using a μPorasil silica column (250 mm × 7.8 mm I.D.) with hexane at 1 ml/min. Separation was monitored on RI and UV (254 nm) detectors.

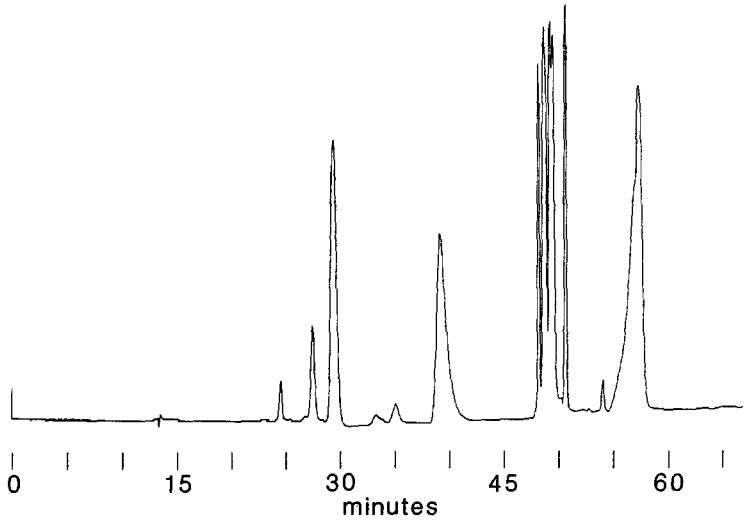

Fig. 3. HPLC–UV chromatogram. Separation of components of the PAH standard solution using the μPorasil silica column (250 mm × 7.8 mm I.D.), backflush, μBondapak amine column (250 mm × 7.8 mm I.D.) and solvent gradient.

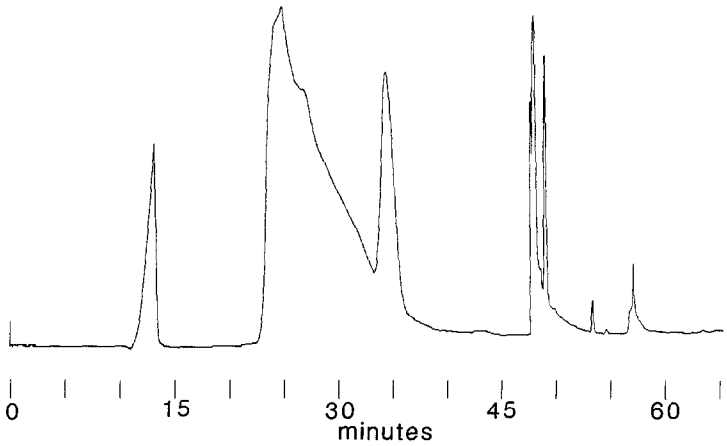

Fig. 4. HPLC–UV chromatogram. Separation of spiked base oil sample using the μPorasil silica column (250 mm × 7.8 I.D.), backflush, μBondapak amine column (250 mm × 7.8 mm I.D.) and solvent gradient.

TABLE II

PROVISIONALLY IDENTIFIED COMPOUNDS FOUND IN FRACTION TWO OF BASE OIL A1 BY USING GC–MS AND RETENTION INDICES

See Fig. 5.

Peak No.	*Compound*[a]	*Retention index*	*MW*
1	Dibenzothiophene	295.4	184
2	Phenanthrene	300.0	178
3	C2-Fluorene	308.3	194
4a	Methyldibenzothiophene/methylnaphthothiophene	312.2	198
4b	8-Methylnaphtho[1,2-*b*]thiophene	315.8	198
4c	1-Methyldibenzothiopene/ 6-methylnaphtho[1,2-*b*]thiophene	319.6	198
5	4-Methylphenanthrene/1-methylanthracene	323.3	192
6a	4,6-Dimethyldibenzothiopene	329.2	212
6b	C2-Dibenzothiophene/naphtothiophene	332.2	212
6c	2,8-Dimethyldibenzothiopene/ 3,7-dimethyldibenzothiopene	335.8	212
6d	C2-Dibenzothiophene/naphthothiophene	338.4	212
7a	C2-Phenanthrene/anthracene	341.5	206
7b	C2-Phenanthrene/anthracene	342.6	206
7c	C2-Phenanthrene/anthracene	344.6	206
8a	C3-Dibenzothiophene/naphthothiophene	346.5	226
8b	C3-Dibenzothiophene/naphthothiophene	348.9	226
8c	C3-Dibenzothiophene/naphthothiophene	350.2	226
8d	C3-Dibenzothiophene/naphthothiophene	351.4	226
8e	C3-Dibenzothiophene/naphthothiophene	354.6	226
8f	C3-Dibenzothiophene/naphthothiophene	356.7	226
9	C3-Phenanthrene/anthracene	359.5	220
10a	C4-Dibenzothiophene/naphthothiophene	361.9	240
10b	C4-Dibenzothiophene/naphthothiophene	366.6	240
10c	C4-Dibenzothiophene/naphthothiophene	368.6	240
10d	C4-Dibenzothiophene/naphthothiophene	370.5	240
10e	C4-Dibenzothiophene/naphthothiophene	374.9	240
10f	C4-Dibenzothiophene/naphthothiophene	377.1	240

[a] - / represents possible isomers.

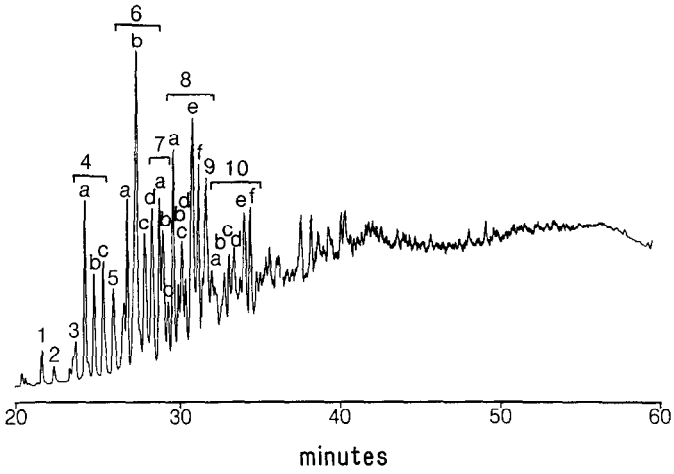

Fig. 5. GC-FID chromatogram. Separation of fraction 2 of base oil A1 on a DB-5 (30 m × 0.32 mm I.D.) column using the temperature programme from 80°C hold 1 min to 300°C at 3.5°C/min hold 10 min.

Base oil C4 was spiked with four PAHs: naphthalene, phenanthrene, chrysene, and picene, representing 2 to 5 fused ring PAHs, respectively. The sample fractions were collected according to the UV trace (Fig. 4) and the rough fraction cut times determined using the PAH standard. The final fraction cut times obtained were 20–30.5, 40, 50, and 65 min.

Analysis of the base oils

A series of four base oils samples (A1, A2, C3 and C4) were separated on the HPLC system and fractions were collected using the optimized HPLC parameters. The aromatic composition of the four base oils was seen to be different according to

TABLE III

PROVISIONALLY IDENTIFIED COMPOUNDS FOUND IN FRACTION 3 OF BASE OILS A1, A2 AND 10W30 OIL USING GC–MS AND RETENTION INDICES

Compound[a]	*Retention index*			
	A1	*A2*	*10W30*	*MW*
2-/3-/8-Methylbenzo[*b*]naphtho[2,1-*d*]thiopene			407.6	248
2-/3-/8-/9-Methylbenzo[*b*]naphtho[2,1-d]thiopene	407.7			248
C2-Benzonaphthothiophene			424.9	262
C2-Benzonaphthothiophene	427.0			262
C3-Benzonaphthothiophene			441.2	276
C3-Benzonaphthothiophene		442.1		276
C3-Benzonaphthothiophene	443.2			276
C3-Benzonaphthothiophene	446.3			276
C3-Benzonaphthothiophene		451.3		276
C4-Benzonaphthothiophene	456.4			290
C4-Benzonaphthothiophene	464.5			290

[a] - / represents possible isomers.

their UV traces. Base oils A1 and A2 appeared to have greater proportion of PAHs than C3 and C4, assuming similar UV response.

Base oil A1 was separated by HPLC and the fractions were collected. GC–MS analysis of fractions 1 and 4 of base oil stock A1 showed an absence of PAHs. Fraction 2 of base oil A1 contained 27 PAHs having three fused rings including a C2-fluorene, dibenzothiophene, alkylated dibenzothiophenes/naphthothiophenes, phenanthrene and alkylated phenanthrenes/anthracenes (Table II, Fig. 5). Six alkylated benzonaphthothiophenes (four fused rings) were found in fraction 3 (Table III). Eleven PAHs having three fused rings were found in fraction 2 of base oil A2, similar to those in fraction 2 of base oil A1 (Table IV). Two alkylated dibenzonaphthothio-

TABLE IV

PROVISIONALLY IDENTIFIED COMPOUNDS FOUND IN FRACTION 2 BASE OIL A2 AND 10W30 OIL USING GC–MS AND RETENTION INDICES

Compound[a]	*Retention index*		
	A2	*10W30*	*MW*
1-Methylfluorene		288.8	180
4-Methyldibenzothiophene	312.7	312.6	198
2-Methyldibenzothiophene/3-methyldibenzothiophene	316.2		198
3-Methylphenanthrene	319.6		192
2-Methylphenanthrene		320.1	192
1-Methylphenanthrene		324.0	192
3-Ethyldibenzothiophene	328.5		212
C2-Dibenzothiophene/naphthothiophene		329.4	212
3,6-Dimethyldibenzothiophene/2-ethyldibenzothiopene	332.8		212
Methoxyanthracene		334.5	208
3,8-Dimethyldibenzothiophene	336.1		212
C2-Dibenzothiophene/naphthothiophene	338.4		212
C2-Phenanthrene/anthracene		339.5	206
C2-Phenanthrene/anthracene	342.0		206
C2-Phenanthrene/anthracene		342.5	206
C2-Phenanthrene/anthracene		343.0	206
C2-Phenanthrene/anthracene		343.8	206
C2-Phenanthrene/anthracene		345.0	206
C3-Dibenzothiophene/naphthothiophene	346.9	347.0	226
C3-Dibenzothiophene/naphthothiophene	349.7		226
C3-Dibenzothiophene/naphthothiophene		350.0	226
C3-Dibenzothiophene/naphthothiophene	354.3		226
C3-Phenanthrene/anthracene		359.0	220
C3-Phenanthrene/anthracene		361.9	220
C4-Phenanthrene/anthracene		377.1	234
C4-Phenanthrene/anthracene		380.5	234
9,10-Dimethyl-3-ethylphenanthrene		381.7	234
Unidentified		465.2	231
Unidentified		474.3	231
Unidentified		481.6	231
Unidentified		485.4	231
Unidentified		494.4	231

[a] - / represents possible isomers.

phenes (four fused rings) were found in fraction 3 (Table III). Again, no PAHs were found in fraction 1 or 4 and no PAHs were found in either base oil C1 or C4.

Analysis of 10W30 oil

A commercial 10W30 oil was analyzed in the same manner as the lubricating oil base stocks. No PAHs were found in fractions 1 and 4 of the sample. Fraction 2 contained 18 PAHs including methylfluorene, alkylated dibenzothiophenes/naphthothiophenes, alkylated phenanthrenes/anthracenes, a methoxyanthracene, and five unidentified compounds with molecular weight 231 (Table IV). Three alkylated benzonaphthothiophenes were found in fraction 3 (Table III).

CONCLUSION

Baseline separation of saturated and aromatic compounds in the lubricating oil base stocks was achieved by using an HPLC system equipped with a silica column. PAHs in the aromatic fraction were subsequently separated into fractions based on the increasing number of fused rings using an amine derivatized silica column. To perform both separations, an HPLC method was developed using a single injection analysis, two semi-preparative HPLC columns, a six-port two-position switching valve and a solvent gradient. The separation can be completed in 65 min. This HPLC system can also be automated for the rapid and routine analysis of oils.

The separation of PAHs into compound class fractions according to the increasing number of fused rings was demonstrated using the spiked base oil sample. Base oil analyses demonstrated the effectiveness of the method since fraction 2 of the oils A1, A2 and 10W30 contained only PAHs having three fused rings, while fraction 3 of these oils contained PAHs having four used rings. In total, 67 PAHs were provisionally identified at low-ppb concentrations in the oil samples A1, A2 and 10W30 by using GC–MS analysis with PBM library search and the use of retention indices. No PAHs were found in base oils C3 and C4. This result correlates with the low signal strength observed in their UV traces when compared with base oils A1 and A2.

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