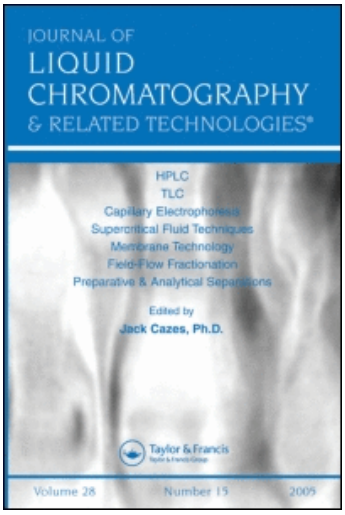

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HYDROCARBON TYPE SEPARATION OF LUBRICATING BASE OIL IN MULTIGRAM QUANTITY BY PREPARATIVE HPLC

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ABSTRACT

A preparative High Pressure Liquid Chromatography (HPLC) method has been developed to separate lubricating base oil into its three major hydrocarbon fractions: saturates, aromatics, and polars. The results are directly comparable to ASTM Method D2007, hydrocarbon type analysis by gradient elution liquid chromatography. The new method employs a preparative HPLC unit with dual, radially compressed columns consisting of clay and alumina/silica gel columns. Multigram quantities of minor components (1 to 2% by wt.) of a base oil can be isolated for further study.

INTRODUCTION

Under American Petroleum Research Project No. 6 (1) many chromatographic methods were developed including liquid-solid, liquid-liquid, and gas-liquid chromatography for hydrocarbon type separation (2). The effects of adsorbent activity and different solvent elution schemes on separation of petroleum fractions are discussed in detail by Snyder et al. (3,4). A general solvent scheme for gradient elution adsorption chromatography such as pentane/toluene/methanol is used to isolate the paraffin, cycloparaffin, aromatic, and polar fractions in lubricating base oil.

Under API Project 60 (5,6,7,8) various adsorption chromatographic methods were developed for the high boiling petroleum distillate,

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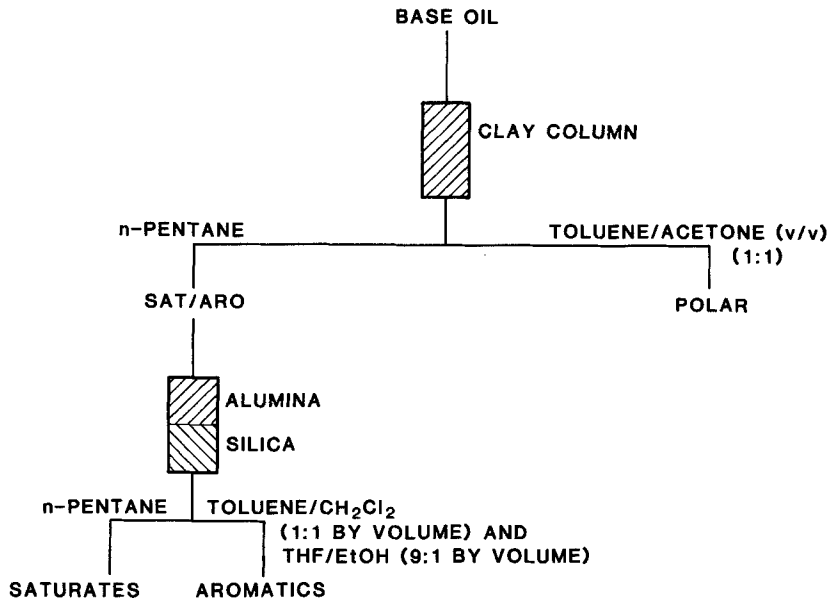
using silica gel and/or alumina adsorbents. The chromatographic methods developed for high boiling distillate are usually open-column chromatography with step gradient elution. The main difficulty has been the amount of time required to complete a separation (as much as 50 hours of continuous operation). The success of such methods is also critically dependent on column dimensions, adsorbent activity, sample loading capacity, and the volume and flow rate of the solvent eluent.

In 1976, the Energy Policy and Conservation Act 142 (U.S.C. 6363 (c); PL 94-163, section 383C) required the National Bureau of Standards to develop test procedures for the determination of substantial equivalency of re-refined or otherwise processed used oil with new oil. One of the tasks is to isolate and identify the possible "contaminants/impurities" present in the re-refined base oils. The possible contaminants may include sulfur from sulfurized cutting oils, oxidized products for the previous oxidation or other additives. It is essential to isolate these "Polar" compounds from re-refined base oils in multigram quantitites in order to assess their effect on performance.

Separation in this laboratory of 4 liters of a medium viscosity (250 N) base oil on a 6-foot-long and 2-inch-diameter preparative LC column packed with 2 kg of alumina yielded multigram quantities of polar compounds which proved to have a significant impact on oil stability (9). However, the scheme required four weeks for separation, raising the posibility of oxidative degradation of the isolated fractions. A faster preparative liquid chromatographic method for isolating multigram quantities of polar constituents in a base oil is needed.

With the advent of High Performance Liquid Chromatography (HPLC), the time-consuming aspect of the open column chromatography has been reduced (10). At present, HPLC methods, either analytical or preparative, generally have limited sample loading capacities in the range of one gram or less (11,12,13,14, 15,16). The amount of polar fraction separated from a run will be in the milligram range, which is not sufficient for performance testing. Therefore,



1. Separation scheme of the preparative HPLC method.

an effort was initiated to develop a rapid multigram chromatographic method for the isolation of "active" species in lubricating base oils in sufficient quantities for performance testing. In this respect, mass balance becomes a critical factor and the criteria for such a preparative chromatographic method must include rapid separation, multigram quantity yield of minor components, good resolution, and good mass balance. The separation method developed in this study satisfies these criteria.

The separation scheme for the method is shown in Figure 1. The process is divided into two steps: (a) the polar fraction is separated from the base oil on an attapulgus clay column, generating a polar fraction and a saturate/aromatic hydrocarbon fraction; (b) the saturate/aromatic hydrocarbon fraction is then separated into pure saturate and aromatic hydrocarbon fractions on a dual packed alumina/silica gel column. Division of the method into two steps

was necessary in order to optimize the separation of the lubricating base oils.

EXPERIMENTAL

Chemicals and Instrumentation (17)

All solvents used in this study were glass distilled solvents and used as received. The clay adsorbent, attapulgus clay, conforms to ASTM D2007 clay specifications. The silica gel used was Davidson's silica gel 621 (60/200 mesh). The alumina adsorbent was obtained from Fisher Scientific Corp. The preparative High Performance Liquid Chromatography unit used was Waters Associates. The columns were packed in our laboratory.

The following instrumentation and methods were used in the characterization of the fractions. A Perkin-Elmer Model 283B with data station was used for IR spectrograms. For refractive indices measurements, ASTM method D1218 was followed. A Bruker CX P200 Pulse NMR Spectrometer was used to obtain C^{13} NMR spectrograms. The samples were dissolved in chloroform with deuterated chloroform as marker for the NMR analysis.

For Gel Permeation Chromatography (GPC), a modular GPC unit was used. It consists of an LDC Constametric Pump (Model III); a Waters Differential Refractometer (Model R401); a Rheodyne Injection Valve (Model 7125) with a 2 ml sample loop. A series of five Styragel columns (1 meter long) from Waters Associates was used to provide ch eparation. The columns were placed in the following series: two 60 Å pore size, one each of 10^3, 10^4, and 10^5 Å pore size. HPLC grade of tetrahydrofuran was used throughout the GPC experiments. The samples are dissolved in tetrahydrofuran before the injection.

Lubrication Base Oil Samples

Three re-refined base oil and five virgin base oils were chosen for this study. They represent typical base oils used in the production of engine lubricants. Table 1 lists the physical properties of these oils.

TABLE 1

CHEMICAL AND PHYSICAL PROPERTIES OF BASE OIL SAMPLES

	Density g/cm ^{3}	Refractive Index D	Viscosity at 40°C Cst	Viscosity Index	Cl ppm	S %wt	Total Acid Number mg KOH/g Oil	N ppm
Re-refined								
A Acid/clay 380N	0.87802	1.4849	73.30	104	197	0.18	0.18	18
B Vacuum Distillation 280N	0.87595	1.4842	60.26	108	7.9	0.19	0.14	17
C Acid/clay 210N	0.88114	1.4865	41.42	102	906	0.29	1.69	24
Virgin								
D Mid-Cont SX 210N	0.86364	1.4770	40.59	100	0.136	0.01	0.18	19
E Mid East SX 600N	0.88749	1.4904	107.62	94	2.9	0.65	0.022	114
F Mid East SX 150N	0.86923	1.4819	30.25	103	0.12	0.30	0.00	42
G Mid East SX 300N	0.87124	1.4814	53.16	102	2.9	0.36	0.00	58
H Mid-Cont SX 250N	0.86952	1.4798	45.63	100	0.068	0.01	0.016	18

*Re-refined base oil "C" received minimum re-refining treatment and was used as a reference oil for method development only.

Column Packing Procedures

Empty polyethylene columns (Waters Associates) have a frit embedded at one end, while the other end remains open. The columns were dry packed using the "tap and fill" method with small increments of adsorbent added until the column was filled to its rim. After packing, a frit was inserted into the open end of the column by pressing gently with a rubber mallet in order not to damage the pores of the frit. The end of the column containing the frit embedded by the manufacturer was used as the column outlet. Each column packed with clay contained approximately 450 g of adsorbent. Silica gel and alumina were activated in a 110 °C oven overnight, then cooled in a desiccator. In the dual packed column silica gel (approximately 300 gm) was packed to the mid-point of the column, then the remainder was packed with alumina (approximately 300 g).

Chromatographic Procedures

Separation of the polar fractions. The packed clay column was placed in the chromatographic chamber of the preparative HPLC and the chamber was closed with a stainless steel cap. After the chamber had been radially compressed to 30 atmospheres the instrument was flushed with 1 liter of n-pentane. The sample solution was then pumped onto the column at the rate of 0.05 l/min. The sample solution was prepared by dissolving the base oil in n-pentane in the ratio of 1:1 by volume. After the sample had been completely pumped through the column, 4 liters of n-pentane equivalent to 8 column volumes were pumped through at the same flow rate. This is sufficient to elute saturate/aromatic from the clay column, since the refractive index (RI) of the eluent returns to the level of the solvent alone. The fraction eluted by the n-pentane was designated the saturate/aromatic fraction. The polar material remained on the column.

One liter of acetone/toluene (1:1 by volume) was then pumped through the column to elute the polar fraction. Both fractions were separately evaporated to dryness using a Rotavap. When the fractions approached dryness, evaporation was completed under a

nitrogen atmosphere. The fractions were then dried to a constant weight and their weights recorded. To determine mass balance, the sample at the detector outlet of the instrument was also collected and weighed.

Separation of the saturate and aromatic fractions. After flushing the chromatograph with 1 liter of n-pentane, a freshly packed column containing alumina and silica gel was oriented in the chamber so the eluent first passed through the alumina, then through the silica gel. Approximately 75 g of the saturate/aromatic fraction obtained from the first separation were weighed out and dissolved in 500 ml of n-pentane. This solution was pumped onto the column as described in the previous section. An additional 1000 ml of n-pentane was then pumped through the column to elute the fractions. The first 500 ml of eluent collected was designated the saturate fraction. The remaining eluent was designated the aromatic fraction. After the elution with n-pentane, 1 liter of methylene chloride in toluene (50 percent), followed by 1 liter of 20 percent ethanol in tetrahydrofuran, was pumped through the column. The fractions were again evaporated to dryness on a Rotavap (under nitrogen atmosphere in the final state).

Method Development

Column Adsorbent Selection. Silica gel and alumina adsorbents tested strongly adsorbed the polar compounds and gave low mass balances (typically 80 to 90 percent). The clay adsorbent finally selected clearly separated the base oils into polar and saturate/aromatic fractions and had a mass balance of 98 percent. Hirsch et al. (5) demonstrated that a dual alumina-silica gel column effectively separated the saturates from the aromatics. After considerable experimentation a two-stage, dual column separation scheme consisting of a clay column and a dual packed alumina/silica gel column was developed. This scheme allows separation of more than 5 g of the polar fraction and 15 g of the aromatic fraction in a single run requiring less than eight hours for completion. The charge of polar fraction to clay ratio of the column

is approximately 1:100 and the charge of saturate/aromatic fraction to gel ratio for the dual column is 1:8.

Separation Optimization

The three factors involved in the optimization of a preparative liquid chromatographic separation are: speed of the separation, sample load capacity, and resolution of the peaks. In the chromatographic separation of polar compounds from the saturate/ aromatic fraction, the resolution factor is large and so a larger load size and faster elution rate can be used. However, in separating the combined saturate/aromatic fractions into pure saturate and aromatic fractions, the resolution factor becomes comparatively small, necessitating a decrease in load size in order to obtain complete separation. Hence, the two stage method was necessary due to the difference in resolution factors and to the small amount of polar fraction present in the base oil relative to the saturate and aromatic fractions.

RESULTS AND DISCUSSION

A total of eight lubricating base oils were separated. Three re-refined base oils and five virgin base oils with viscosity range from 30 cst (150N) to 110 cst (600N) at 40 °C. Table 2 shows that the mass balance and precision achieved with the preparative HPLC method is excellent. The recovery is better than 99 percent by weight in duplicate runs for the clay column and 98 percent for the dual alumina/silica gel column. Table 3 shows that the values obtained from the preparative LC method agree well with those obtained with the ASTM D2007 method. ASTM D2007 method is a clay-gel liquid chromatographic method used for rubber extender and processing oils. Although the ASTM method was not originally designed for lubricating base oil, it agreed with mass spectroscopy data (18). The agreement of the data suggests that the new preparative method yields results which are quantitatively comparable with the ASTM analytical method. At low polar concentrations, e.g., oil "H," the new method appeared to recover less polar materials.

TABLE 2

MASS BALANCE AND PRECISION OF THE PREPARATIVE HPLC METHOD

Sample	Clay Column Separation (Gram)			Alumina/Silica Gel Column Separation (Gram)		
	Injected	Recovered	Wt. % Rec.	Injected	Recovered	Wt. % Recovery
"A"	251.88	250.72	99.5	70.2	68.9	98
	251.83	251.29	99.8	70.4	68.8	98
"B"	250.6	249.8	99.7	70.3	69.0	98
	251.0	250.5	99.8	70.5	69.3	98
"C"	250.0	248.7	99.5	70.5	69.1	98
	249.8	248.3	99.4	70.1	68.7	98
"D"	251.2	250.9	99.9	70.1	68.3	97.4
	251.5	250.5	99.6	70.1	69.2	98.7

TABLE 3

COMPARISON OF PREP HPLC WITH ASTM METHOD D2007

Sample	Saturate wt.% Prep HPLC	Saturate wt.% D2007	Aromatic wt.% Prep HPLC	Aromatic wt.% D2007	Polar wt.% Prep HPLC	Polar wt.% D2007
A	76.4	75.3	21.5	22.5	2.0	2.2
B	76.0	77.6	22.7	20.7	1.3	1.7
C	72.5	72.5	24.8	24.1	2.9	3.4
D	82.9	83.4	16.7	16.2	0.3	0.4
E	64.5	62.9	34.5	35.4	0.8	1.7
F	65.8	67.4	32.6	32.1	0.32	0.5
G	74.8	78.0	24.5	21.4	0.4	0.6
H	78.8	80.7	19.6	19.0	0.05	0.3

TABLE 4

SATURATE AND AROMATIC FRACTIONS SEPARATION AS INDICATED BY REFRACTIVE INDICES

Sample		Refractive Indices
A	Saturate	1.4738
	Aromatic	1.5209
B	Saturate	1.4727
	Aromatic	1.5204
C	Saturate	1.4713
	Aromatic	1.5290
D	Saturate	1.4703
	Aromatic	1.5076

At high viscosity grade, e.g., oil "E" (600N), again less polar materials was recovered. Further method development employing solvent recycling and successive injections may be needed.

Several tests were performed to determine if the fractions designated saturate, aromatic, and polar were free of other types of hydrocarbons. These tests included refractive index determinations, infrared spectroscopy, C^{13} NMR, mass spectroscopy (both high and low resolution), and gel permeation chromatography. All tests suggested good separation by the preparative HPLC method.

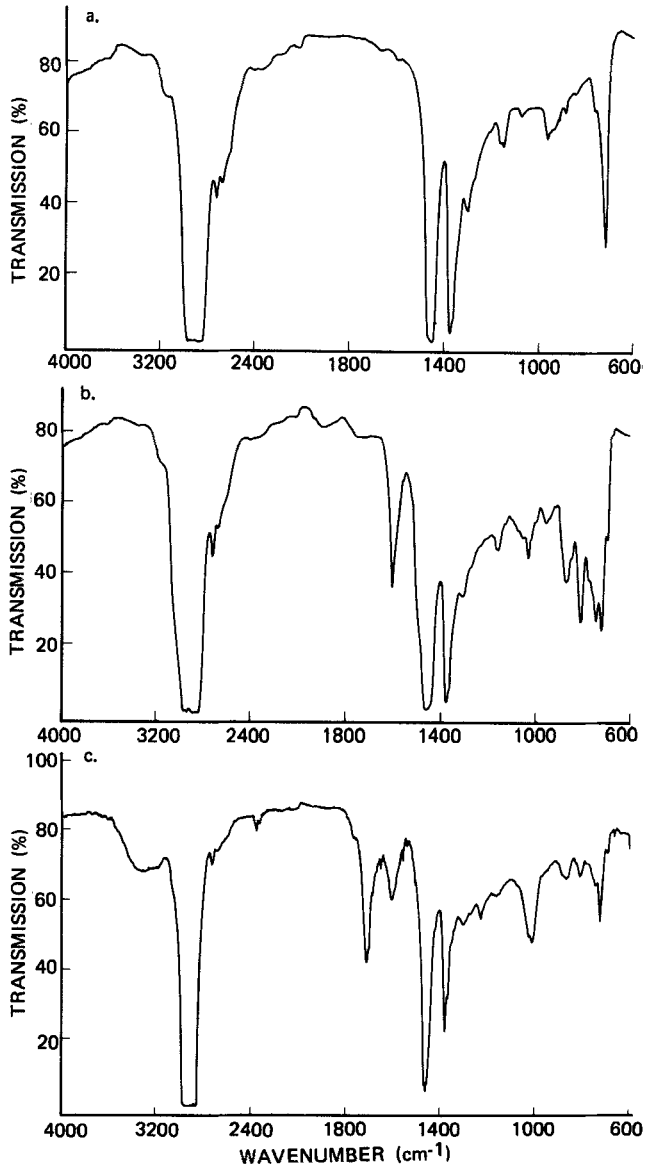
Table 4 shows the refractive index values of the saturate and aromatic fractions of four oils. The refractive indices of the saturate fractions are distinctly lower than those of the aromatic

fractions, as would be expected if the saturate fractions were relatively free of contamination by aromatic hydrocarbons. The dark color of the polar fractions prevented accurate determination of high precision refractive indices.

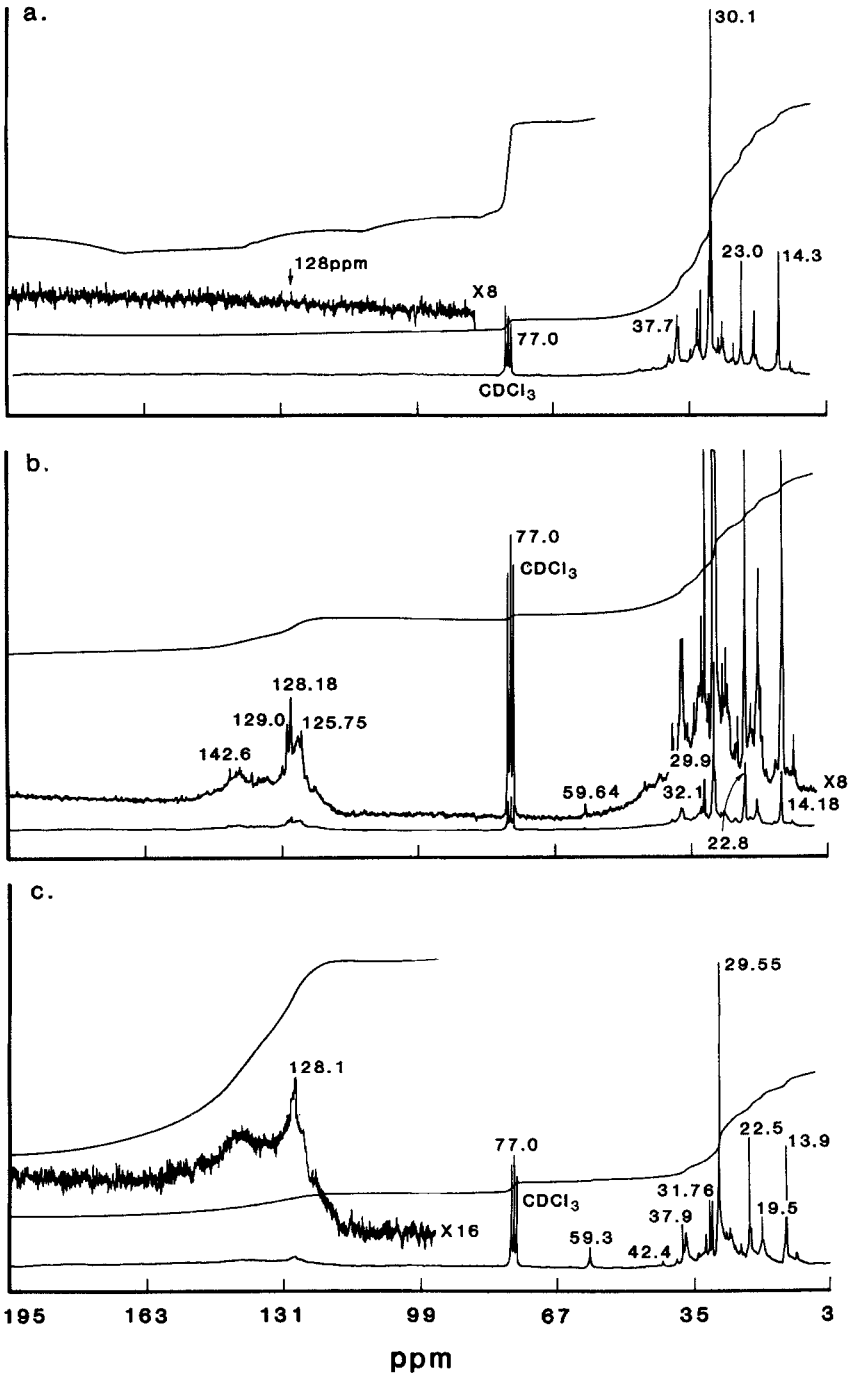
The IR spectra of the fractions of oil samples "A" is shown in Figure 2. The aromatic carbon-carbon stretch band at 1600 cm^{-1} is absent in the IR spectra of the saturate fractions (Figure 2a) but is strongly present in the IR spectra of the aromatic fraction (Figure 2b), indicating that the saturate fraction consists mainly of straight chain hydrocarbons. The strong absorption band observed at the C=O stretch frequency (1700 cm^{-1}) in the IR spectra of the polar fractions shows that most of the oxygenated compounds such as esters, acids, ketones, and other active components of the base oil are concentrated in the polar fractions (Figure 2c).

C^{13} NMR of the fractions of re-refined oil "A" are shown in Figure 3. The absence of aromatic C^{13} (120 to 170 ppm) in the NMR spectra of the saturated fraction is again consistent with the purity of the fraction. The integral ratio of linear carbon to the total carbon is 0.23 in the saturate fraction. The ratio of aromatic carbon to aliphatic carbon is 0.27 in the aromatic fraction. The ratio of aromatic carbon to aliphatic carbon in the polar fraction is 0.18. The extra peak at 89.3 ppm in the aromatic and polar fractions is due to the presence of a viscosity improver, polyisobutylene, which is not completely removed when the used oil is re-refined. The preparative HPLC separation of the base oil concentrated most of the polyisobutylene in the polar fraction, as it is very likely to be an oxidized form of polyisobutylene.

Low resolution mass spectroscopy was performed on the saturate fraction to determine the percentage of aromatic rings in the fraction. The values found in each saturate fraction are listed in Table 5. The values found, approximately two percent, are considered normal for a saturate fraction. High resolution mass spectroscopy was performed on the polar fraction of two re-refined base oils ("A" and "C") and a virgin base oil ("D") in order to determine their content of major trace polar compounds. The re-



2. Infrared spectra of oil "A" fractions: (a) saturates, (b) aromatic, (c) polar.

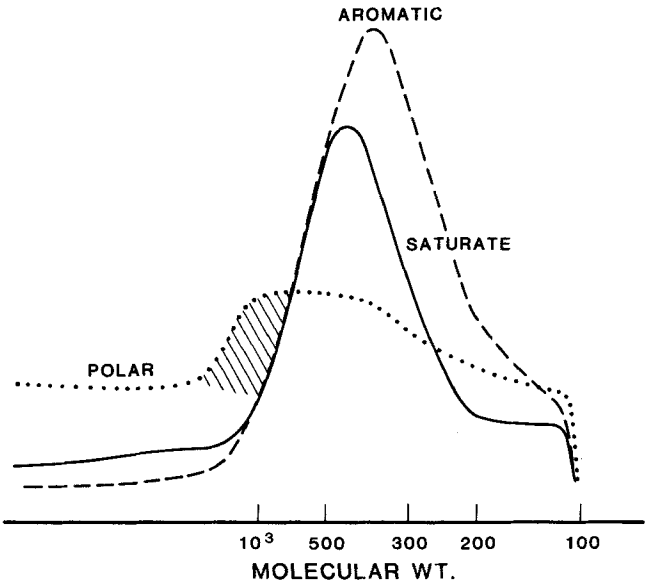


3. C^{13} NMR spectra of oil "A" fractions: (a) saturates, (b) aromatic, (c) polar.

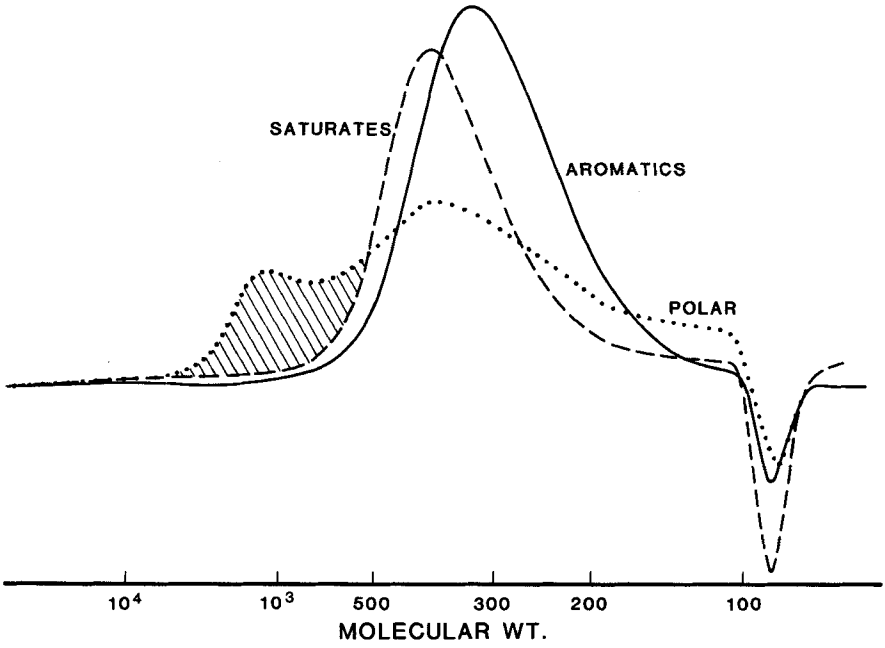
TABLE 5

THE PURITY OF THE SATURATE FRACTION AS MEASURED BY LOW RESOLUTION MASS SPECTROMETRY

Sample	Napthenes (%) in the saturate fraction					Aromatics (%) in the saturate fraction
	Paraffins	1-ring	2-ring	3-ring	4-ring	
A	26.0	28.6	18.1	11.7	13.4	2.2
B	26.4	29.6	17.5	11.0	13.6	1.8
C	24.6	27.0	18.1	12.9	14.9	2.5
D	28.0	30.4	18.1	10.1	11.9	1.4



4. GPC chromatograms of oil "A" fractions (re-refined oil).



5. GPC chromatograms of oil "D" fractions (virgin oil).

refined base oil, "C," is a "minimally re-refined" oil, while "A" is a typical "re-refined" oil. The polar fractions of samples "A" and "D" were found to be very complex mixtures, consisting primarily of hydrocarbons and possibly alkylated phenols. With a probe temperature at 100 °C, considerable residue remained. However, the polar fraction of sample "C" contained free fatty acids, indicating that the feedstock of this re-refined base oil was contaminated by trace amounts of grease. The total acid number of "C" was also found to be unusually high at a value of 1.69 mg KOH/g of oil (Table 1). This is quite interesting, as sample "C" is a "minimally re-refined" oil.

Figure 4 is the molecular weight profile, determined by gel permeation chromatography, of the fractions collected from sample "A." The molecular weight standards used in the calibration of the gel permeation chromatography are polystyrene in the molecular weight range of 233,000 to 3,000 and hydrocarbons of C_{12} to C_{44} in the molecular range of 170 to 618. The profile of the aromatic fraction shows the presence of smaller molecular weight compounds while the profile of the polar fraction is broad, therefore containing both the highest and lowest molecular weight portion of the base oil. For comparison, Figure 5 shows the molecular weight profile of fractions from virgin base oil (sample "D"). The general appearance is the same although some details differ.

CONCLUSIONS

A preparative multigram HPLC method has been developed for the separation of lubricating base oils according to hydrocarbon types. The multigram fractions produced are saturates, aromatics, and polar compounds. In comparison to open column methods, the step-wise elution scheme described here is a much quicker and more efficient means of separating the hydrocarbon fractions contained in large samples (up to 250 g) of lubricating base oils. The method is especially effective for the isolation of large quantities of minor components in complex hydrocarbon mixtures. The base oil fractions obtained by this method were analyzed by spectrometric

methods for purity of contents, and very little overlap was found among fractions. The multigram quantities of minor fractions of lubricating oil prepared by this method are sufficient not only for chemical characterization, but also for performance studies such as oxidation, and friction and wear characteristics. Such a fractionation will also greatly simplify subsequent separation and characterization by analytical HPLC, GC, and GC/MS and will serve as a first step toward a scheme for detailed characterization of lubricating oils.

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