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Friction and Wear Characteristics of Molecular Compound Classes From Lubricating Base Oils

Part 1
Separation and Chemical Characterization

ECUT

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Materials Science
Inorganic Materials Division
Washington, DC 20234

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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Part 1

Separation and Chemical Characterization

1. INTRODUCTION

Tribology is the science and technology concerned with the control of
friction and wear of interacting surfaces in relative motion. It is
a generic technology which supports the manufacturing industries, power
industries, and transporation industries. As such, tribology plays a
key role in energy conversion and utilization technology concepts.

One of the most widely used means to control friction and wear is the
use of lubricants. Most lubricants today are derived from petroleum
which is relatively low cost and abundant. As the energy conversion
and utilization technologies continue to advance, lubrication
environments and demands become more difficult, and new generations of
lubricants are needed to meet the high temperature and sometimes
corrosive environments. In addition, as new classes of materials are
being developed for advanced heat engines (high temperature, high
thermal efficiency engines), lubricant-material compatibility and
interactions need to be understood. Lack of basic knowledge of how
lubricants function and the mechanisms of friction control often
impedes the technology advance. Molecular design basis for lubricants
is not available at present.

Lubricants consist of base oils and additives. While the additives
control the initial friction and wear characteristics of the lubricant,
the base oils control the breakdown and failure mechanisms, as well as
the additive response. Industry has reported that different base oils
with the same additive treatment could perform significantly different
in engine performance tests [1]. Yet, no basic understanding of the
phenomenon is available. Oftentimes, the search for new base oils
and additives for new lubricants becomes a process of trial and error
using expensive full-scale engine tests.

A clear understanding of the lubrication mechanism in existing
technologies and a systematic data base linking molecular structures to
lubricating properties related to various materials are clearly needed
to build new advanced lubricants for high efficiency energy conversion
concepts in the future. Such understanding and data base could yield
significant savings in existing technologies as well.

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1.1 TECHNICAL APPROACH

In lubricated contacts, friction and wear are governed by load, speed, lubricant film thickness, surface topography, metallurgy, and contact geometry. Under low and moderate loads, the lubricating oil film is relatively thick and continuous, and the surface asperity-asperity contacts are often elastic in nature. Frictional forces are governed mostly by the viscous drag of the fluid and the frequency and magnitude of elastic collisions of the surface asperities. The coefficient of friction is generally between 0.01 and 0.06. Predictive models have been developed [2-4]. For most engineering surfaces on gears and bearings, the load is sufficiently high that the lubricating oil film is very thin. In this region, the surfaces are in constant contact, and the asperity-asperity inter-actions result in plastic, as well as elastic deformations. Friction and wear are influenced by adhesion, abrasion, displacement, intermolecular forces, and the chemical compositions of the lubricating film. Surface temperature and surface chemistry [5] are important in controlling the amount of plastic collisions and the properties of the surface film. Coefficient of friction in this region ranges from 0.08 to 0.15.

It is in this region of highly loaded lubricated contact that most advances can be made through systematic research, because the lubricant-surface interactions are complex and the least understood. Lubrication in this region is controlled by surface topography and lubricant chemistry. Bowden and Tabor [6] in 1964 summarized a series of experiments demonstrating the effects of chain length of fatty acids on friction and wear. Greenhill [7] and Sanders [8] studied the effects of esters, alcohols, and long chain polar compounds on friction and wear in various simple sliding experiments. Goldblatt [9,10] studied the antiwear behavior of polynuclear aromatics in basestocks and their influence on antiwear additives. Groszek [11,12] measured heats of adsorption of various molecular structures of surfactants and some phosphorous and sulfur additives on solid surfaces and was able to explain some observed lubrication phenomena.

In developing the basic data linking molecular structures to friction and wear characteristics, one of the most difficult questions is what molecular structures are significant in friction and wear control. Model compounds seldom provide the practical link to actual lubricants. Obviously lubricating base oils and additives are important, yet it is not clear which structures in the lubricants control the tribochemical reactions.

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Our work on recycled base oils provided some interesting results.
In an effort to isolate and identify contaminants in re-refined
lubricating base oils, we developed a separation scheme to isolate
the polar fractions using liquid chromatography. Characteristics
of the fractions are shown in Table 1. The polar fraction (1 to 2%
by wt.) contains most of the sulfur, nitrogen and acidic species and
at the same time possesses almost all of the antioxidant capacity
of the oil (Table 2). Figures 1 and 2 demonstrate the effect of
this fraction on friction and wear. As shown in Figure 1, at low
concentrations in pure saturates, the polar fraction lowers the wear.
With some antiwear additive added, the polar fraction increases the
wear by reducing the effectiveness of the additive. Figure 2 shows that
addition of polar fraction to pure saturates can influence friction.
These data suggest that the polar structures in base oils exert a
large influence on friction and wear characteristics.

If the antiwear additives in oils provide antiwear performance, i.e,
wear and friction control, as long as the additives remain in the
system, then the natural polar structures in the base oil control the
friction and wear failure. Identification of these polar fraction
structures could provide a basis for model compounds selection.

Therefore, the approach that we have chosen is to separate three
lubricating base oils, as illustrated in Figure 3, to provide basic
structural information on the constituents in base oil that control
friction and wear. After careful characterization of these compound
classes, model compounds of various molecular structures will be used
to measure their effects on friction and wear under different load/
speed combinations.

1.2 TEST DEVELOPMENT AND STANDARDIZATION

Within the general framework of the technical approach, many
significant technical challenges exist in spite of recent advances.
Compound separation, isolation, and identification of a particular specie
from a complex mixture such as base oils remain formidable. Conventional
liquid chromatographic methods are time consuming and yield only
milligram quantities of separated materials. Large scale and rapid
separation techniques need to be developed. Micro-characterization of
limited quantities of materials in terms of compound identification is
difficult. Various analytical instrumentations run in tandem such as
GC-FTIR, GC-MS, HPLC-FTIR may be required for positive compound
identification.

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Table 1

Physical and Chemical Properties of Separated Fractions

Re-refined Base Oil

	Base Oil	Pure Fraction	Pentane Fraction	Polar Fraction
Viscosity at 40 °C, cSt	73.	65.	73.	560.
Viscosity at 100 °C, cSt	9.4	8.8	9.0	20
VI	104	108	97	< 0
Refractive Index	1.4850	1.4798	1.4864	1.5682
Density, g/cm^3	0.8780	0.8696	0.8797	1.0071
TAN, mg KOH	0.18	0.03	0.10	0.74
Basic Nitrogen, ppm	0.4	0.9	1.7	45
Sulfur, ppm	1750	600	2710	27.500
Percolation Technique, %	--	58.2	38.8	2.9
ASTM 2007 Clay-Gel	--	75.3	22.5	2.2
HC Type by n-d-m				
Paraffinic C, %	67.5	68.3	65.3	40.4
Naphthenic C, %	26.5	28.5	26.9	17.1
Aromatic C, %	6.0	3.2	7.8	42.5

Table 2

Antioxidant Capacity of Various Base Oil Fractions

ANTIOXIDANT CONCENTRATION, 10^{-3} MOLAR

OILS	ORIGINAL	"PURE"	PENTANE	POLAR ACETONE
A	12	2	1	420
B	7	1	1	210
C	-	1	1	270
D	-	1	1	260
E	8	2	1	230

Apparatus: NBS Modified 4-Ball Wear Tester
Speed: 600 RPM
Load: 40 kg
Temperature: 75 °C
Duration: 60 minutes
Atmosphere: 0.25 ℓ/min dry Air
Lubricant: Purified Fraction Blended with Polars

FIGURE 1. EFFECTS OF ZDDP - POLAR FRACTION
           INTERACTIONS ON WEAR

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Apparatus: NBS Modified 4-Ball Wear Tester
Speed: 600 RPM
Load: 40 kg
Temperature: 75 °C
Duration: 60 minutes
Atmosphere: 0.25 ℓ/min air atmosphere
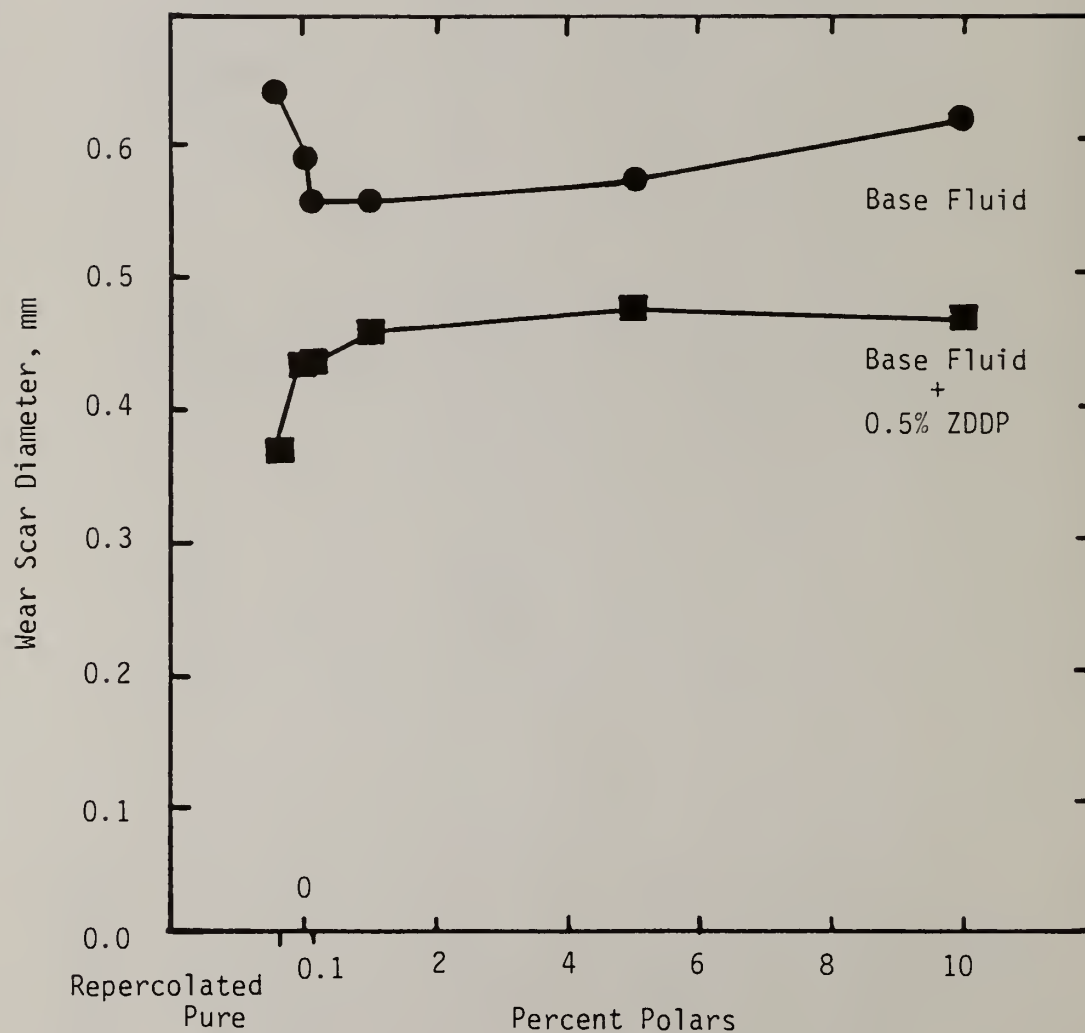Lubricant: 10 ml Purified Fraction Blended with Polars
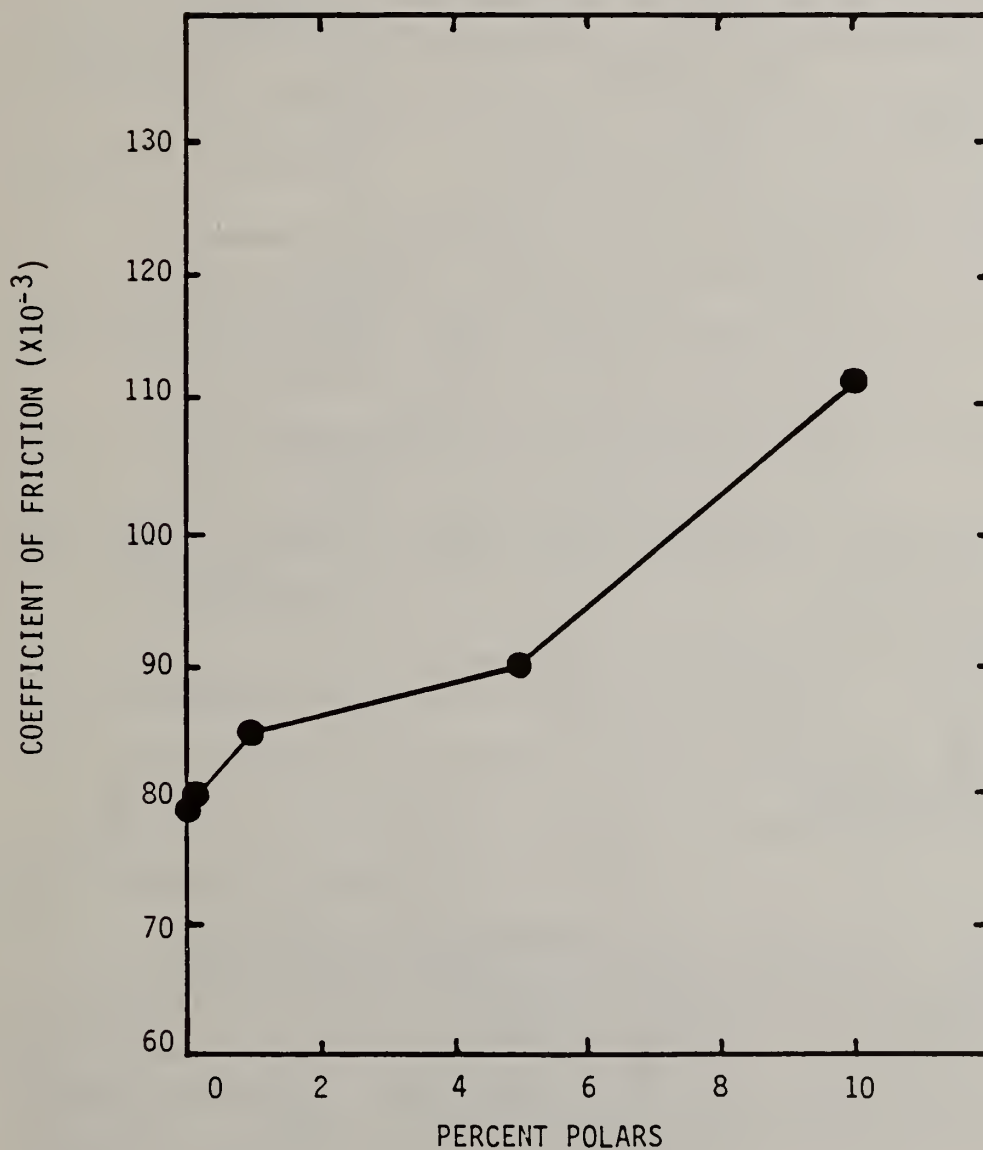
FIGURE 2.   COEFFICIENT OF FRICTION AS A FUNCTION
            OF POLAR CONCENTRATION
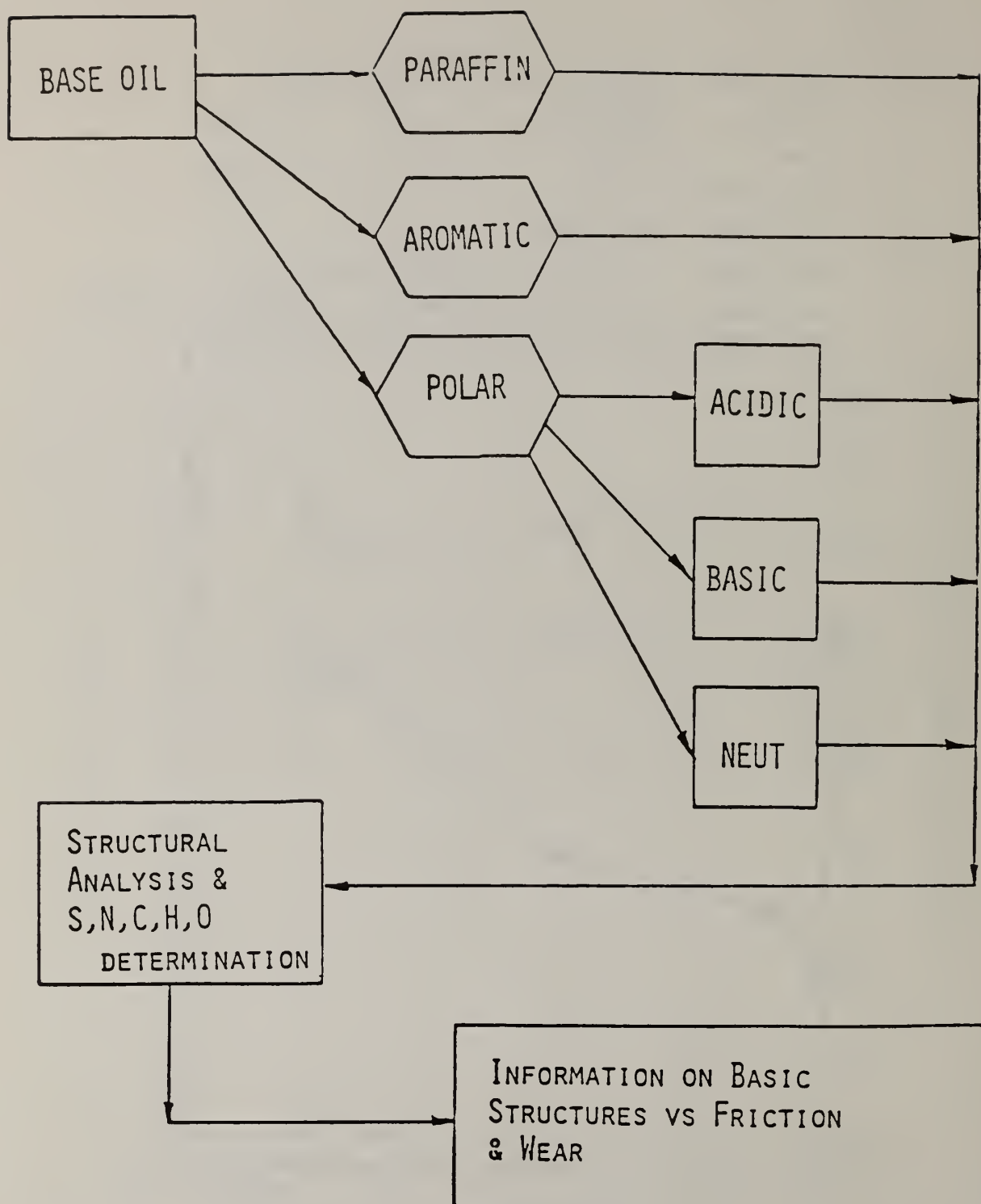
FIGURE 3

MOLECULAR STRUCTURE SEPARATION/CHARACTERIZATION SCHEME

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Performance characterization techniques for lubricants are usually conducted using laboratory simulation tests. These are usually oxidation and wear tests. However, the significance of these test results is often questioned. A methodology needs to be established to link laboratory test results to actual field experience.

These tests, once developed, have to be standardized to provide comparable data base by different workers. In an interdisciplinary subject such as tribology, the necessity of standardization for technological advancement is crucial.

This report describes in part, the technical activities associated with the ECUT project from March 15, 1982 to June 30, 1983. The emphasis is restricted to separation science and test method development.

The scope of the overall long-term project goals can be described as follows:

1. Increase the understanding of the basic lubrication and friction mechanisms and develop predictive models.

2. Specifically, understand how the molecular structure of lubricants interact with surfaces to control friction.

3. Develop an understanding of the chemistry taking place at lubricated surfaces and its effect on lubricity.

4. Understand the effects of lubricant molecular structure on adsorption, and the dependence of friction on different surface materials.

5. Develop measurement techniques and standardized test methods on friction.

6. Technology transfer through cooperative study with industries.

A schematic of the technical objectives is shown in Figure 4.

1.3 TECHNOLOGY TRANSFER

In addition to the normal publications and society presentations, many cooperative research programs have been initiated with universities and industries. Details are shown in Figure 5. An industrial working group comprised of nine major oil companies and five additive companies has been formed to conduct base oil research. Industry supplied over 100 base oil samples with extensive analytical data, and NBS conducted simulation tests to assess the effects of base oil compositions on oxidation stability [13].
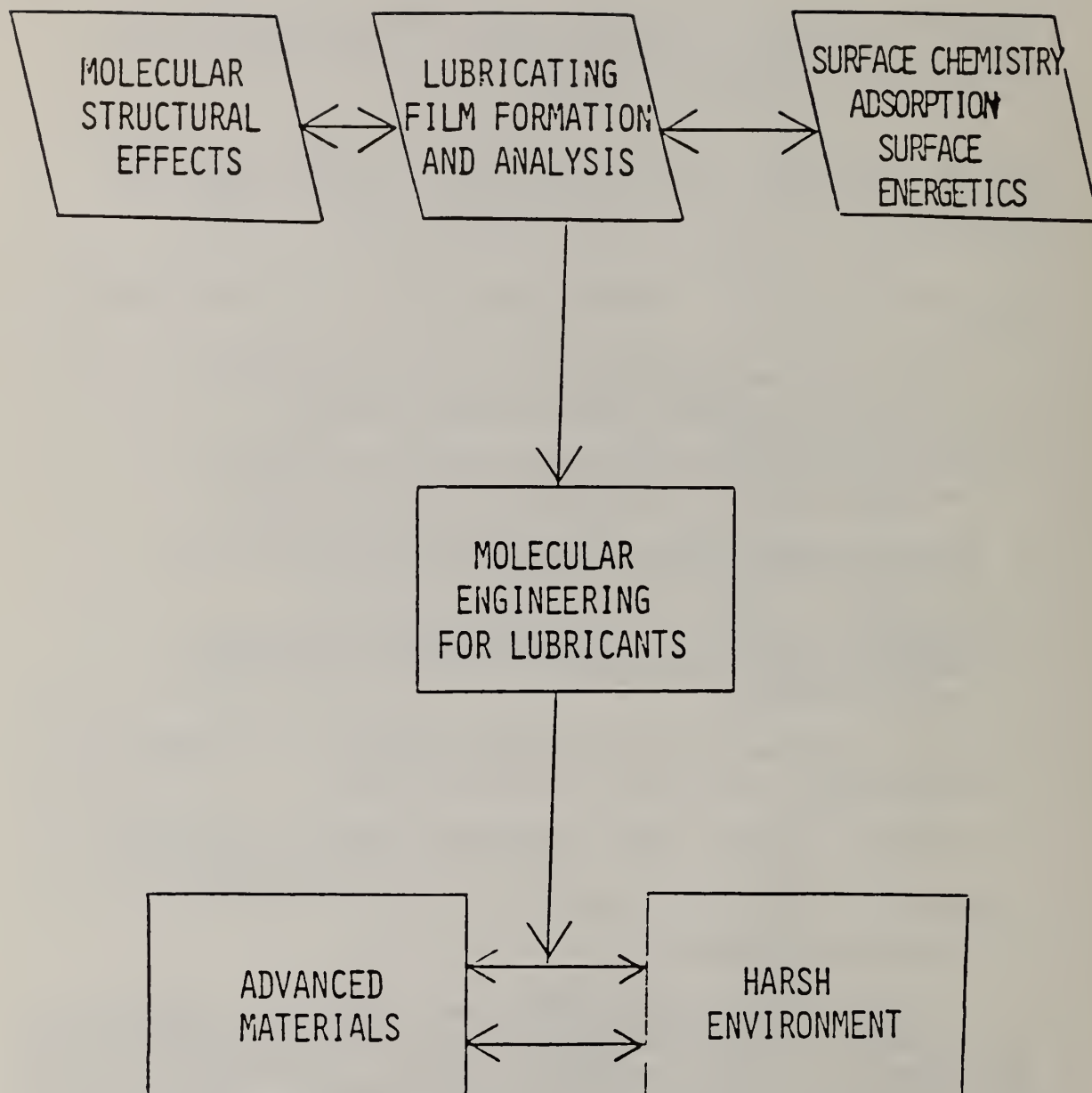
FIGURE 4. NBS/ECUT TECHNICAL PROGRAM OBJECTIVE

UNIVERSITIES   INDUSTRIES

PA. STATE (GRAD. COOP.)   MARTIN MARIETTA (ADSORPTION)
NORTHWESTERN (IPA)   CUMMINS ENGINE (CERAMICS)
MINNESOTA (IPA)   HUGHES AIRCRAFT (BEARINGS)
                             GEO CENTERS   (ORGANIC SYNTHESIS)
                             LUBRIZOL   (ADDITIVE RESEARCH)
                             BENDIX   (CERAMICS)
                             MACK TRUCK   (DIESEL)
                             CATERPILLAR   (DIESEL)

                        ┌─ ─ ─ ─ ─ ─ ─ ─┐
                        │   │
                        │   NBS/ECUT   │
                        │ TRIBOLOGY PROGRAM │
                        │   │
                        └─ ─ ─ ─ ─ ─ ─ ─┘

AGENCIES   INDUSTRIAL WORKING GROUP

DOE   EXXON   PARAMINS
U.S. ARMY   MOBIL   ORONNITE
U.S. AIRFORCE   TEXACO   AMOCO CHEMICALS
U.S. NAVY   AMOCO   LUBRIZOL
                             CHEVRON   CIBA GEIGY
                             IMPERIAL
SAE   SHELL
ASLE   ARCO
ASTM   UNION
ASME

FIGURE 5.   NBS/INDUSTRY/UNIVERSITY INTERACTIONS

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2. SEPARATION METHOD DEVELOPMENT

A variety of lubricating base oils were used to develop the separation method. These oils represent the current technologies and are the most widely available commercially. Detailed characterization results are shown in Table 3.

Several separation techniques were examined. These included: activated alumina column chromatography, clay-silica gel combination column chromatography, ion exchange column chromatography, and preparative High Performance Liquid Chromatography (HPLC) methods. The final separation scheme uses the HPLC apparatus and is a three stage process: (1) a clay column to separate the oil into polar and saturate/aromatic fractions, (2) silica-gel/activated alumina combination column to separate the saturate/aromatic fraction into its respective fractions, and (3) a neutral alumina column to separate the polar fractions into four major subfractions (P-2, P-3, P-5, and P-6). The following sections discuss the advantages and disadvantages of each separation technique examined.

2.1 LARGE SCALE ACTIVATED ALUMINA COLUMN

To isolate a large quantity of the polar fraction (1 to 2% by wt.) in a base oil, a large scale activated alumina column of 182 cm length and 5 cm internal diameter was used. About 2000 gram of a 80/200 mesh alumina adsorbent, which was activated at 200 $^{\circ}$C for 6 hours, was employed for each separation. About 3.5 kg of oil was charged under one atmosphere of nitrogen pressure. The conditions and the apparatus are shown in Table 4 and Figure 6. The procedure produced purified saturate fraction, and a polar fraction. The purified oil fraction was collected until the infrared aromatic absorbance at 1605 cm-[1] reached 6.3 x 10^{-2} absorbance units. This gave a good balance of yield and purity in the first fraction. The remaining nonabsorbed material in the column was removed by eluting with pentane. The end point for the pentane fraction elution was determined using a Refractive Index (RI) detector. When the RI value of the column eluent matched the RI value of n-pentane, only the polar materials remained on the column. Acetone was used to remove the absorbed material from the column, and was collected as the polar fraction.

Pentane and acetone were removed from the respective fractions by evaporation at 60 $^{\circ}$C under vacuum in a rotary evaporator, followed by stripping with nitrogen. Completion of solvent removal was checked by the constant weight method, followed by analysis of the fractions by gas chromatography.

TABLE 3

CHEMICAL AND PHYSICAL PROPERTIES OF BASE OIL SAMPLES

	Density g/cm³	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.

Table 4

Experimental Conditions for the Activated
Alumina Column

Column Dimension	:	182 cm long 5 cm ID with 2 liter capacity reservoir
Wt. of Alumina Used	:	1847 g to 2000 g
Wt. of Base Oil Charged:		3530 g
Pressure	:	0.1 MPa (1 Atm)
Pentane Used to Elute	:	4 liters
Acetone Used to Elute	:	4 liters
Wt. Recovered	:	∿99%
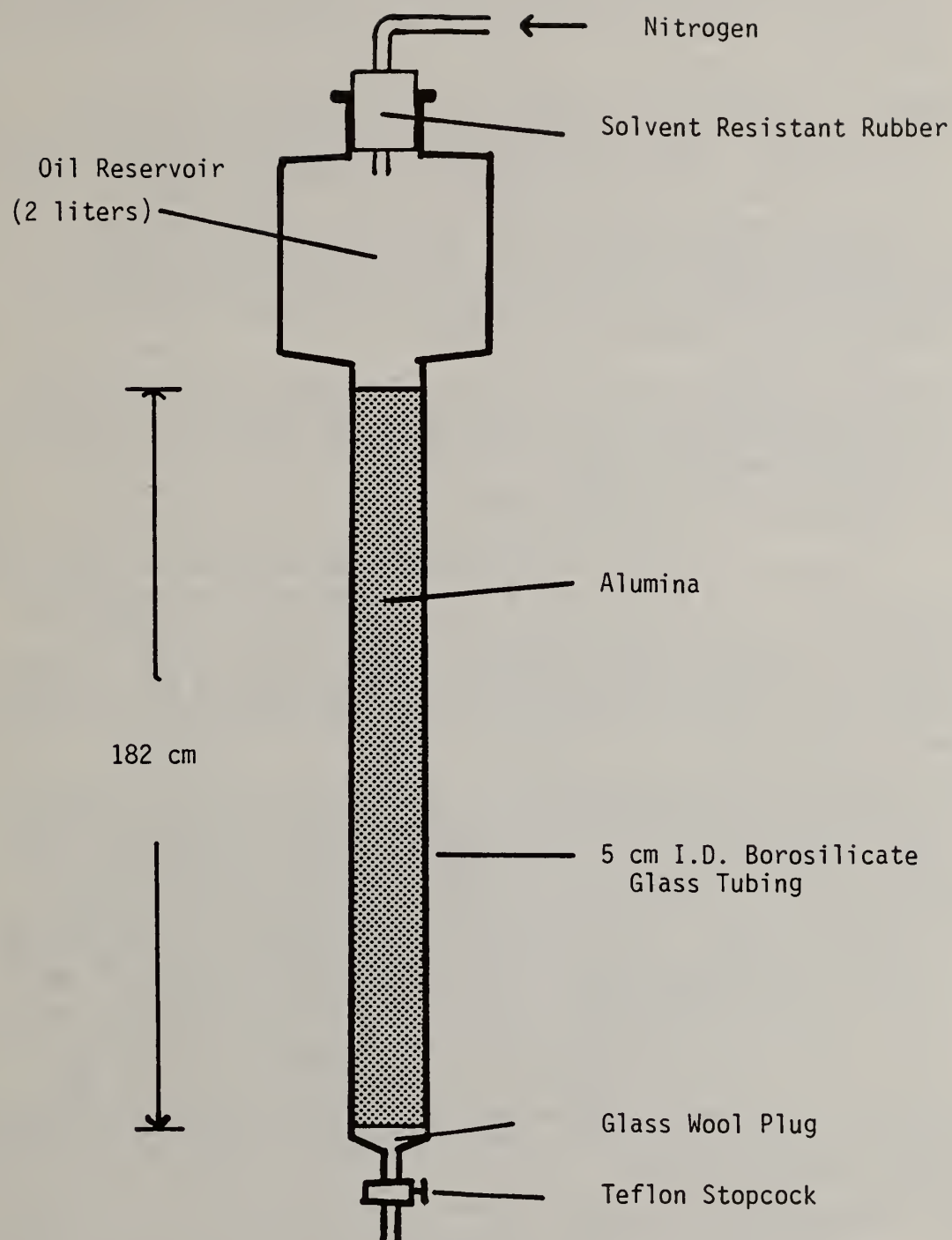
FIGURE 6.   LARGE SCALE ACTIVATED ALUMINA LIQUID CHROMATOGRAPHY
COLUMN FOR BASE OIL SEPARATION

Nitrogen

Solvent Resistant Rubber

Oil Reservoir
(2 liters)

182 cm

Alumina

5 cm I.D. Borosilicate
Glass Tubing

Glass Wool Plug

Teflon Stopcock

This procedure takes 3 to 4 weeks per oil sample. The physical and chemical characteristics and the infrared spectra of the three base oils and their fractions separated on activated alumina are listed in appendix A.

Chemical analyses and IR spectra show the acetone eluted polar fraction contains large amounts of oxygen and sulfur compounds. This is indicated by a high weight percent of elemental sulfur, and high total acid number, as well as the presence of strong hydroxy (3450 cm-[1]) and carbonyl peaks (1700 cm-[1]) in the infrared absorbance spectrum. The pure fraction contains a small amount of aromatic compounds as shown by the aromatic band at 1600 cm-[1] in the IR spectrum. The pentane eluted oil fraction is free of any carbonyl compounds as no carbonyl band is observed at 1700 cm-[1].

The main difficulty with this preparative method is the long period of time required to separate one oil into its compound fractions. During the 3 to 4 weeks time, undesirable oxidation of the base oil constituents may also occur.

2.2 CLAY/SILICA GEL CHROMATOGRAPHY

A clay-gel adsorption chromatographic method based on ASTM D-2007 was examined. The method uses a dual column (silica gel and clay adsorbents) to separate oils into three fractions: (1) saturated compounds, which are not adsorbed on either the silica gel or clay columns, (2) aromatic compounds which are adsorbed on the silica gel column, and (3) polar compounds which are adsorbed on a clay column of specific activity.

This method offers a rapid means to separate base oils into major hydrocarbon types such as polar compounds, aromatics and saturates. A base oil was evaluated by this method and found the method useful as an analytical tool. The fractions obtained by this method are characterized by infrared spectroscopy. The fractions are found to be relatively pure. The IR spectra of the fractions of the sample are shown in appendix B. The polar fraction contains most of the sulfur and acidic compounds. The advantages of this method are its simplicity and the excellent recovery of all three hydrocarbon fractions. However, the quantity recovered from the separation is very small because the starting oil feed to the column is limited to 10 gm. A scaled up version of this method requires 4 to 6 weeks to complete testing one oil. Therefore, a fast preparative scale liquid chromatographic method is sought.

2.3 PREPARATIVE HPLC METHOD

With the advent of High Performance Liquid Chromatography (HPLC), the time consuming aspect of the open column chromatography has been reduced. A modification of Hirsh's method was reported by Sawatzky

et. al [14], which consists of using high pressure to give enhanced separation in a much shorter period of time. At present, HPLC methods, either analytical or preparative, generally have limited sample loading capacities in the range of one gram or less [15-20]. This means the amount of polar fraction separated from a run will be in the milligram range, not sufficient for performance testing. Therefore, an effort was initiated to develop a rapid multigram chromatographic method for the isolation of active species in base oils. In this respect, good mass balance becomes an important factor, since loss of a significant amount of the active species in an oil will render the separation unacceptable.

A commercial preparative HPLC unit with dual 5 cm I.D. radially compressed column was used. The first column was packed with 450 grams of attapulgus clay as specified by ASTM D-2007 clay specifications. The second column was packed with 300 gm of silica gel (60/200 mesh) and 300 gm of activiated alumina successively.

The separation scheme developed is shown in Figure 7. The process is divided into two steps: (1) the polar fraction is separated from the base oil on an attapulgus clay column, generating a polar fraction and a saturate/aromatic hydrocarbon fraction, and (2) the saturate/aromatic hydrocarbon fraction is then separated into pure saturate and aromatic hydrocarbon fractions on a dual packed alumina/silica gel column.

2.3.1 POLAR FRACTION SEPARATION

The packed clay column was placed in a stainless steel chromatographic chamber, and the chamber was pressurized to 3.0 MPa (440 psi). After flushing the column with 1 liter of n-pentane, the sample solution (50:50 oil and pentane) was pumped onto the column at the rate of 50 mL/min. After the sample has been pumped onto the column, four liters of n-pentane were used to sweep the clay column at the same flow rate. The fraction eluted by the n-pentane was designated the saturate/aromatic fraction. One liter of acetone/toluene (1 to 1 by volume) was then pumped through the column to elute the polar fraction. Both fractions were evaporated to dryness using a rotary evaporator. 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.

2.3.2 SEPARATION OF THE SATURATE/AROMATIC FRACTION

After flushing the preparative unit with one 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
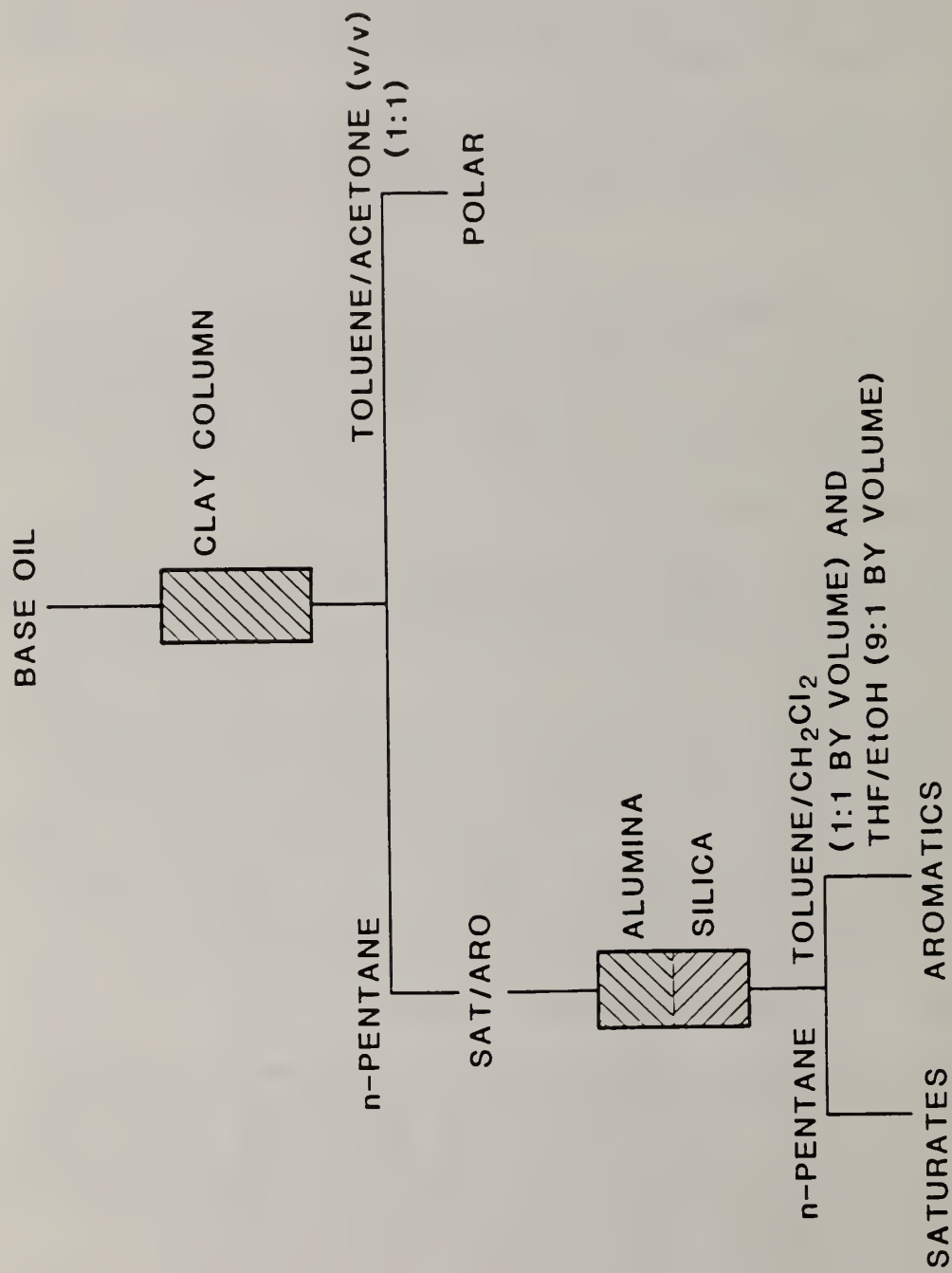
FIGURE 7. PREPARATIVE HPLC SEPARATION SCHEME

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. After the elution with n-pentane, one liter of
methylene chloride in toluene (50%), followed by one liter of 10% ethanol
in tetrahydrofuran, was pumped through the column. The fractions were
again evaporated to dryness on a Rotavap under nitrogen atmosphere. The
final two elution volumes were combined for the aromatic fraction as
shown in Figure 7.

2.3.3 SEPARATION OPTIMIZATION

The three factors involved in the optimization of a preparative liquid
chromatographic separation are: (1) speed of the separation, (2) sample
load capacity, and (3) resolution of the peaks. If improved resolution
of peaks is required, some sacrifice in speed and load size is necessary,
such as decreasing the sample size placed on the column and/or slowing the
elution rate of the mobile phase. 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 the small amount of polar fraction present in
the base oil relative to the saturate and aromatic fractions. By utilizing
this two-step process 5 gm of the polar fraction, 15 g of the aromatic
faction, and 60 g of the saturate fraction can be obtained in a single
run requiring less than 8 hours for completion.

2.3.4 PURITY OF THE SEPARATED FRACTIONS

A total of eight lubricating base oils were studied: three re-refined base oils
and five virgin base oils with viscosity range from 30-110 Cst (150-600N).
Table 5 shows that the mass balance and precision achieved with the preparative
HPLC method is excellent. The recovery is better than 99% by wt. in duplicate
runs for the clay column and 98% for the dual alumina/silica gel column.
Table 6 shows that the values obtained from the preparative HPLC method
agree well with those obtained with the ASTM D2007 method.

The agreement of the data suggests that the new method, while preparative
in nature, yields results which are quantitatively comparable with an
analytical method.

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 spectro-
scopy, 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 5

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 6

COMPARISON OF PREP HPLC WITH ASTM METHOD D2007

Sample	Saturate wt.%		Aromatic wt.%		Polar wt.%	
	Prep HPLC	D2007	Prep HPLC	D2007	Prep HPLC	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

The IR spectra of the fractions of oil samples 'A' and 'D' are shown in Figures 8 and 9. The aromatic carbon-carbon stretch band at 1600 cm^{-1} is absent from the IR spectra of the saturate fractions (Figures 8a and 9a) but is strongly present in the IR spectra of the aromatic fraction (Figures 8b and 9b), indicating that the saturate fraction contains very little aromatic hydrocarbon. The strong absorption band observed at the C = O stretch frequency (1700 cm^{-1}) in the IR spectra of the polar fraction 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 fraction (Figures 8c and 9c).

C^{13} NMR of the fractions of one re-refined oil 'A' are shown in Figure 10. The absence of aromatic C^{13} (120-170 ppm) in the NMR spectra of the saturated fraction is again consistant 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 contamination by a residual additive, polyisobutylene, which is not completely removed during the re-refining process.

Low resolution mass spectroscopy was performed on the saturate fraction to determine the percentage of aromatic rings. The values found in each saturate fraction are listed in Table 7. Approximately 2%, monoaromatics are found in the saturate fraction, which is considered acceptable for such separation. High resolution mass spectroscopy was performed on the polar fraction of three base oils to determine the major constituents of the polar compounds. Results suggest that the polar fractions remain too complex a mixture for accurate identification. By this technique with a probe temperature at 100 $^\circ$C, considerable residual remained. Further separation of the polar fraction is required.

Figure 11 shows the molecular weight profile, determined by gel permeation chromatography, of the fractions collected from oil 'D'. The molecular weight standards used in the calibration of the gel permeation chromatography are polysytrenes of known molecular weight. The profile of the aromatic fraction shows the presence of smaller molecular weight compounds while the profile of the polar fraction is broad, since it contains both the highest and lowest molecular weight portion of the base oil.
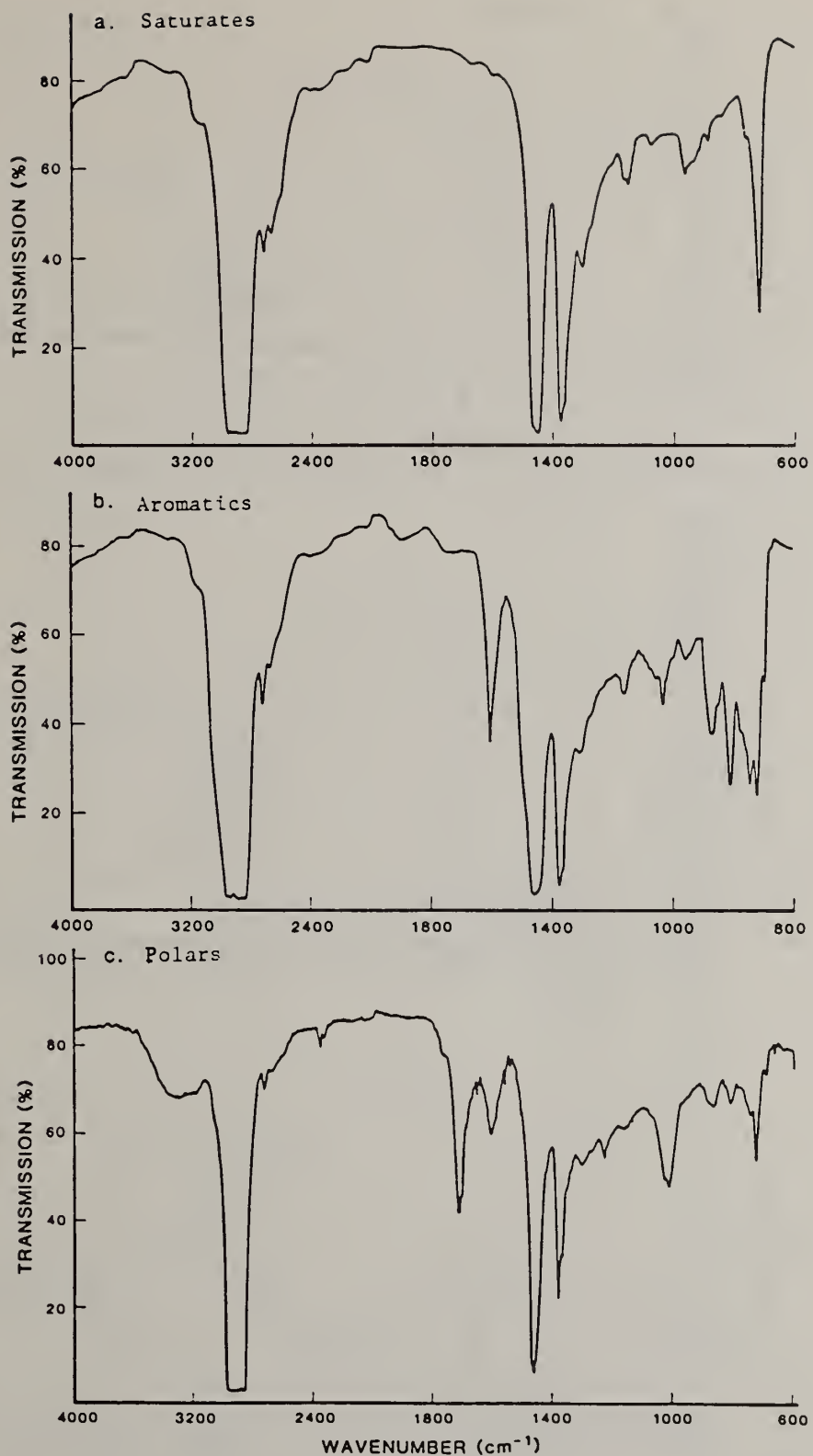
FIGURE 8.   INFRARED SPECTROGRAMS OF OIL A FRACTIONS
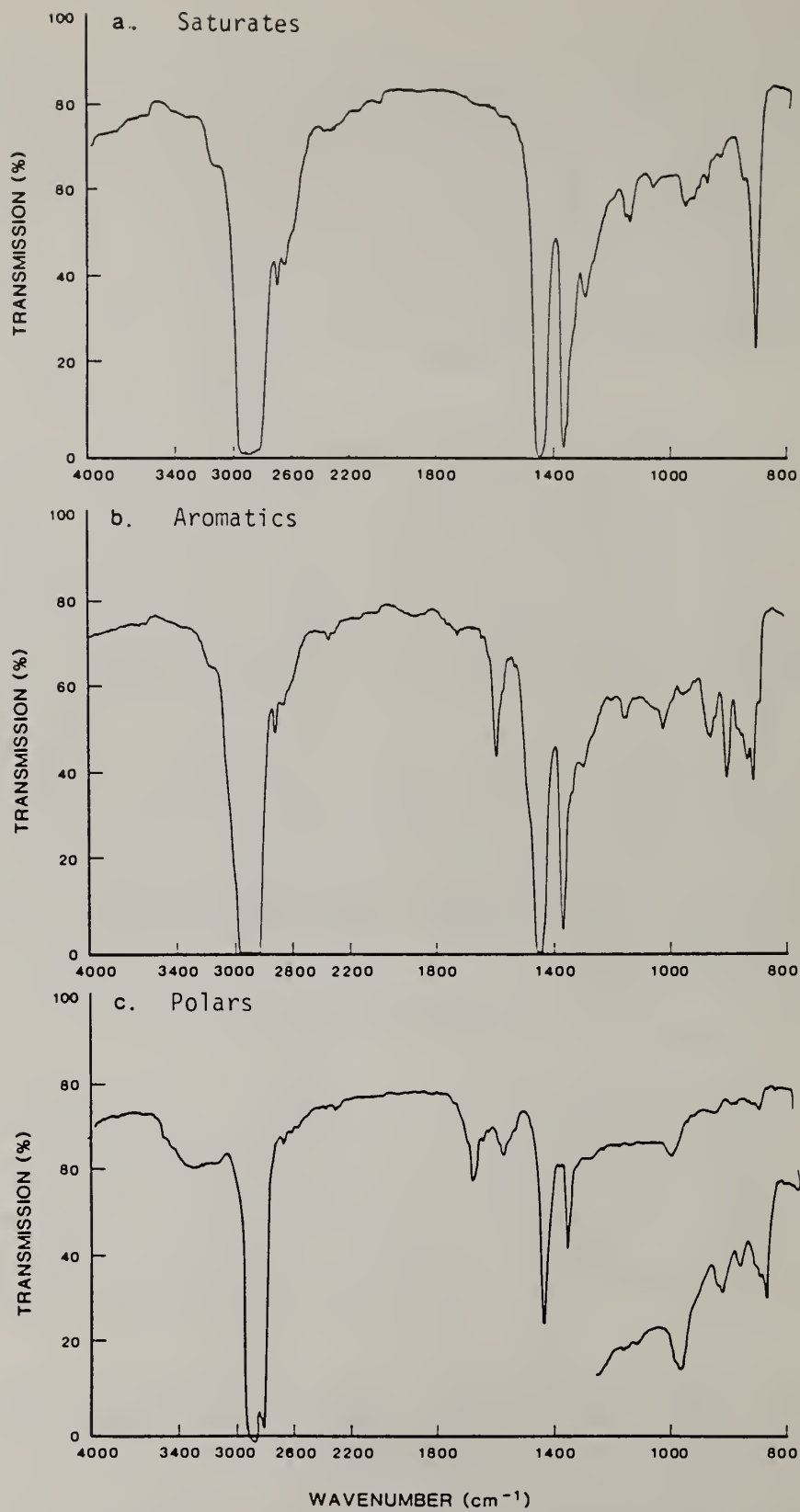
FIGURE 9. INFRARED SPECTROGRAMS OF OIL D FRACTIONS
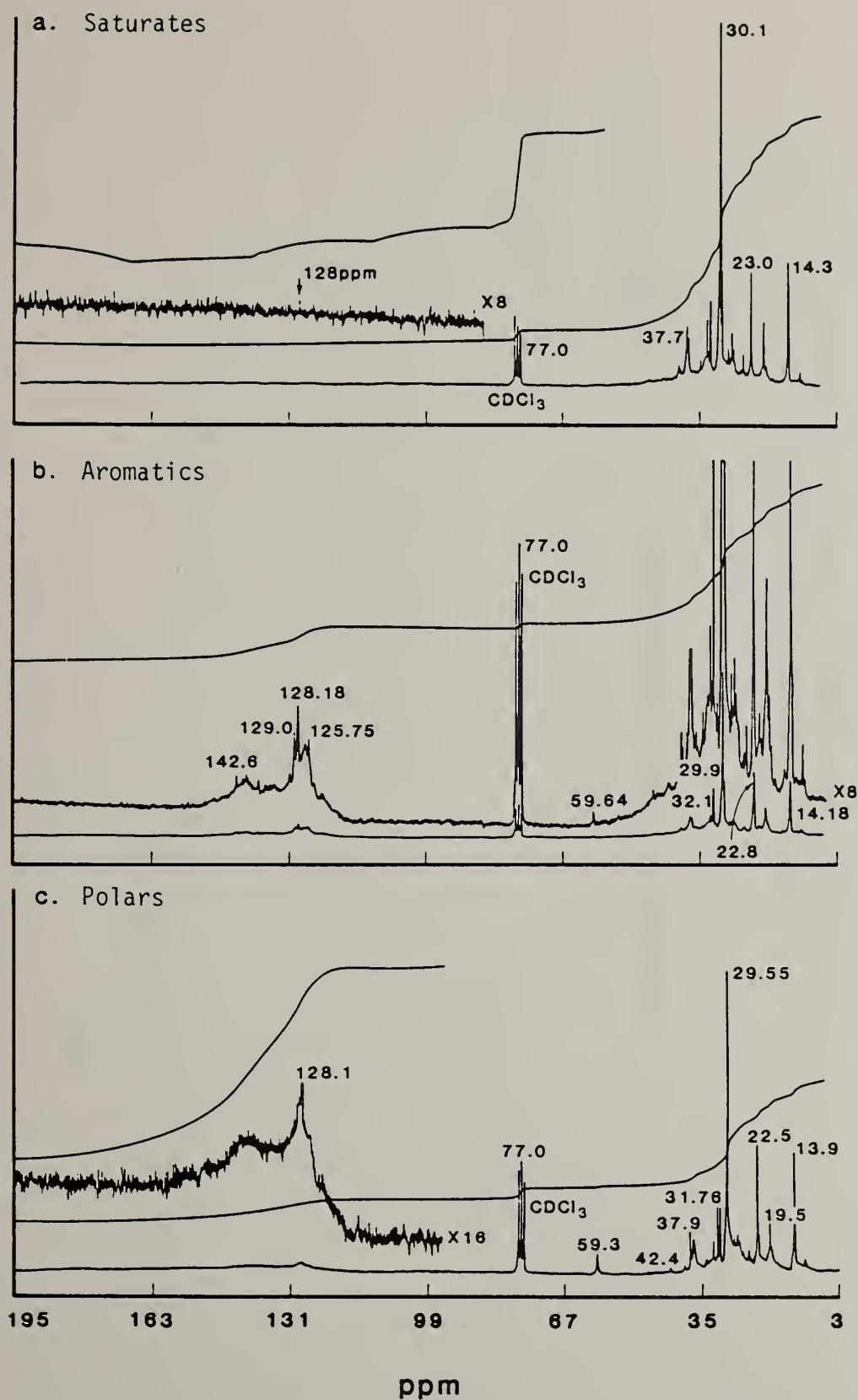
FIGURE 10. C^{13} NMR SPECTROGRAMS OF OIL A FRACTIONS

TABLE 7

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

	Napthenes (%) in the saturate fraction				Aromatics(%) in the saturate fraction
Sample	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
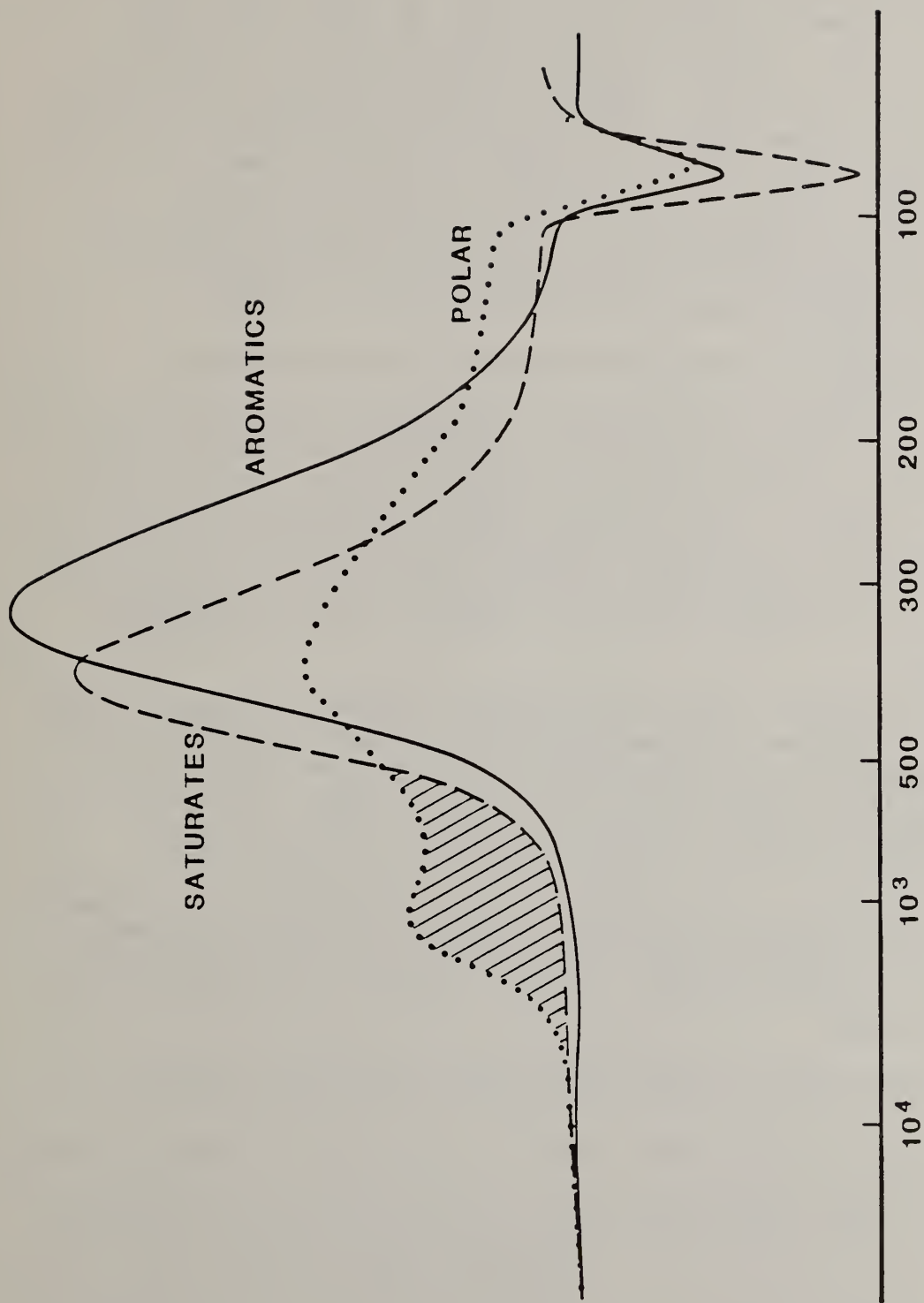
MOLECULAR WT.

FIGURE 11. MOLECULAR WEIGHT DISTRIBUTION
OF FRACTIONS FROM OIL D

2.3.5 SUMMARY OF THE HPLC SEPARATION

A preparative multigram HPLC method has been developed
for the separation of lubricating base oils according to hydrocarbon
types. This preparative method can produce multigram quantities of
various hydrocarbon/compound types. The fractions produced are
saturates, aromatics and polar compounds. In comparison to open
column methods, the step-wise scheme described here is rapid and
efficient. The method is especially effective for the isolation of
large quantities of minor components in complex hydrocarbon mixtures.
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, friction, and
wear. Such a fraction scheme greatly simplifies subsequent
separation and characterization by analytical HPLC, GC, and GC/MS
and will serve as a first step toward a scheme for isolating
molecular compound classes in a base oil.

2.4 ION-EXCHANGE COLUMN CHROMATOGRAPHY FOR POLAR SEPARATION

Jewell et al. [21] reported an ion-exchange, coordination and
adsorption chromatographic method for separation of heavy-end petroleum
distillates into acids and bases, neutral-nitrogen, saturates, and
aromatic fractions. Both cationic and anionic exchange resins were
used to isolate the acids and bases while the neutral-nitrogen fraction
was separated by coordination complex formation with ferric chloride
supported on attapulgus clay. Silica gel was used to separate the
remaining hydrocarbon and nonpolar compounds into saturates and
aromatics.

A modified version of the separation was examined to further separate
the polar fraction. The separation scheme illustrated in Figure 12
was attempted on the polar fraction of a 350N re-refined base oil.
The last acid fraction (POLA-5), and base fractions POLB-4 were not
characterized chemically due to negligible recovery. Detailed
characterization data and discussion are shown in appendix C.

Preliminary data on this separation method were encouraging. However,
Holmes [22] reported some artifacts and molecular rearrangement of
materials separated by this method. Controlled experiments in our
laboratory confirmed Holmes' finding. Therefore, this method was not
pursued further.

2.5 NEUTRAL ALUMINA COLUMN CHROMATOGRAPHY FOR POLAR SEPARATION

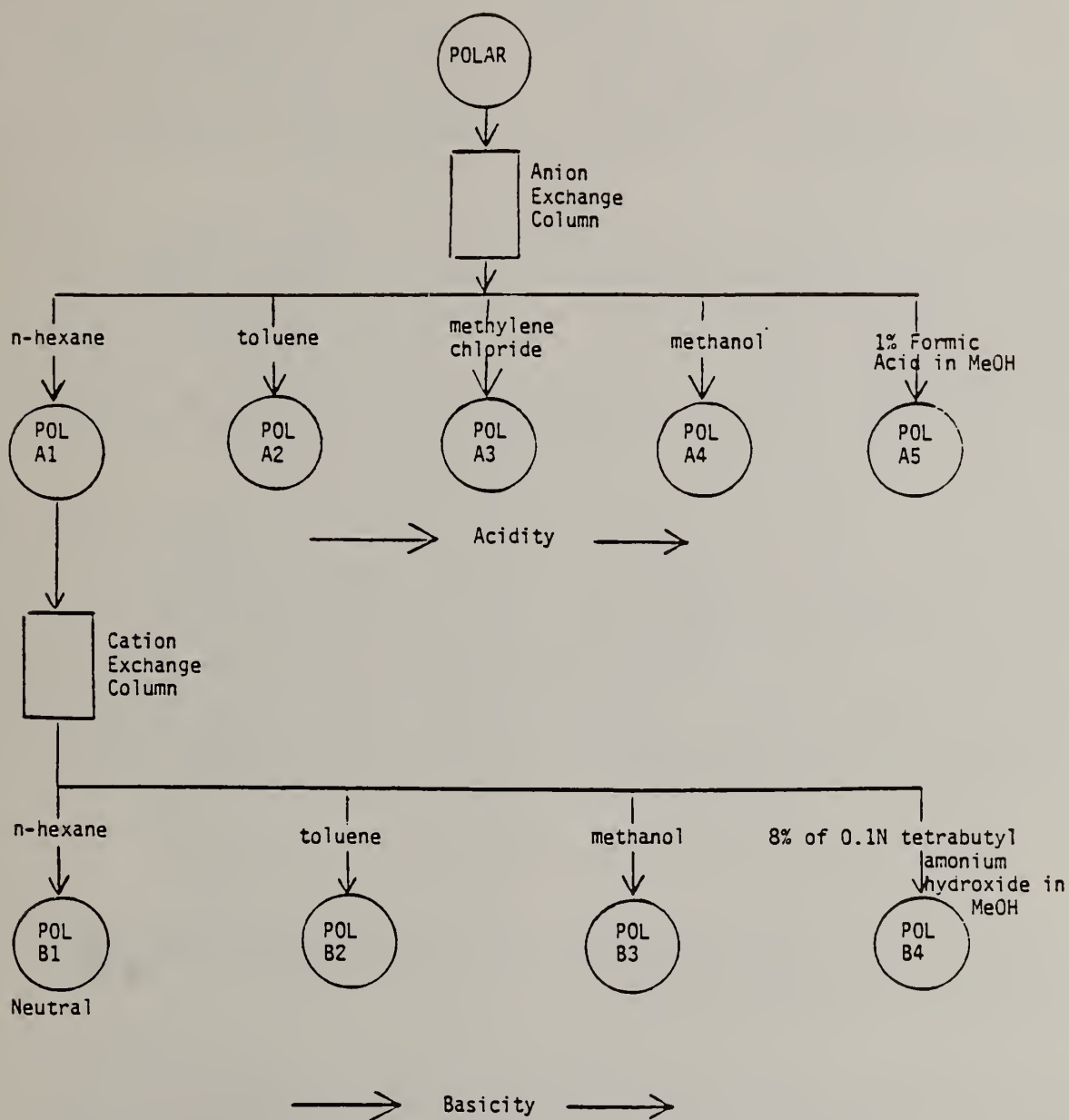A new separation scheme using a neutral alumina column was developed.

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FIGURE 12. SEPARATION SCHEME OF THE ION–EXCHANGE COLUMN

CHROMATOGRAPHIC METHOD

A glass column, 45 cm long by 1 cm I.D. having a 100 mL reservoir was used for the separation of the polar fraction. The column has a tapered-end tip. The other end of the column is fitted with a 100 mL reservoir, on top of which is a ground-glass socket so that 4 psig of back pressure can be applied to the column. A glass wool plug is placed at the bottom of the column. Another glass wool plug is placed on the top of the packed adsorbent to protect it from flow disturbances when eluting solvents are added. Twenty-five grams of neutral alumina adsorbent are added to the column in small increments, and the column is packed uniformly with the aid of a vibrator.

Approximately 1 gram of the polar fraction was dissolved in 50 mL n-hexane. The solution was then charged onto the alumina in the glass column. The following step-gradient elution scheme was used to elute the polar sub-fractions according to their polarities: 125 mL n-hexane, 100 mL toluene, 200 ml chloroform with 0.75 percent ethanol, 200 mL of 10 percent ethanol in tetrahydrofuran, and 200 ml methanol. Five subfractions were obtained. However, the first subfractions contain only a negligible amount of saturates, and the last two subfractions were combined due to small quantities eluted. As a result, three subfractions were isolated and studied.

The three polar subfractions were carefully characterized using infrared, high resolution mass spectroscopy, and elemental analysis. The first subfraction was found to consist of mainly polynuclear aromatics with esters, phthalates, and amides. The second subfraction consisted of amines and amides, and the third subfracation was found to be mainly oxygenated molecules with phenolic structures (oxygen content 25.4% by weight). There were some nitrogen compound classes overlapping among the subfractions, but no molecular rearrangement occurred on the column. The major limitation of this method appears to be the small size of the isolated sample. Thus, effort in developing a HPLC version of this procedure was underway.

2.6 PREPARATIVE HPLC NEUTRAL ALUMINA COLUMN SEPARATION PROCEDURE FOR POLAR SEPARATION

A preparative HPLC method based on the neutral alumina column method was developed. The separation scheme is shown schematically in Figure 13. The procedure is described below.

About 770 grams of neutral alumina is used to pack a column 33 cm long by 5 cm I.D. The packed column is placed in the chromatographic chamber of the preparative HPLC unit. After the chamber has been radially compressed to 3.0 MPa (30 atm.), 100 mL of n-hexane was pumped onto the column. Then a sample of 5 g of polar fraction dissolved in 100 m of n-hexane was pumped onto the column at the rate of 50 mL/min. After the sample has been pumped onto the column, 40 mL of n-hexane was pumped through at the same rate. One liter of toluene followed.

FIGURE 13. SEPARATION SCHEME OF THE NEUTRAL ALUMINA COLUMN
CHROMATOGRAPHIC METHOD
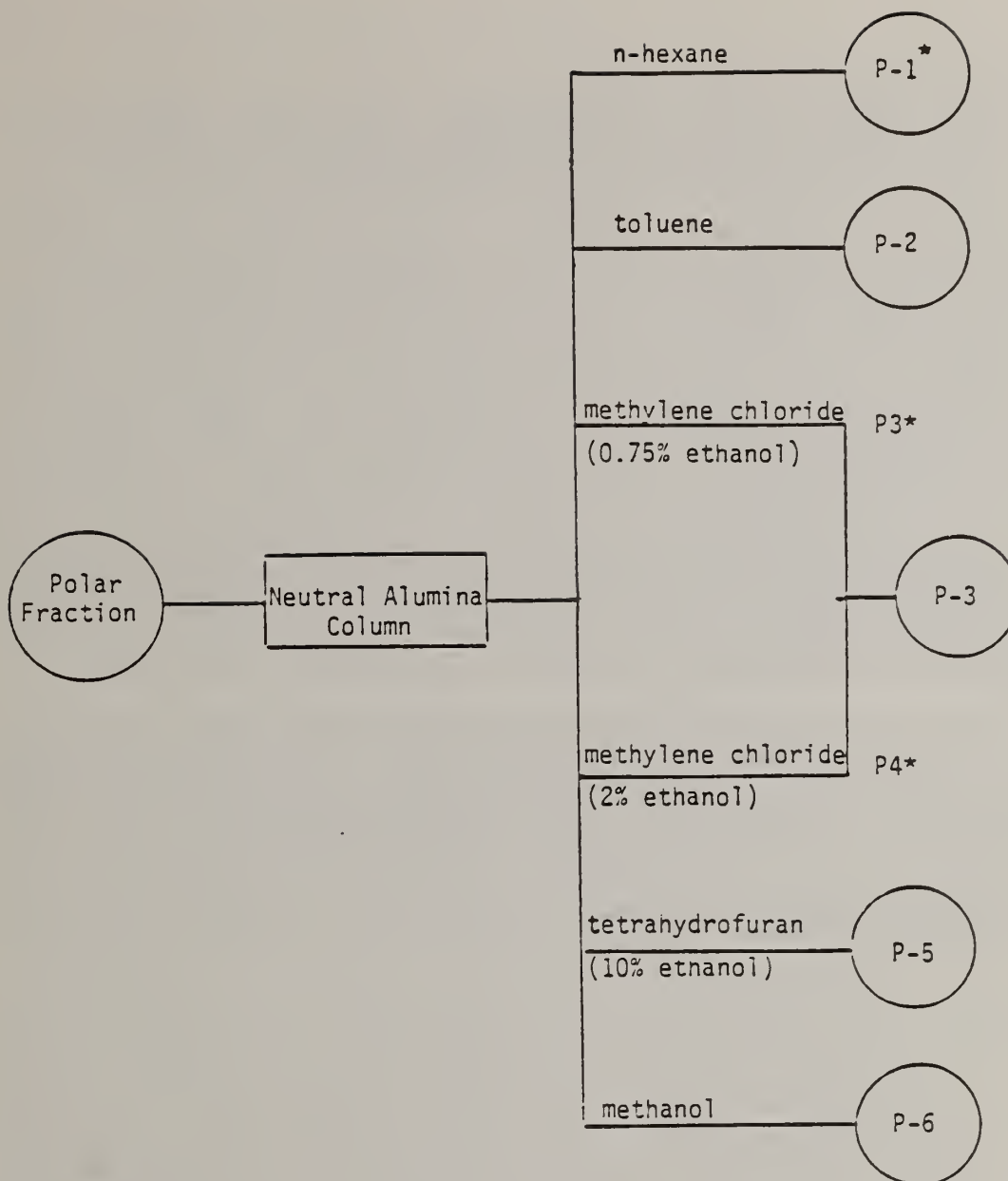
*P-1 contains only a small amount of saturates, therefore, it is not
characterized P3 and P4 are combined into one P3 fraction due to
similar characteristics.

After the toluene, the following solvent systems were sequentially
pumped onto the column at the 50 mL/min rate.   They are :
one liter of 0.75% ethanol in methylene chloride; 2% ethanol
in methylene chloride; 10% ethanol in tetrahydrofuran; and finally
two liters of methanol. All together six subfractions were collected.
The first subfraction collected was the 600 mL n-hexane and it is
designated as P1 subfraction. This subfraction was found to contain only an
insignificant quantity of saturate compounds and therefore was not
studied. The second subfraction designated as P2 is the one liter of
toluene eluent. The third and fourth subfractions are the two liters
of methylene chloride with 0.75% and 2% ethanol. These two subfractions
were combined to produce the P3 subfraction. One liter of 10% ethanol
in tetrahydrofuran was collected as P5 subfraction. The remaining
1.5 liters of methanol is collected as P6 subfraction. All five sub-
fractions were separately evaporated to dryness using a Rotavap. When
the fraction approached dryness, evaporation was completed under a
nitrogen atmosphere. The fractions were dried to a constant weight
and their weights recorded. To determine mass balance, the sample
from the detector was also collected, evaporated, and weighed.

Three base oils of 150N, 300N, and 600N from mid-eastern crude were
separated using the HPLC method described in section 2.3 to generate
the polar fractions. The polar fractions were then separated using
the method described above. Detailed characterization of the polar
subfractions is described in the next section and will not be
duplicated here. It is suffice to say that the separation is found
to be satisfactory in isolating molecules of varying polarity for
subsequent testing.

3. ANALYTICAL CHARACTERIZATION OF FRACTIONS

Three lubricating base oils were selected for detailed characterization and evaluation. These base oils represent the typical commercially available base oils of 150N, 300N, and 600N viscosity grades from mid-eastern crudes. Detailed physical and chemical properties of these oils are shown in Table 8.

The schematic separation scheme for these three base oils is shown in Figure 14. Each oil is first separated into a saturate/aromatic hydrocarbon fraction and a polar fraction on a clay column. The saturate/aromatic hydrocarbon fraction is further separated into a saturates fraction and an aromatics fraction on a dual packed, alumina/silica gel column. The detailed separation procedures have been described in section 2.3 The polar fraction is further separated on a neutral alumina absorbant to obtain four subfractions containing mainly four different compound classes such as polynuclear aromatic compounds, nitrogen-containing compounds, ester, and phenol type of compounds, and carboxylic acidic type of compounds. The detailed separation procedures are described in section 2.6. These three steps provide the flexibility necessary to optimize the separation of the base oils and the isolation of the major polar molecular compounds.

The weight percent data of each fraction of the original base oil are shown in Table 9. It can be seen that the polar molecules are generally less than one percent of the base oils, yet they exert significant influence on oxidation stability and friction performance of the base oils.

Each major fraction and compound class was characterized chemically by analytical methods such as IR, mass spectroscopy, gel permeation chromatography. In addition to analytical characterization, performance evaluation tests were performed on these fraction and compound classes. The performance tests include antioxidant capacity titration method and micro sample step loading wear tests which determine oil's resistance to wear under boundary lubricating conditions. This section will describe the detailed analytical characterizations of the fractions and their subfractions. High resolution mass spectroscopy data for all the fractions and subfractions are shown in appendix D for reference.

3.1 150N MID-EAST BASE OIL

3.1.1 150N SATURATE FRACTION CHARACTERIZATION

The physical properties of the saturate fraction are shown in Table 10. The Viscosity Index (VI) of the saturate fraction increases
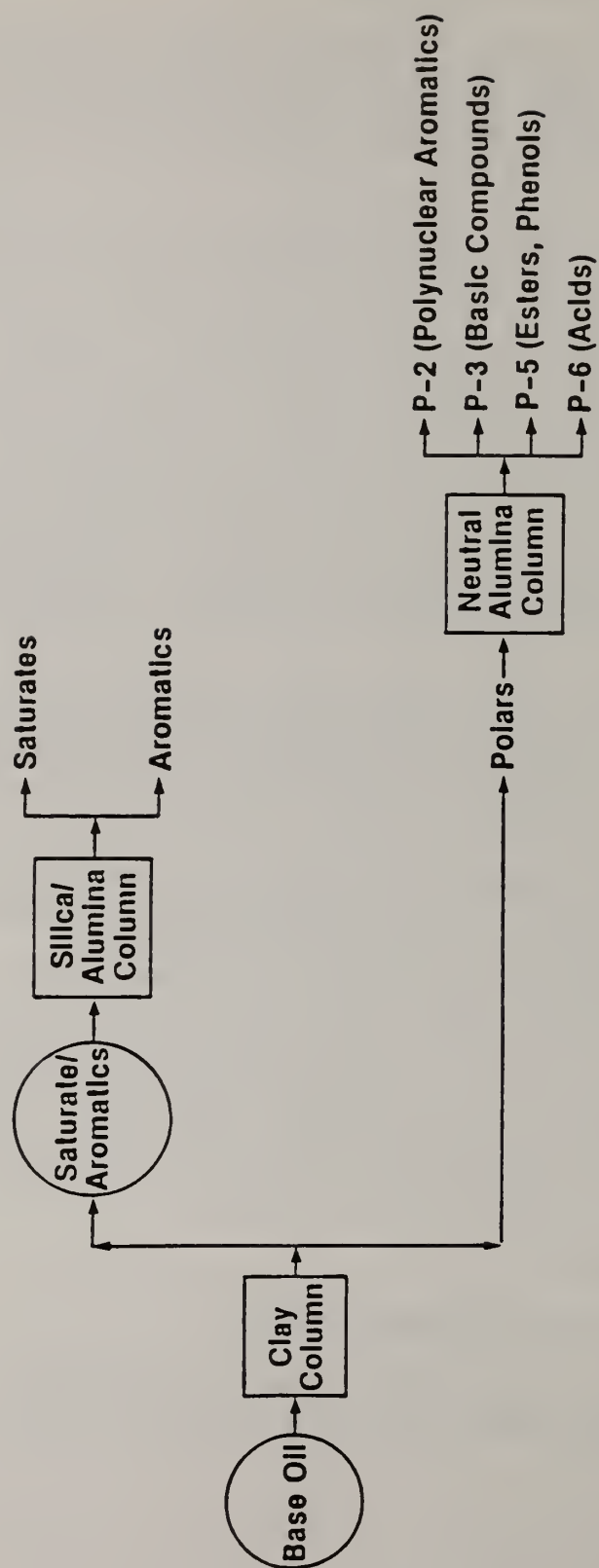
FIGURE 14. SEPARATION SCHEME of the BASE OIL INTO FRACTIONS and COMPOUND CLASSES

Table 8

Chemical and Physical Properties of the Base Oils

	150N Mid-East	300N Mid-East	600N Mid East
Kinematic Viscosity 40 ^{o}C	30.25	53.16	107.65
Kinematic Viscosity 100 ^{o}C	5.23	7.48	11.53
Refractive Index	1.4819	1.4814	1.4904
Density (gm/cm^3)	0.86990	0.87151	0.88749
Pour Point (^{o}C)	-15	-7	-10
Flash Point (^{o}C)	235	241	244
Sulfur (wt. %)	0.49	0.36	0.67
Tan (mg KOH/g)	0	0	0.022
TBN (mg KOH/g)	-	-	0.343
Moisture ppm	95	139	65
Chlorine (ppm)	0.16	2.9	2.9
Bromine (ppm)	0	< 0.02	0.02
Sulfated Ash (wt %)	0	0	0
Carbon Residue	0.03	0.03	0.16
Total Nitrogen (ppm)	42	58	114
Boiling Point, ^{o}C IBP	286	343	313
5% off	349	410	405
10% off	375	426	434
50% off	451	477	498
90% off	498	532	552
Hydrocarbon Types			
Saturates, wt%	67.0	78.0	63.0
Aromatics, wt%	32.5	21.4	35.3
Polars, wt%	0.5	0.6	1.7

Table 9

Weight Percentage Distribution of Fractions and Polar Subfractions

				Polar Subfractions			
Oil Sample	Saturates	Aromatics	Polars	P2	P3	P5	P6
150N	65.8	32.8	0.32	0.04	0.14	0.09	0.03
300N	74.8	24.5	0.40	0.08	0.08	0.19	0.02
600N	64.5	34.5	0.80	0.17	0.45	0.04	0.01

Table 10

Physical Properties of the Base Oils
and the Base Oil Fractions

	Viscosity, cSt 40 °C	100 °C	Viscosity Index	Avg. Molecular Weight	Refractive Index
150N					
Base Oil	30.3	5.2	103	402	1.4830
Saturate	25.1	4.8	116	404	1.4693
Aromatic	60.0	7.0	58	396	1.5134
300N					
Base Oil	53.2	7.5	102	459	1.4816
Saturate	46.1	7.0	109	457	1.4749
Aromatic	162.4	11.7	34	436	1.5214
600N					
Base Oil	107.7	11.5	93	520	1.4907
Saturate	73.4	9.7	109	520	1.4769
Aromatic	95.5	11.0	99	524	1.5039

from 103 to 116 when compared to the original base oil. The refractive index (RI) of the fraction decreases from 1.4819 to 1.4693. Both data indicate that the saturate fraction has predominately paraffinic molecules. The average molecular weight derived from the viscosity data suggests that the saturate fraction is similar to base oil (402 vs. 404).

However, the measured molecular weight distribution profile by gel permeation chromatography (Figure 15) of the saturate fraction shows that the saturate fraction has more of the higher molecular weight distribution within the base oil molecular weight profile. The molecular weight scale of the gel permeation chromatography is calibrated with polystyrene and hydrocarbon standards of known molecular weight.

The saturate fraction as separated is found to be relatively free of aromatic and heteroatom compounds. The infrared (IR) spectrum of the saturate fraction (shown in Figure 16b) is free of aromatic band at 1600 cm^{-1} and also the carboxyl and hydroxyl bands at 1700 and 3400 cm^{-1}. The presence of CH_2 band at 720 cm^{-1} is strong. The purity of the saturate fraction is again confirmed by the elemental analysis results as shown in Table 11. The carbon and hydrogen content of the fraction has accounted for about 99.9% of the material, and so there are relatively no heteroatom compounds detected in the saturate fraction.

3.1.2   150N AROMATIC FRACTION CHARACTERIZATION

The physical properties of the aromatic fraction are shown in Table 10. The VI of the fraction has decreased from 103 (base oil) to 58 (aromatic) indicating the decrease of the paraffinic content, and the RI has increased from 1.4830 (base oil) to 1.5134 (aromatic) suggesting predominately the presence of aromatic compounds. The average molecular weight derived from the viscosity data of the fraction is similar to that of the base oil, but the measured molecular weight profile of the fraction as shown in Figure 15 indicates that the aromatic fraction contains more lower molecular weight compounds than the saturate fraction. Elemental analysis results (Table 11) indicate a large concentration of sulfur compounds associated with the aromatic structures. The sulfur content of the fraction is 1.5%. These sulfur compounds appear to be thiophenes. The IR spectrum of the aromatic fraction is shown in Figure 16c. The aromatic band at 1600 cm^{-1} is very pronounced. It does not have carbonyl and hydroxyl bands at 1700 cm^{-1} and 3400 cm^{-1}.
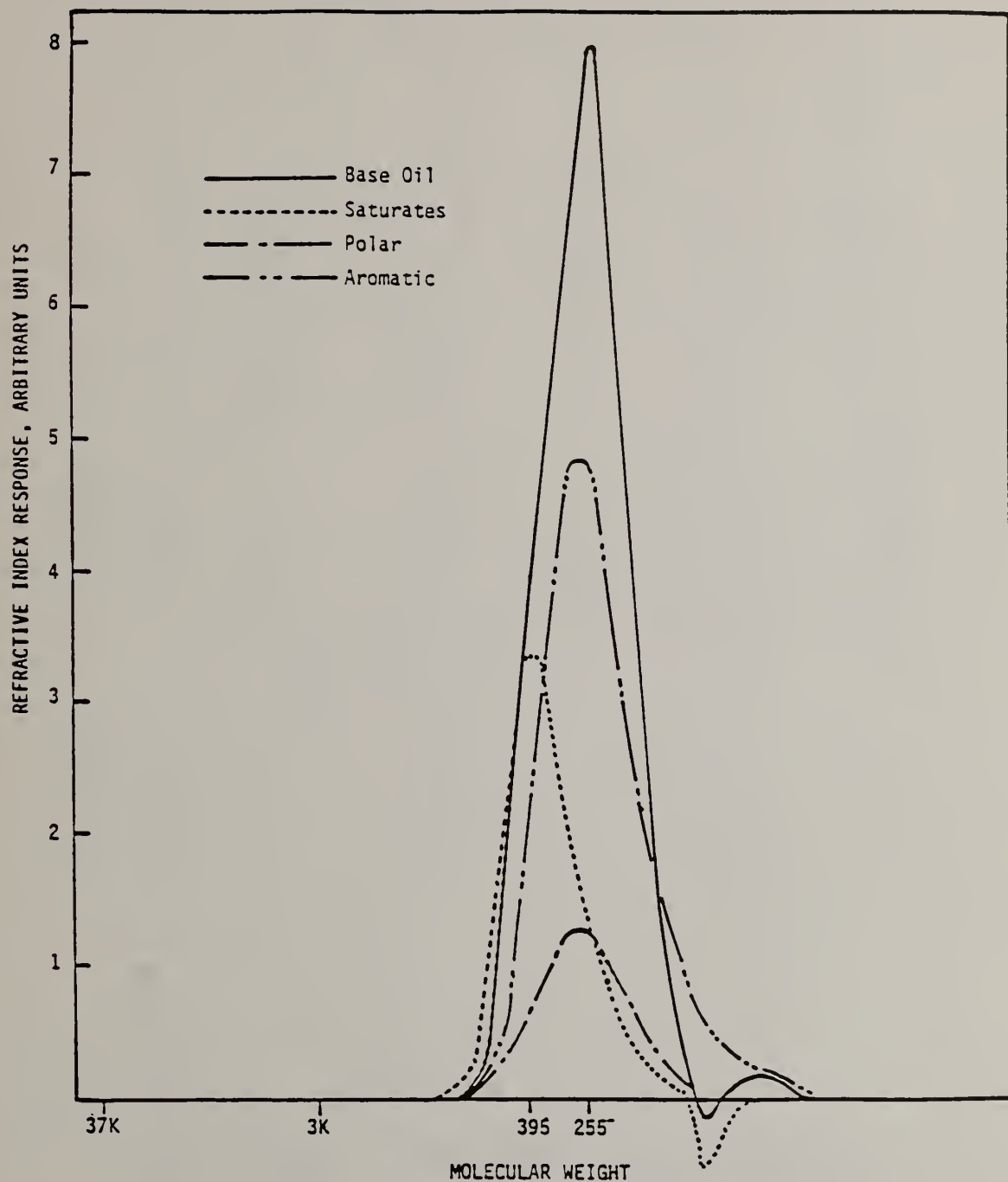
FIGURE 15. MOLECULAR WEIGHT DISTRUBITON OF 150N
BASE OIL AND BASE OIL FRACTIONS
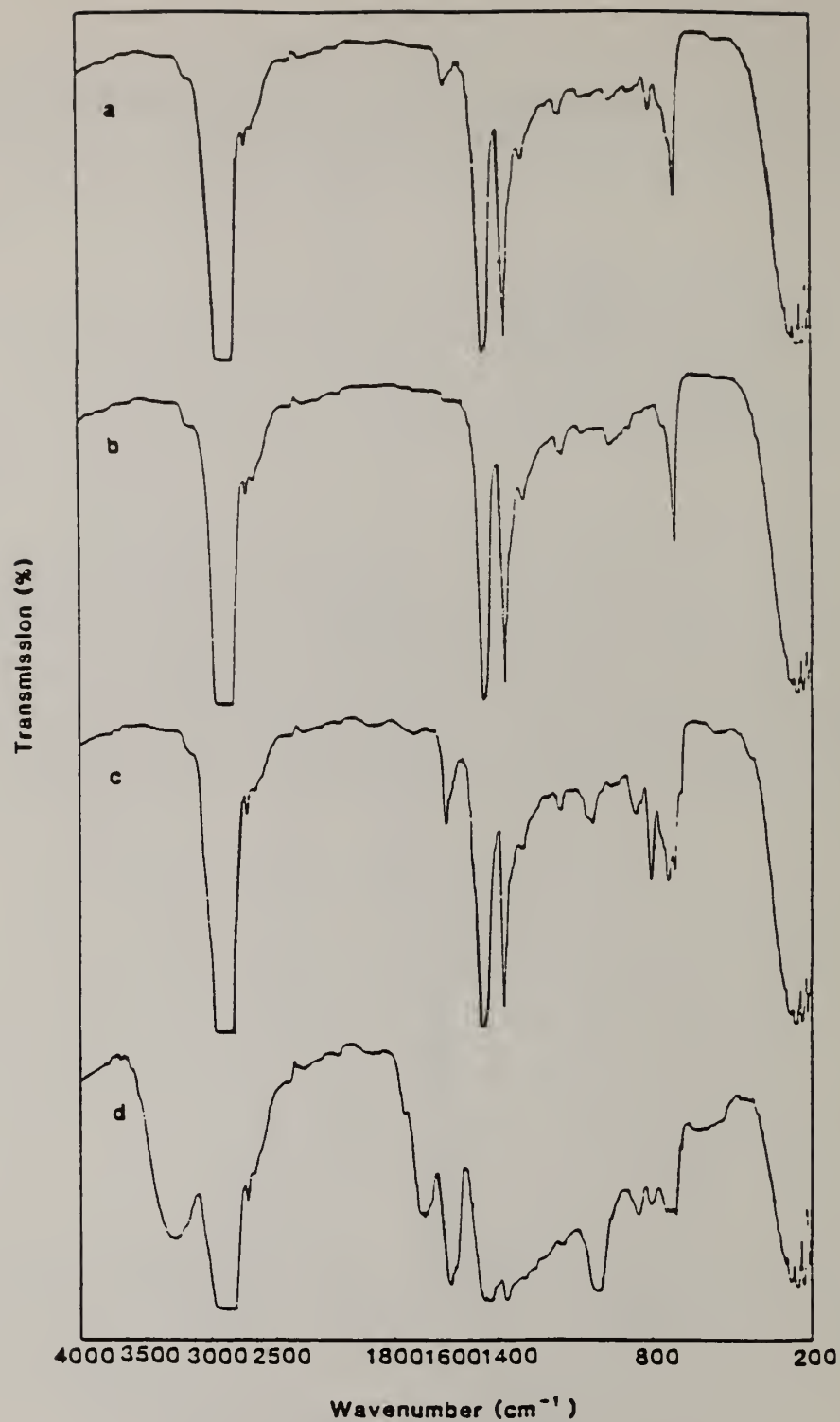
FIGURE 16. INFRARED SPECTRA OF HYDROCARBON
FRACTIONS OF THE 150N BASE OIL:

a) BASE OIL; b) SATURATE FRACTION;
c) AROMATIC FRACTION; d) POLAR FRACTION

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Table 11

Elemental Analyses of the Base Oils and the Base Oil Fractions

	Weight %				
150N	C	H	N	S	O
Base Oil	86.2	13.2	< 0.01	0.42	< 0.3
Saturate	85.9	14.0	< 0.01	0.01	< 0.3
Aromatic	86.7	11.8	< 0.01	1.54	< 0.3
Polar	82.6	11.3	1.8	2.83	1.6
300N					
Base Oil	86.2	13.2	< 0.01	0.33	0.34
Saturate	86.3	13.8	< 0.01	0.01	< 0.3
Aromatic	86.3	11.8	< 0.01	2.26	< 0.3
Polar	83.2	11.5	1.4	1.68	1.5
600N					
Base Oil	86.1	13.2	0.02	0.69	< 0.3
Saturate	86.4	13.5	< 0.01	0.09	< 0.3
Aromatic	85.9	13.0	0.01	1.24	< 0.3
Polar	84.3	11.5	1.2	2.19	0.8

3.1.3 150N POLAR FRACTION CHARACTERIZATION

The polar fraction is dark, viscous, and available in very small quantities. Therefore, kinematic viscosities and refractive index measurements are not made. The molecular weight profile of the polar fraction is approximately in the same range as the base oil.

For chemical characterization of the polar fraction, elemental analysis, High Resolution Mass Spectrometry (HRMS), and Infrared Spectrophotometry (IR) were used. The polar fraction appears to contain large amount of sulfur-, nitrogen-, and oxygen-containing molecules relative to other fractions, as evidenced by the elemental analysis results in Table 11. The infrared spectrum shown in Figure 16 indicates the following bonds are distinctly present: NH/OH at 3400 cm^{-1}, C=O at 1700 cm^{-1}, and aromatic structure at 1600 cm^{-1}.

The existence of these molecular bonding is further supported by HRMS results (Appendix D). Substituted thiophene, pyridine, indoles, quinoline, carbazoles, phthalates, phenols, and carboxylic acids functional groups have been identified. At this stage, the polar fraction is still very complex and further separation is needed to identify molecular compound classes.

3.1.4 COMPARISON OF THE 150N FRACTIONS

The separation of the 150N base oil into saturates, aromatics, and polars is relatively clean as evidenced by the IR and elemental analyses. Most of the heteroatom compounds appear to be concentrated in the polar fraction. Sulfur compounds appear in two groups: the non-polar sulfur compounds such as thiophenes collected in the aromatic fraction and the polar sulfur compounds are collected in the polar fraction.

Molecular weight profiles of the fractions as shown in Figure 15 show that the saturates have slightly higher molecular weight than the aromatic and the polar fractions, which have nearly the same molecular weight range as the base oil.

3.1.5 150N P-2 POLAR SUBFRACTION

The polar fraction of the 150N is separated on a neutral alumina HPLC column as described in section 2.5.1. The four subfractions collected are designated as P-2, P-3, P-5, and P-6. P-2 is the subfraction eluted with toluene and therefore should contain predominately aromatic structures. Elemental analysis results shown in Table 12 suggest that P-2 contains the least amount of oxygen. The molecular weight distribution as shown in Figure 17 indicates that P-2 contains more low molecular weight compounds compared with other polar subfractions from the same base oil. The infrared spectrum in Figure 18a suggests little or no oxygen-hydrogen bonds at 3400 cm^{-1} or carbon-oxygen carbonyl bonds at 1700 cm^{-1} wavenumbers. The aromatic structure at 1600 cm^{-1} wavenumber is very

Table 12

Elemental Analyses of the Polar and the Polar Subfractions

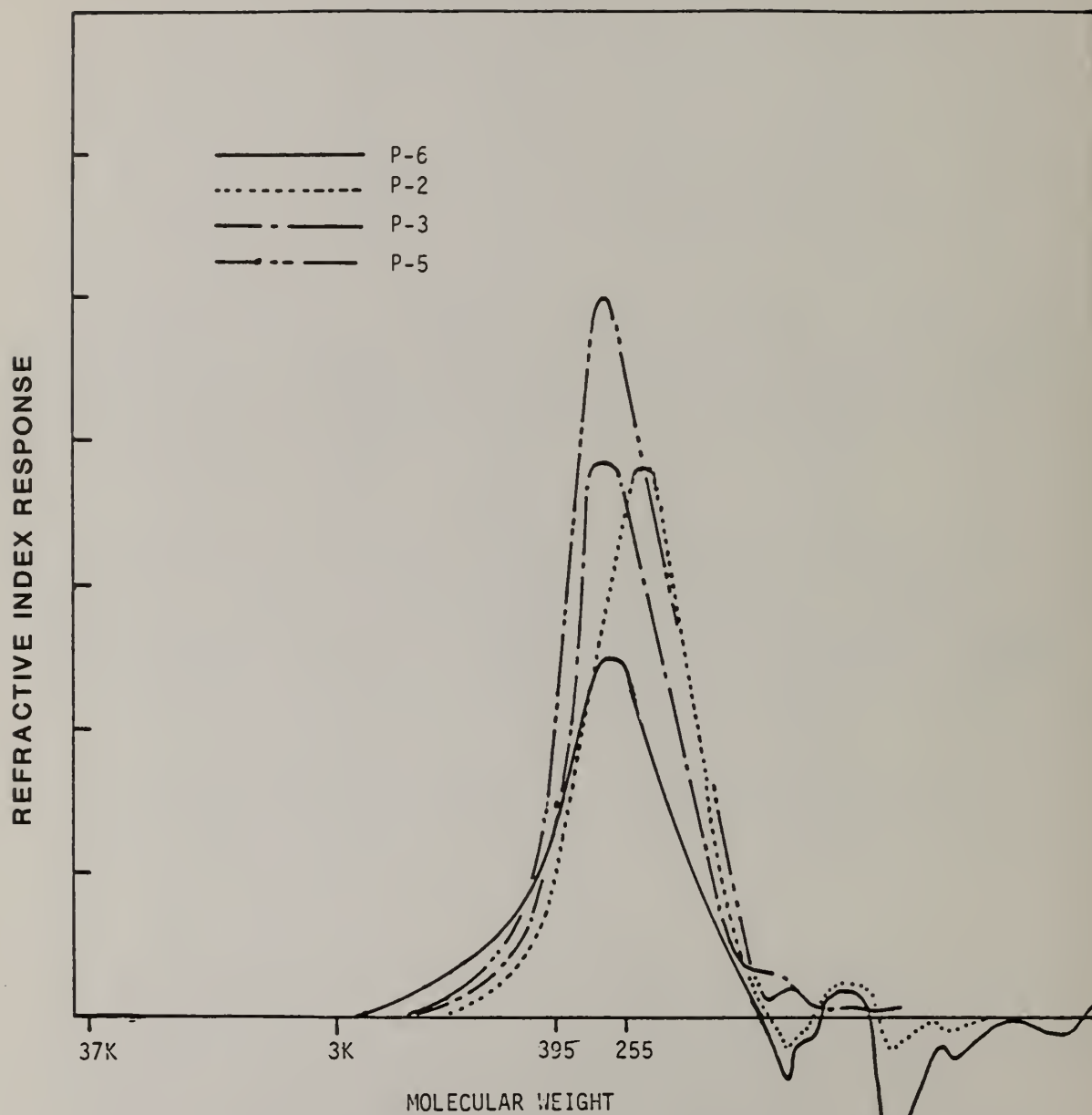|	Weight %				
	C	H	N	S	O
150N					
Polar	82.6	11.3	1.8	2.83	1.6
P-2	84.1	11.2	1.6	2.71	0.7
P-3	82.4	11.4	1.6	2.66	2.1
P-5	81.0	11.3	1.2	3.52	3.2
P-6	75.3	10.0	1.0	3.11	7.3
300N					
Polar	83.2	11.5	1.4	1.68	1.5
P-2	85.0	11.4	< 0.01	1.60	0.4
P-3	83.9	10.9	1.9	2.28	1.2
P-5	83.7	11.5	1.3	1.65	1.8
P-6	82.5	12.7	0.2	0.47	4.3
600N					
Polar	84.3	11.5	1.2	2.19	0.8
P-2	84.5	11.6	1.1	2.53	0.6
P-3	84.0	11.7	1.3	1.78	1.1
P-5	82.1	11.4	0.8	2.53	2.9
P-6	67.9	9.8	0.8	1.21	17.0

FIGURE 17. MOLECULAR WEIGHT DISTRIBUTION OF THE
POLAR SUBFRACTIONS OF THE 150N BASE OIL

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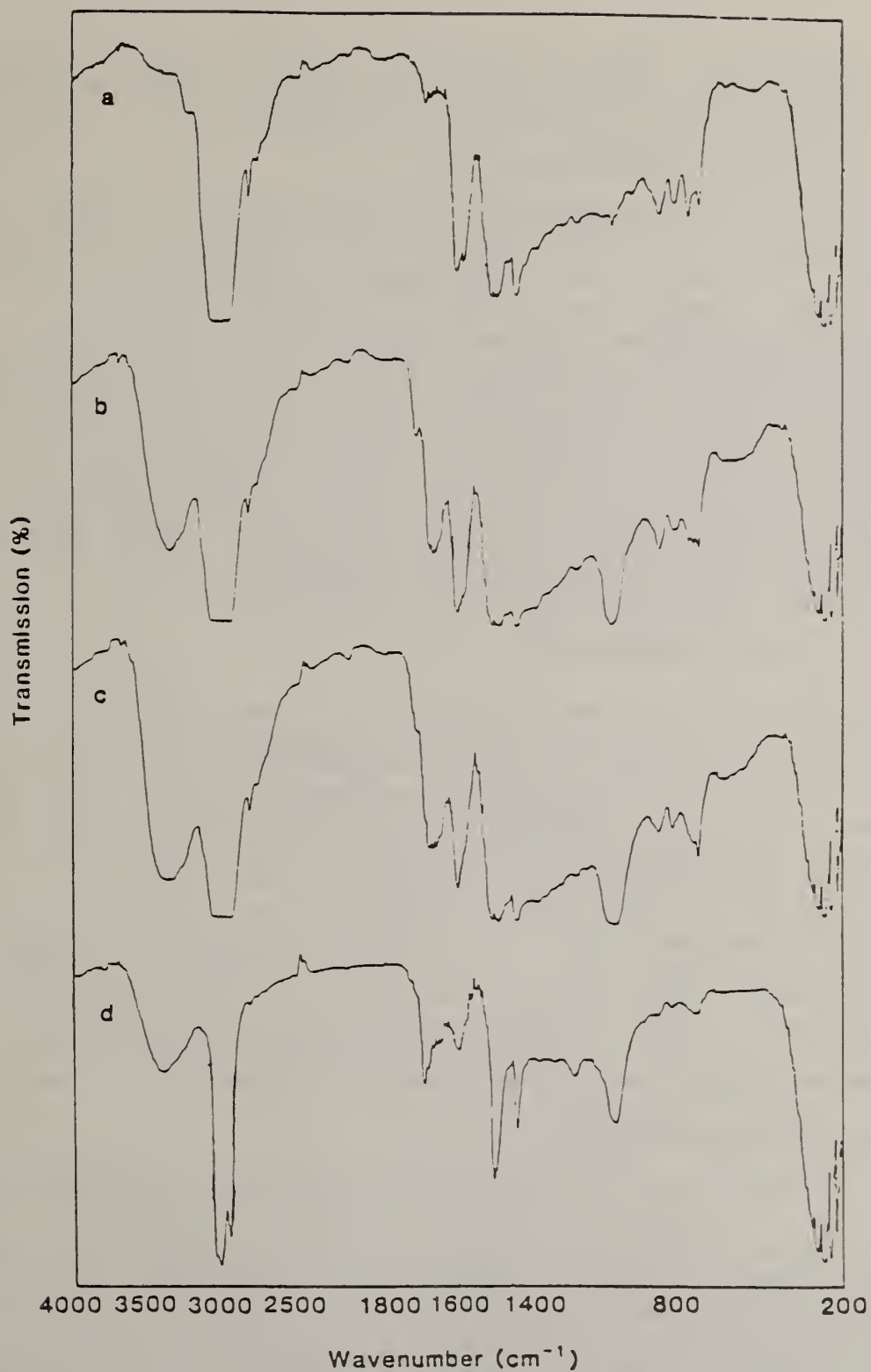
FIGURE 18. INFRARED SPECTRA OF POLAR SUBFRACTIONS
OF THE 150N BASE OILS:

a) P-2 SUBFRACTION; b) P-3 SUBFRACTION
c) P-5 SUBFRACTION; d) P-6 SUBFRACTION

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strong, thus confirming the predominately aromatic nature of the P-2 subfraction. High resolution mass spectroscopy results suggest the presence of thiophenes and benzothiophenes.

3.1.6 150N P-3 POLAR SUBFRACTION

Subfraction P-3 is eluted from the neutral alumina column with methylene chloride solution containing low concentrations of ethanol (0.75% - 2% by weight) and should contain moderately polar compounds. Elemental analysis results in Table 12 suggest that the oxygen content has increased significantly from 0.7% to 2.1% relative to P-2. The molecular weight distribution (Fig. 17) indicates that P-3 contains mostly the same molecular weight compounds from the same base oil but with a tailing distribution of high molecular weight materials to about 1500. The infrared spectrum in Figure 18b suggests possible nitrogen-hydrogen amine bond at 3300 cm^{-1} and strong carbonyl bonds in the 1690 cm^{-1} region indicating possible amides, Possibly sulfoxides are present in P-3, as indicated by the strong 1030 cm^{-1} bond. High resolution mass spectroscopy results suggests the presence of quinolines, and carbazoles as nitrogen compounds.

3.1.7 150N P-5 Subfraction

Subfraction P-5 is eluted from the neutral alumina column with a stronger polar solvent of 10% ethanol in tetrahydrofuran. This sub-fraction should contain more polar compounds which have higher oxygen and sulfur content as indicated by the elemental analysis results shown in Table 12. The molecular weight distribution as shown in Figure 17 indicates that P-5 contains more higher molecular weight compounds than P-2 and P-3 subfractions from the same base oil. The infrared spectrum of the P-5 subfraction in Figure 18c is similar to the IR spectrum of the P-3 subfraction, suggesting the presence of nitrogen-hydrogen, amine bond at 3300 cm^{-1}; carbon-oxygen bond at 1700 cm^{-1}; aromatic carbon at 1600 cm^{-1}; and sulfur-oxygen bond at 1030 cm^{-1}. High resolution mass spectroscopy of the P-5 subfraction suggest the presence of quinolines and carbazoles for nitrogen compounds and thiophenes for sulfur compounds.

3.1.8 150N P-6 SUBFRACTION

The P-6 subfraction is eluted from the neutral alumina column with methanol. This subfraction contains the most polar compounds of the polar fraction and consists predominately of oxygenated compounds. Elemental analyses shown in Table 12 confirm that P-6 contains the highest proportion of oxygen (7.3%) among the polar subfractions. The molecular weight distribution of the P-6 subfraction as shown in Figure 17 indicates that P-6 contains the most high molecular weight compounds (about 3000) compared to the other polar subfractions from the same base oil. The infrared spectrum shown in Figure 18d shows a strong IR absorption at 3350 cm^{-1}, suggesting that a phenolic-OH group for the high

oxygen content of this subfraction. This is confirmed by the high resolution mass spectroscopy results (Appendix D) indicating the presence of phenolic alcohol in the P-6 subfraction. The absorption peak at 1735 cm^{-1} suggests the presence of esters and sulfoxide peak (1030 cm^{-1}) is also present. High resolution mass spectroscopy results suggest the presence of quinolines, thiophenes, and phenols.

3.1.9 SUMMARY OF 150N POLAR SUBFRACTIONS

The chromatographic separation of the 150N polar fraction was achieved on a neutral alumina column and various molecular compounds were eluted off the column with solvents of different polarity. P-2 subfraction contains the least polar compounds and P-6 subfraction contains the most polar compounds. Elemental analysis results shown in Table 12 suggest the P-2 subfraction has the least amount of oxygen while the P-6 sub-fraction has the most, while sulfur and nitrogen molecules are distributed evenly among the four subfractions. Infrared spectra shown in Figure 18 suggest that P-2 subfraction contains predominantly aromatic compounds; P-3 and P-5 subfractions contain amides, sulfoxides, and esters; P-6 sufraction contains phenols, and esters. High resolution mass spectroscopy data (Appendix D) suggests the presence of the following probable compounds in each subfraction:

1. P-2, aromatic compounds;

2. P-3, thiophenes, amides, and sulfoxides;

3. P-5 carbazoles, quinolines, amides, and sulfoxides; and

4. P-6, phenols, esters, acids, and sulfoxides.

3.2 300N MID-EAST BASE OIL

3.2.1 300N SATURATE FRACTION CHARACTERIZATION

The 300N is a heavier cut than the 150N, i.e., the boiling points and molecular weights are higher. The saturate fraction of the 300N is obtained by the HPLC separation scheme (section 2.3). It has higher viscosities and average molecular weight than the 150N saturates. The physical property data are presented in Table 10.

Again, the saturate fraction of the 300N oil is pure when compared to the base oil. The paraffinic content is high as evidenced by the increase of viscosity index from 102 to 109 and the decrease of refractive index from 1.4816 to 1.4749. The molecular weight distribution of the saturate fraction is similar to those of the base oil as shown in Figure 19.
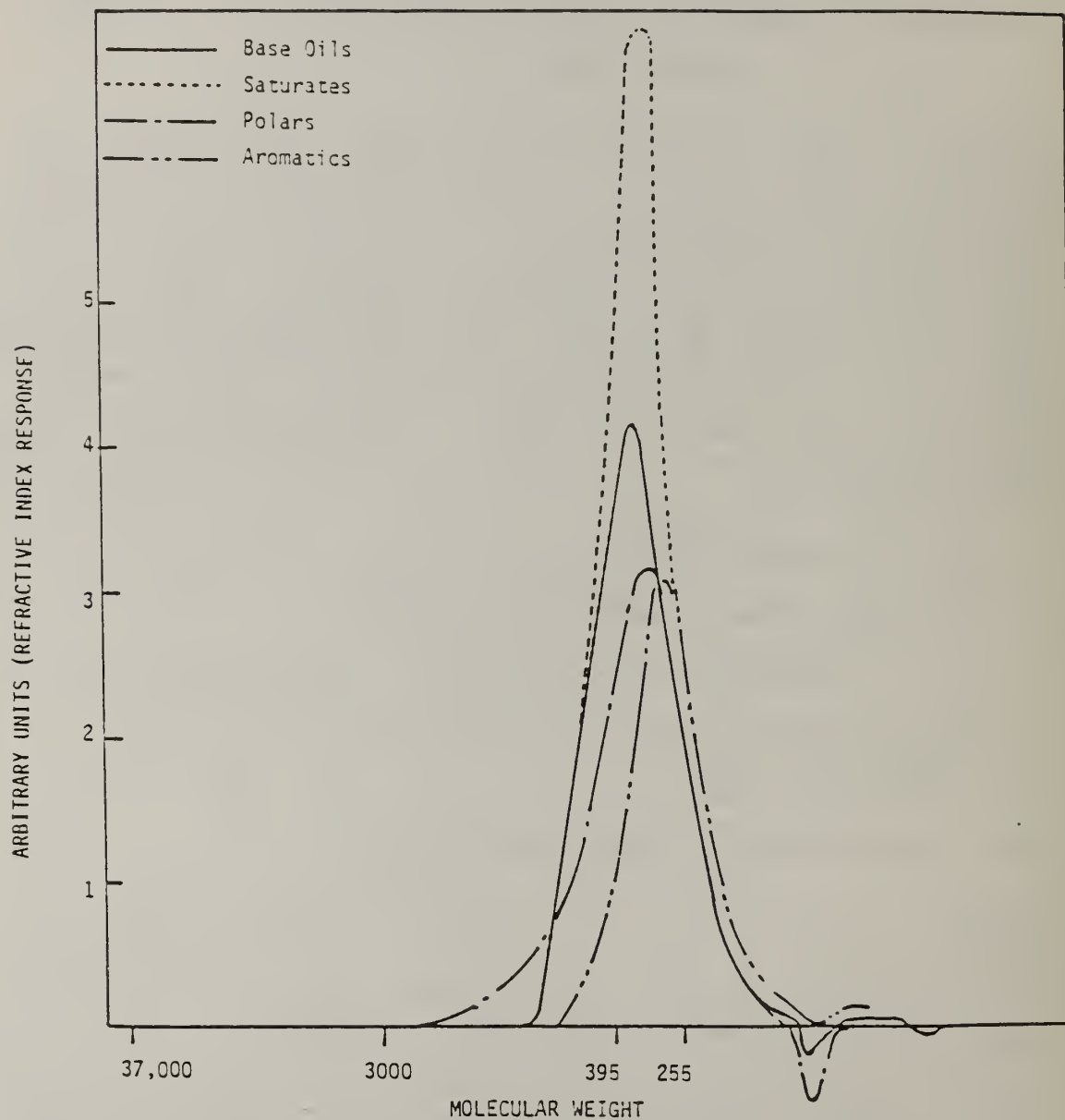
FIGURE 19. MOLECULAR WEIGHT PROFILE OF THE 300N BASE OIL
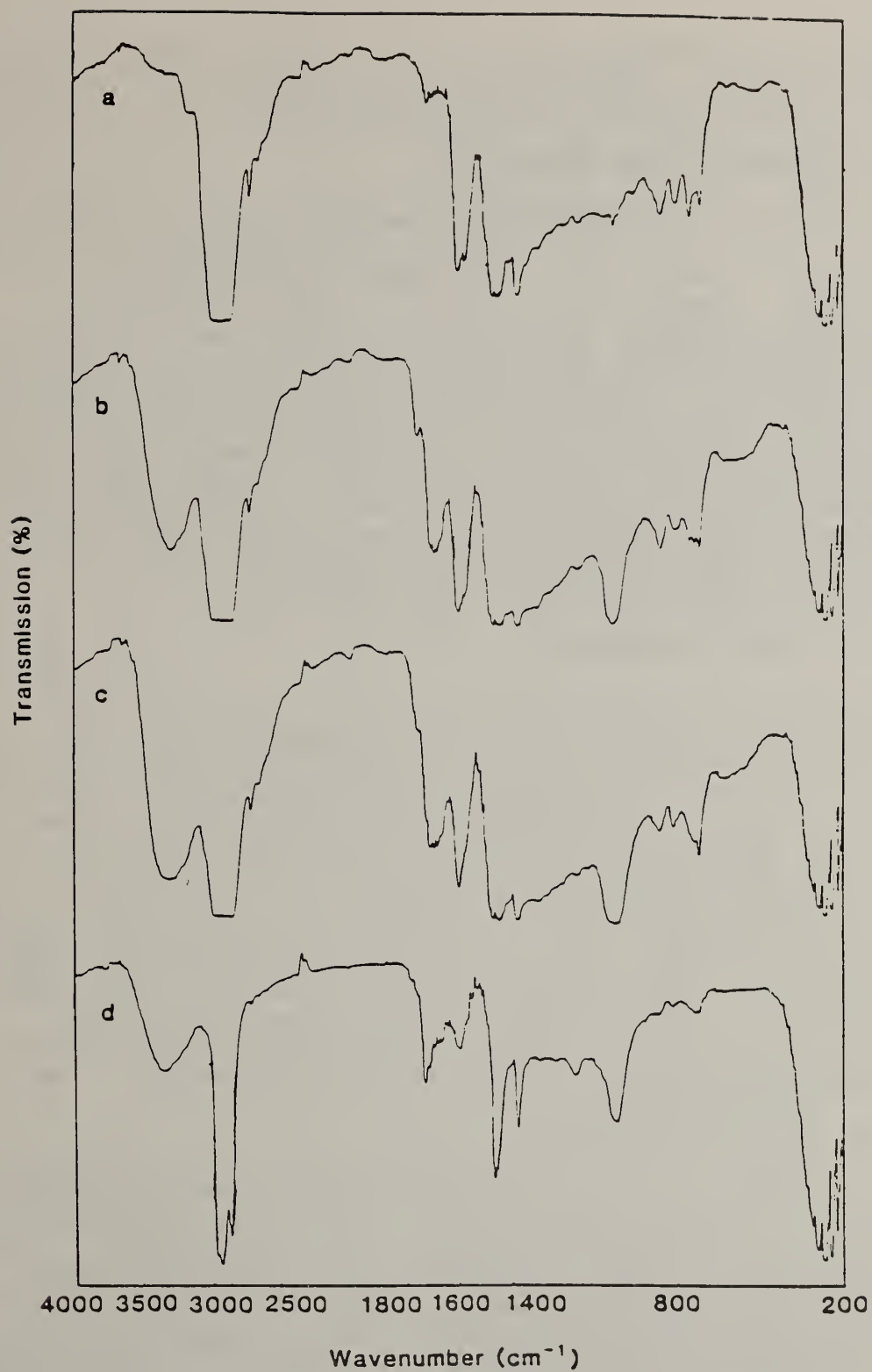AND ITS FRACTIONS

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FIGURE 18.   INFRARED SPECTRA OF POLAR SUBFRACTIONS
OF THE 150N BASE OILS:

a) P-2 SUBFRACTION; b) P-3 SUBFRACTION
c) P-5 SUBFRACTION; d) P-6 SUBFRACTION

strong, thus confirming the predominately aromatic nature of the P-2 subfraction. High resolution mass spectroscopy results suggest the presence of thiophenes and benzothiophenes.

3.1.6 150N P-3 POLAR SUBFRACTION

Subfraction P-3 is eluted from the neutral alumina column with methylene chloride solution containing low concentrations of ethanol (0.75% - 2% by weight) and should contain moderately polar compounds. Elemental analysis results in Table 12 suggest that the oxygen content has increased significantly from 0.7% to 2.1% relative to P-2. The molecular weight distribution (Fig. 17) indicates that P-3 contains mostly the same molecular weight compounds from the same base oil but with a tailing distribution of high molecular weight materials to about 1500. The infrared spectrum in Figure 18b suggests possible nitrogen-hydrogen amine bond at 3300 cm^{-1} and strong carbonyl bonds in the 1690 cm^{-1} region indicating possible amides. Possibly sulfoxides are present in P-3, as indicated by the strong 1030 cm^{-1} bond. High resolution mass spectroscopy results suggests the presence of quinolines, and carbazoles as nitrogen compounds.

3.1.7 150N P-5 Subfraction

Subfraction P-5 is eluted from the neutral alumina column with a stronger polar solvent of 10% ethanol in tetrahydrofuran. This subfraction should contain more polar compounds which have higher oxygen and sulfur content as indicated by the elemental analysis results shown in Table 12. The molecular weight distribution as shown in Figure 17 indicates that P-5 contains more higher molecular weight compounds than P-2 and P-3 subfractions from the same base oil. The infrared spectrum of the P-5 subfraction in Figure 18c is similar to the IR spectrum of the P-3 subfraction, suggesting the presence of nitrogen-hydrogen, amine bond at 3300 cm^{-1}; carbon-oxygen bond at 1700 cm^{-1}; aromatic carbon at 1600 cm^{-1}; and sulfur-oxygen bond at 1030 cm^{-1}. High resolution mass spectroscopy of the P-5 subfraction suggest the presence of quinolines and carbazoles for nitrogen compounds and thiophenes for sulfur compounds.

3.1.8 150N P-6 SUBFRACTION

The P-6 subfraction is eluted from the neutral alumina column with methanol. This subfraction contains the most polar compounds of the polar fraction and consists predominately of oxygenated compounds. Elemental analyses shown in Table 12 confirm that P-6 contains the highest proportion of oxygen (7.3%) among the polar subfractions. The molecular weight distribution of the P-6 subfraction as shown in Figure 17 indicates that P-6 contains the most high molecular weight compounds (about 3000) compared to the other polar subfractions from the same base oil. The infrared spectrum shown in Figure 18d shows a strong IR absorption at 3350 cm^{-1}, suggesting that a phenolic-OH group for the high

oxygen content of this subfraction. This is confirmed by the high
resolution mass spectroscopy results (Appendix D) indicating the presence
of phenolic alcohol in the P-6 subfraction. The absorption peak at
1735 cm^{-1} suggests the presence of esters and sulfoxide peak (1030 cm^{-1})
is also present. High resolution mass spectroscopy results suggest
the presence of quinolines, thiophenes, and phenols.

3.1.9 SUMMARY OF 150N POLAR SUBFRACTIONS

The chromatographic separation of the 150N polar fraction was achieved
on a neutral alumina column and various molecular compounds were eluted
off the column with solvents of different polarity. P-2 subfraction
contains the least polar compounds and P-6 subfraction contains the most
polar compounds. Elemental analysis results shown in Table 12 suggest
the P-2 subfraction has the least amount of oxygen while the P-6 sub-
fraction has the most, while sulfur and nitrogen molecules are distributed
evenly among the four subfractions. Infrared spectra shown in Figure 18
suggest that P-2 subfraction contains predominantly aromatic compounds;
P-3 and P-5 subfractions contain amides, sulfoxides, and esters; P-6
sufraction contains phenols, and esters. High resolution mass spectroscopy
data (Appendix D) suggests the presence of the following probable compounds
in each subfraction:

1. P-2, aromatic compounds;

2. P-3, thiophenes, amides, and sulfoxides;

3. P-5 carbazoles, quinolines, amides, and sulfoxides; and

4. P-6, phenols, esters, acids, and sulfoxides.

3.2 300N MID-EAST BASE OIL

3.2.1 300N SATURATE FRACTION CHARACTERIZATION

The 300N is a heavier cut than the 150N, i.e., the boiling points and
molecular weights are higher. The saturate fraction of the 300N is obtained
by the HPLC separation scheme (section 2.3). It has higher viscosities
and average molecular weight than the 150N saturates. The physical
property data are presented in Table 10.

Again, the saturate fraction of the 300N oil is pure when compared to the
base oil. The paraffinic content is high as evidenced by the increase
of viscosity index from 102 to 109 and the decrease of refractive index
from 1.4816 to 1.4749. The molecular weight distribution of the saturate
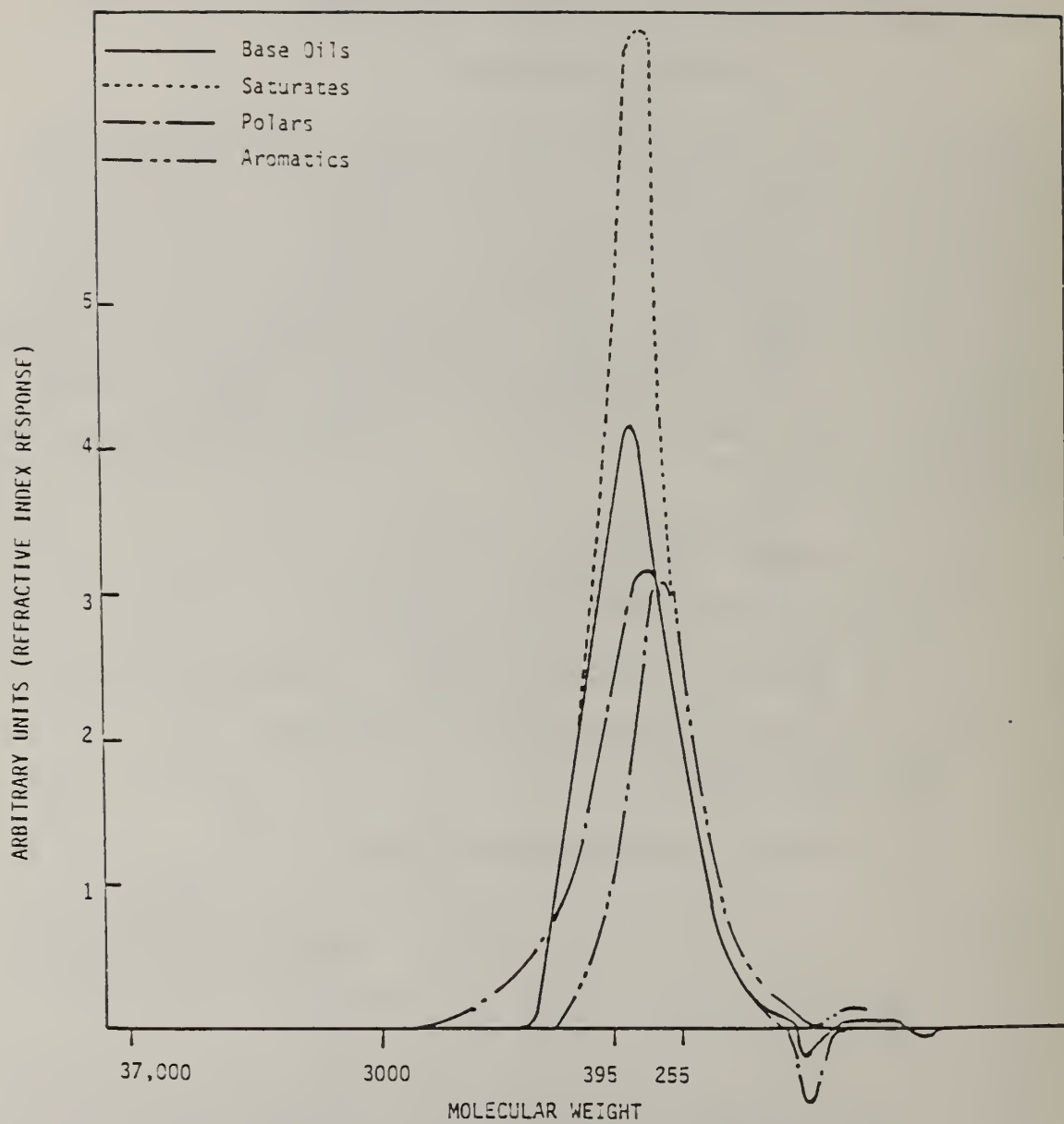fraction is similar to those of the base oil as shown in Figure 19.

FIGURE 19. MOLECULAR WEIGHT PROFILE OF THE 300N BASE OIL
AND ITS FRACTIONS

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Elemental analysis results indicate little or no heteroatoms present, the amount of oxygen, sulfur, and nitrogen is well below 0.01% (Table 11). The IR spectrum of the fraction shown in Figure 20b indicates the absence of the hydroxyl, aromatic, and carbonyl bonds at 3400, 1600, and 1700 cm^{-1}, respectively.

3.2.2 300N AROMATIC FRACTION CHARACTERIZATION

The kinematic viscosity of this fraction at 40 $^{\circ}$C is the highest of the three base oils but the viscosity index is the lowest of all the fractions, which suggests that the aromatic compounds in this fraction have much stronger intermolecular attraction forces. This may be due to the presence of more polar functional groups. The refractive index value again is higher than that of the base oil (1.5214 vs. 1.4816), indicating high aromatic content. The molecular weight profile as shown in Figure 19 indicates smaller molecules than other fractions.

Elemental analysis data in Table 11 show that the aromatic fraction has the highest sulfur content among the major fractions of the 300N. It is essentially free of nitrogen and oxygen-containing molecules. The infrared spectrum in Figure 20c shows strong aromatic absorption at 1600 cm^{-1} and the absence of bands attributable to hydroxyl and carbonyl bonds. These data tend to suggest the aromatic fraction contains monoaromatics and thiophenes of lower molecular weight, hence lower polarity than the aromatic compounds in the polar fraction.

3.2.3 300N POLAR FRACTION CHARACTERIZATION

The molecular weight distribution of the polar fraction presented in Figure 19 shows the presence of high molecular weight compounds in this fraction. The range of molecular weight is from 500 to 2000. Elemental analysis data in Table 11 show most of the nitrogen- and oxygen-containing compounds are concentrated in the polar fraction.

The infrared spectrum of the polar fraction (Figure 20d) shows the presence of very strong hydroxyl, carbonyl, aromatic, sulfur-oxygen, and amide bonds. This is confirmed by high resolution mass spectroscopy results indicating the presence of nitrogen compounds such as homologs of quinoline; sulfur compounds such as homologs of thiophenes and oxygenated compounds such as esters, phenols, and acids.

3.2.4 COMPARISON OF THE 300N FRACTIONS

The separation of the base oil into the three major fractions is relatively clean and most of the polar functional compounds are concentrated in the
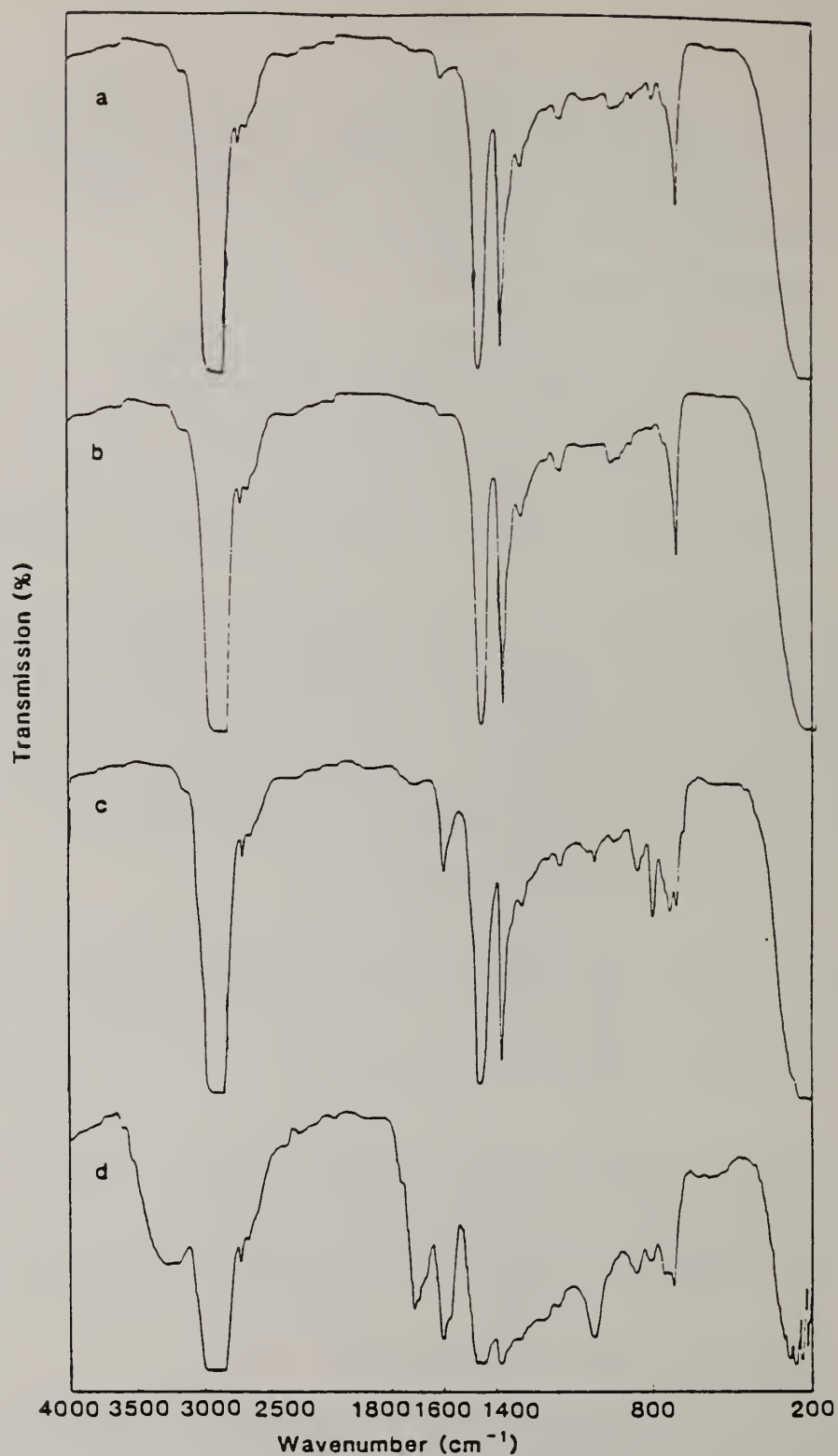
FIGURE 20.   INFRARED SPECTRA OF HYDROCARBON
FRACTIONS OF THE 300N BASE OIL:

a) BASE OIL; b) SATURATE FRACTION;
c) AROMATIC FRACTION; d) POLAR FRACTION

polar fraction. The aromatic fraction of the 300N has the highest sulfur content in contrast with the 150N base oil. The nitrogen, and oxygen distributions are similar to the 150N. Molecular Weight (MW) profiles show that the polar fraction contains a large amount of high MW (2500) materials.

3.2.5 300N P-2 SUBFRACTION

This subfraction is eluted from the column with toluene. Similar to the 150N P-2 subfraction, it has the lowest oxygen content of 0.4%, and negligible nitrogen content (Table 12). The molecular weight distribution curve shown in Figure 21 suggests a higher proportion of high molecular weight materials than the 150N P-2. The infrared spectrum in Figure 22 indicate the presence of strong aromatic peaks at 1600 cm^{-1}, 1500 cm^{-1}, and 1400 cm^{-1}, suggesting mixtures of mono and fused aromatic ring structures. The carbon-oxygen peak at about 1800 cm^{-1} is very distinct and isolated while P-3, P-5, and P-6 subfractions show much broader peaks, indicating the presence of some carbonates and anhydrides. High resolution mass spectroscopy results suggest the presence of phthalates, indoles, and quinolines (Appendix D).

3.2.6 300N P-3 POLAR SUBFRACTION

The P-3 subfraction is eluted with methylene chloride with a small amount of ethanol. Elemental analysis results in Table 12 suggest that P-3 contains the highest sulfur and nitrogen content among the 300N polar subfractions (2.28% sulfur, 1.9% nitrogen). The oxygen content has also increased from 0.4% (P-2) to 1.2% (P-3). The molecular weight distributions in Figure 21 indicate that P-2 is similar to P-3 except that P-3 has a high molecular tail distribution to 3000 MW. Infrared spectrum shown in Figure 22 suggests nitrogen-hydrogen bonds at 3300 cm^{-1}, carbon-oxygen bonds at 1690 cm^{-1} and 1710 cm^{-1}, and sulfur-oxygen bonds at 1030 cm^{-1} wavenumbers. These peaks suggest the presence of carboxylic acids, amides, and aromatic structures. High resolution mass spectroscopy results suggest P-3 contains quinolines, carbazoles, phthalates. However, no significant amount of sulfur compounds were identified. This may be due to the fact that the sulfur containing compounds are not volatile enough to be ionized, hence are not detected in the mass spectrophotometer.

3.2.7 300N P-5 POLAR SUBFRACTION

P-5 Polar Subfraction is eluted from the neutral alumina column with a polar solvent, 10% ethanol in tetrahydrofuran. The elemental analysis results shown in Table 12 indicate that this subfraction has a lower amount of nitrogen and sulfur than P-3 but has higher oxygen content than P-3. The molecular weight distribution shown in Figure 21 has the highest proportion of high molecular weight compounds when compared to polar subfractions. Infrared spectrum of the P-5
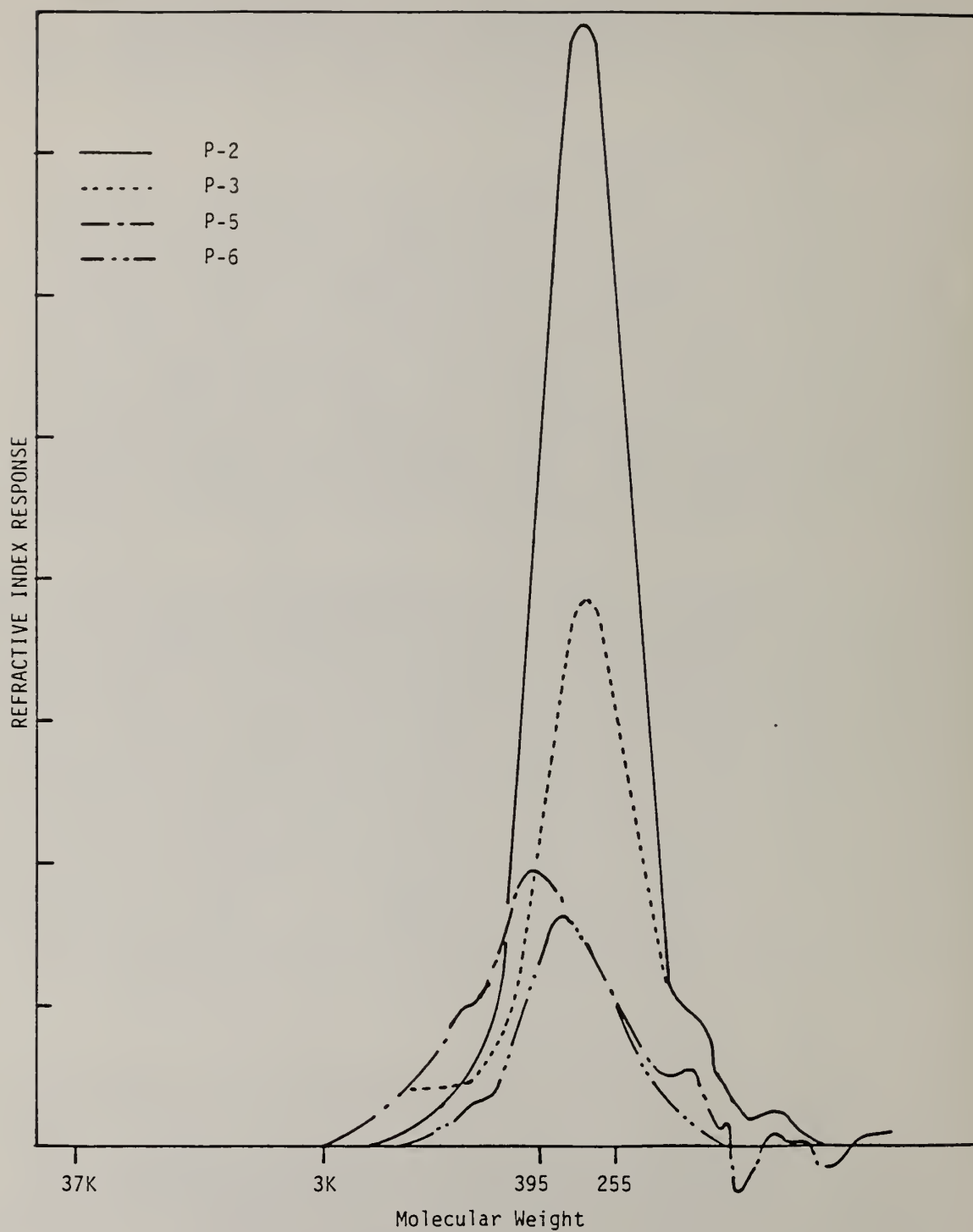
FIGURE 21. MOLECULAR WEIGHT PROFILE OF THE POLAR SUBFRACTIONS
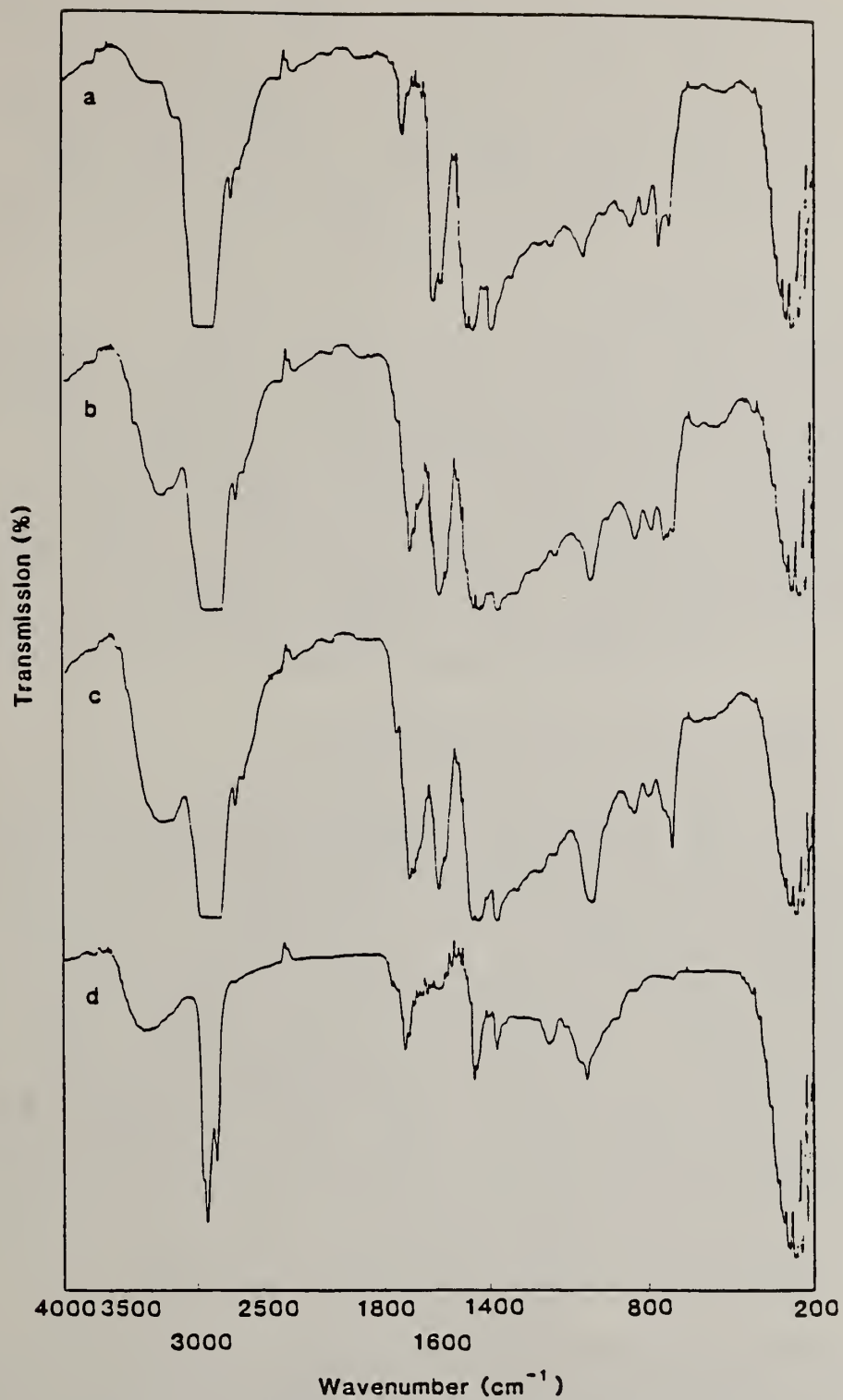OF THE 300N BASE OIL

FIGURE 22. INFRARED SPECTRA OF POLAR SUBFRACTIONS
OF THE 300N BASE OIL:

a) P-2 SUBFRACTION; b) P-3 SUBFRACTION
c) P-5 SUBFRACTION; d) P-6 SUBFRACTION

subfraction shown in Figure 22 is similar to that of the P-3 subfraction suggesting the presence of similar compounds; nitrogen-hydrogen, amine bond at 3300 cm^{-1}; carbon oxygen bond at 1700 cm^{-1}, aromatic carbon at 1600 cm^{-1} and sulfur-oxygen bond at 1030 cm^{-1}. High resolution mass spectroscopy results (Appendix D) suggests the presence of quinolines, carbazoles, indoles, phthalates, and phenols. The increased oxygen content and the high molecular weight are the two main characteristics of P-5 compared with P-3, suggesting higher polarity of the same functional groups.

3.2.8 300N P-6 SUBFRACTIONS

Subfraction P-6 is eluted from the neutral alumina column with methanol and this subfraction should contain the most polar compounds. Elemental analysis results listed in Table 12 suggest that the oxygen content of this subfraction is the highest among the 300N subfractions. The molecular weight distribution shown in Figure 21 suggests that the molecular weight of P-6 subfraction is about the same as that of P-2 and P-3 but higher than the base oil itself. The infrared spectrum shown in Figure 22 strongly indicates hydrogen-oxygen bond at 3400 cm^{-1} and carbon-oxygen bond at 1735 cm^{-1}. Very little or no aromatic structure at 1600 cm^{-1} is apparent. High resolution mass spectroscopy results (Appendix D) of the P-6 subfraction suggest the presence of phenols and carboxylic acids.

3.2.9 COMPARISON OF THE 300N POLAR SUBFRACTIONS

The polarity of compounds in the polar subfractions are in the increasing order of the P-2, P-3, P-5, and P-6. Elemental analysis results shown in Table 12 suggest that the P-2 subfraction has the lowest amount of oxygen compounds while P-6 has the highest oxygen content. Sulfur and nitrogen compounds are present in P-3 and P-5 subfractions. Molecular weight distributions shown in Figure 21 suggest P-2, P-3, and P-6 subfractions have relatively low molecular weight compounds while P-5 has the highest molecular weight compounds. Infrared spectra shown in Figure 22 suggest the variation of the wavenumber of the carbonyl peaks in each subfraction. Possibly the carbon-oxygen bond in P-2 is due to esters; in P-3 and P-5 it is due to aromatic carboxylic acids and amides; in P-6 it is due to esters, and acids. High resolution mass spectroscopy data (Appendix D) suggest the presence of the following possible compounds:

1. P-2, aromatic hydrocarbons, phthalates, quinolines, carbazoles;

2. P-3, phthalates, quinolines, carbazoles;

3. P-5, phthalates, phenol, quinolines, carbazoles, indoles; and

4. P-6, phenols and carboxylic acids.

3.3 600N MID-EAST BASE OIL

3.3.1 600N SATURATE FRACTION CHARACTERIZATION

The 600N is a heavier distillate than the 150N or the 300N. This is
reflected in the higher viscosities of the base oil as shown in
Table 10. The saturate fraction viscosities also reflect this trend
when compared to the 150N saturates and the 300N saturates. The
viscosity index changes from 93 (600N base oil) to 109 (600N saturate)
and the refractive index changes from 1.4907 to 1.4769. Both data again
indicate the paraffinic saturate content has been successfully isolated
by the separation method. The molecular weight distribution shown in
Figure 23 suggests that the saturate has the same distribution profile
as the base oil. Elemental analysis data in Table 11 again suggest
that this fraction contains little or no hetroatoms of nitrogen and oxygen.
The sulfur level is small (0.09%) compared to the other 600N fractions,
but is much higher than the 150N and 300N saturate fractions. The infrared
spectrum in Figure 24 confirms the purity of the saturate fraction.

3.3.2 600N AROMATIC FRACTION CHARACTERIZATION

As the viscosities of the base oil increase from 150N to 600N, the
average molecular weight as well as the molecular weight distribution
will shift to the higher values. The average molecular weight
data in Table 10 reflect this change. As the molecular weight increases,
aliphatic side chains attached to the aromatic or other ring structures
will also increase. The viscosity index of the aromatic fraction is 99,
in fact higher than the base oil itself (93). The refractive index,
however, shows an increase from 1.4907 to 1.5039 suggesting more
aromatic content. The infrared spectrum in Figure 24 confirms this
observation. The aromatic peak at 1600 cm^{-1} is very distinct, but
the rest of the spectrum looks like the saturate fraction. This indicates
there are many mixed molecular structures where the aromatic ring
structures are often hidden in the aliphatic chains. This 600N aromatic
fraction is relatively free of nitrogen and oxygen compounds. Sulfur
in the form of thiophenes is present as evidenced from the elemental
analysis data in Table 11. The molecular weight distribution profiles
in Figure 23 suggest that the aromatic fraction has more low molecular
weight molecules than the 600N base oil and other fractions.

3.3.3 600N POLAR FRACTION CHARACTERIZATION

The 600N polar fraction appears to concentrate most of the heteratoms
present in the base oil, having the highest proportion of nitrogen (1.2%),
sulfur (2.19%), and oxygen (0.8%) compared to the 600N saturate and aromatic
fractions. When compared with the 150N and 300N polar fractions, the 600N polar
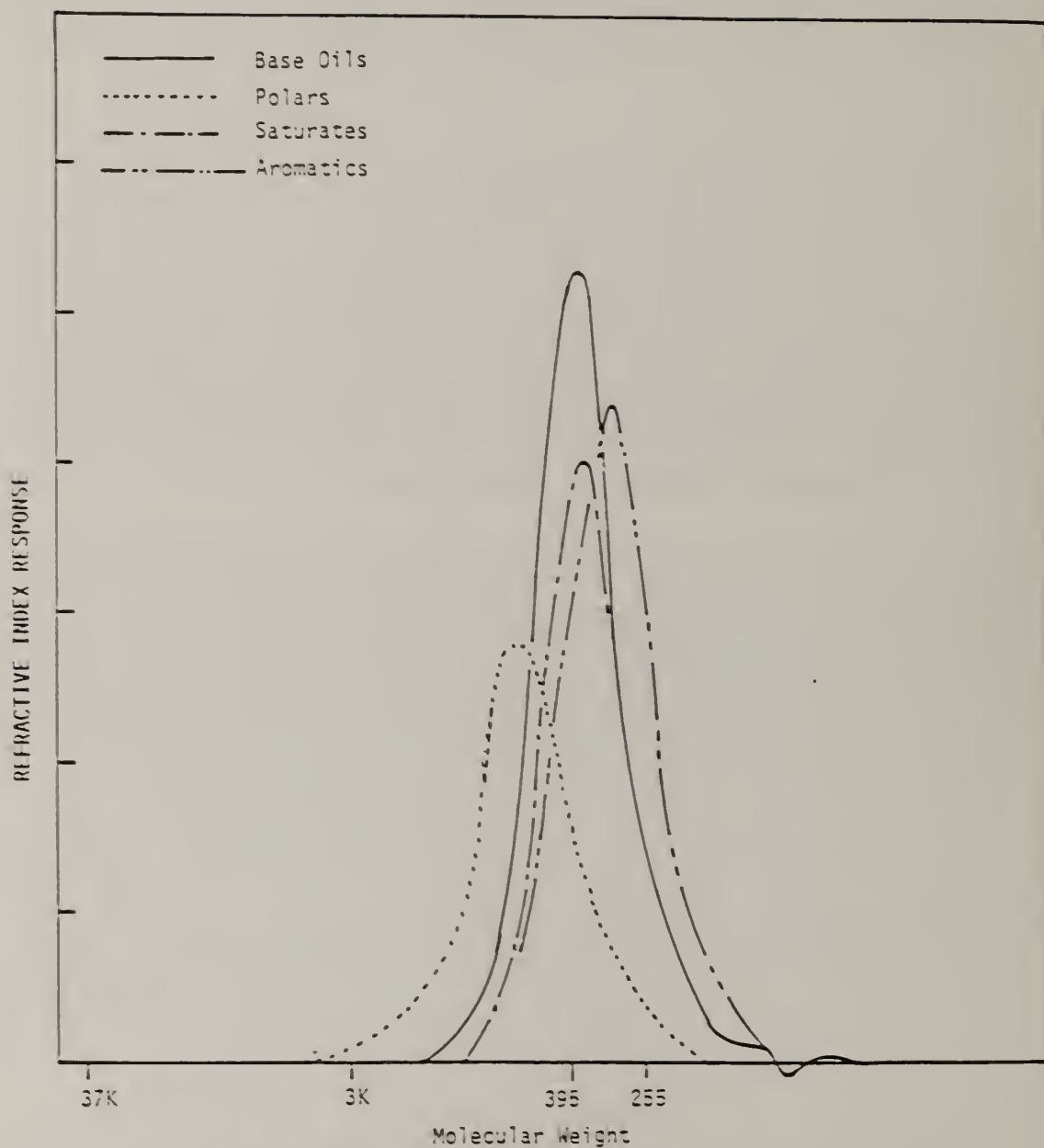fraction has the lowest nitrogen and oxygen content and intermediate sulfur

FIGURE 23. MOLECULAR WEIGHT PROFILE OF THE 600N BASE OIL
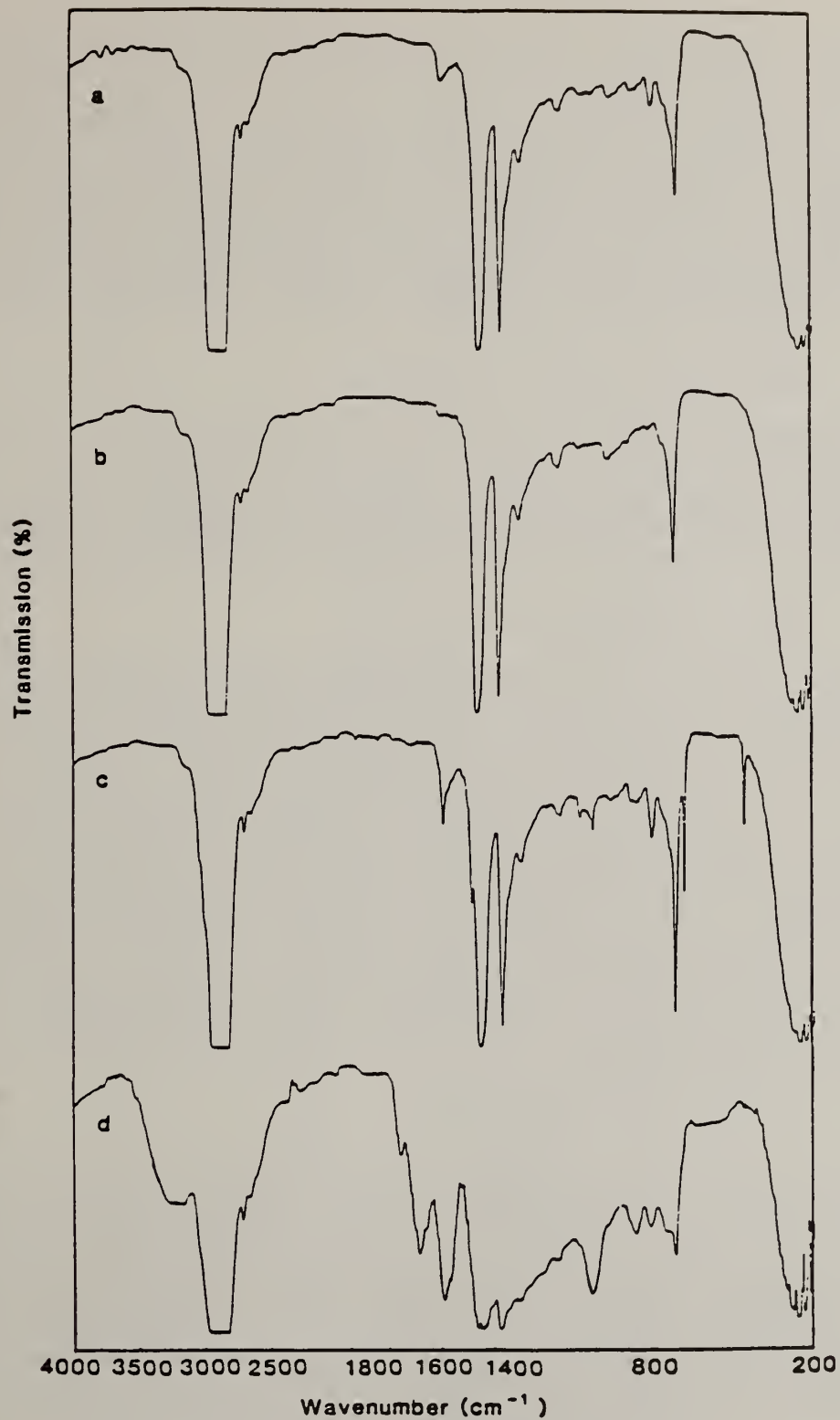AND ITS FRACTIONS

FIGURE 24. INFRARED SPECTRA OF HYDROCARBONS
FRACTIONS OF 600N BASE OIL:

a) BASE OIL; b) SATURATE FRACTION;
c) AROMATIC FRACTION; d) POLAR FRACTION

content. The molecular weight distribution profile of the 600N polar
fraction indicates much higher (up to 3700)   molecular weight than
the other 600N fractions, as shown in Figure 23. Infrared spectrum in
Figure 24 suggests presence of hydrogen-oxygen, aromatic, sulfur-oxygen,
and carbon-nitrogen bondings. When compared with the 150N and 300N polar
fractions, the peak at 1775 cm^{-1} is unique to this 600N polar fraction.
This may be due to the presence of cyclic anhydrides. High resolution
mass spectroscopy results (Appendix D) suggest the probable presence
of carbazoles, quinolines, thiophenes, esters, and organic acids. This
seems to support the infrared data.

3.3.4   COMPARISON OF THE 600N FRACTIONS

The separation of the 600N base oil appears to be clean. The distinction
between the saturate fraction and the aromatic fraction is not as
pronounced as the 150N and 300N. The molecular weight of the polar
fraction is much higher than that of the other fractions. There is a
progressive increase of molecular weights from 150N to 300N and 600N.

3.3.5   600N P-2 POLAR SUBFRACTION

The 600N polar fraction was separated on a neutral alumina HPLC column
as discussed in section 2.6. The four subfractions collected are
designated as P-2, P-3, P-5, and P-6. P-2 subfraction is the fraction
eluted from the neutral alumina column with toluene. Elemental analysis
results in Table 12 show that this subfraction has relatively low oxygen,
high sulfur, and high nitrogen content among the 600N polar subfractions. The
molecular weight distribution of P-2 subfraction as shown in Figure 25
indicates that P-2 contains some high molecular weight compounds up
to 4000 MW. Infrared spectrum of P-2 shown in Figure 26 suggests that
there is little or no hydrogen-oxygen bond at 3400 cm^{-1} but carbon-
oxygen bond and aromatic carbon are strongly indicated at 1700 cm^{-1}
1600 cm^{-1}, and 1570 cm^{-1} respectively. High resolution mass spectro-
scopy results (Appendix D) suggest the presence of phthalates, quinolines,
carbazoles, and thiophenes.

3.3.6   600N P-3 POLAR SUBFRACTION

P-3 subfraction is eluted from the neutral alumina column with methylene
chloride with 0.75% to 2% ethanol. Elemental analysis results in Table 12
shows that sulfur has dropped and oxygen and nitrogen has increased
over P-2. The molecular weight distribution shown in Figure 25
suggests that P-3 subfraction has the highest amount of high molecular
compounds among the 600N polar subfractions. Infrared spectrum of P-3
subfraction in Figure 26b suggests possibly nitrogen-hydrogen bond
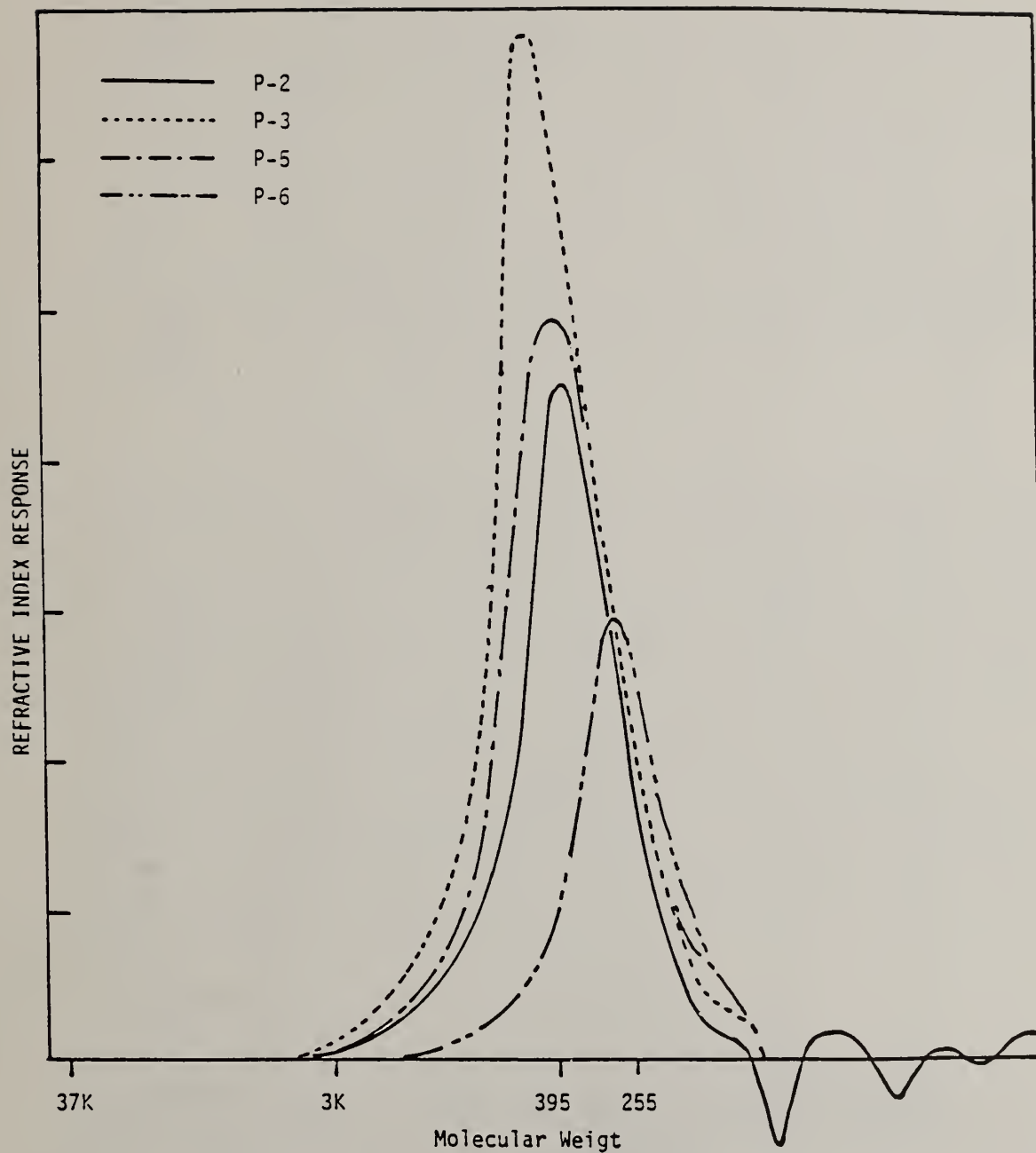at 3300 cm^{-1}, carbon-oxygen bond at 1770 and 1690 cm^{-1} and sulfur-

FIGURE 25. MOLECULAR WEIGHT PROFILE OF THE POLAR
SUBFRACTIONS OF THE 600N BASE OIL
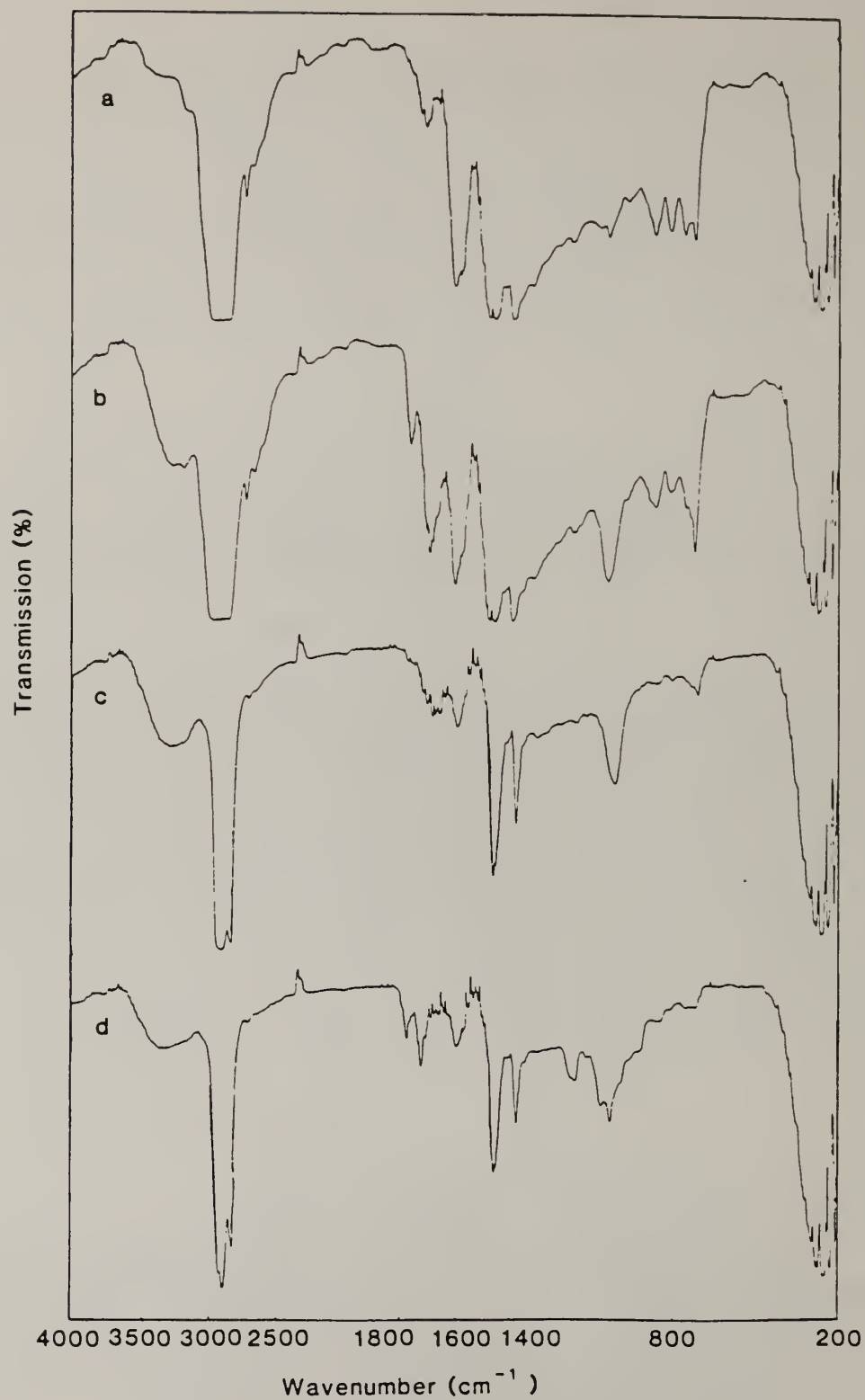
FIGURE 26.   INFRARED SPECTRA OF POLAR SUBFRACTIONS OF 600N BASE OIL:

a) P-2 SUBFRACTION; b) P-3 SUBFRACTION
c) P-5 SUBFRACTION; d) P-6 SUBFRACTION

oxygen bond at 1030 cm^{-1}. High resolution mass spectroscopy data (Appendix D) suggest that phthalates, indole quinolines, carbazoles, and thiophenes are present.

3.3.7 300N P-5 POLAR SUBFRACTION

Subfraction P-5 is eluted from the column with a polar solvent, 10% ethanol in tetrahydrofuran. Elemental analysis results in Table 12 indicate the presence of high sulfur and high oxygen but low nitrogen among the 600N polar subfractions. The molecular weight distribution of P-5 subfraction is similar to P-2 and P-3 subfractions containing high molecular weight compounds. The infrared spectrum shown in Figure 26 suggests hydrogen-oxygen bond at 3300 cm^{-1}, carbon-oxygen bond at 1690 cm^{-1}, aromatic structures at 1600 cm^{-1} and sulfur oxygen bond at 1030 cm^{-1}. The peaks between 1600 to 1800 cm^{-1} and the peaks between 1000 to 1400 cm^{-1} have decreased significantly. This suggests that the functional groups have shifted from aromatic to more alkylated carboxylic structures. High resolution mass spectroscopy data suggest the presence of phenols, esters, indoles, and carbazoles.

3.3.8 600N P-6 POLAR SUBFRACTION

Subfraction P-6 is eluted from the column with methanol, and therefore, this subfraction contains the most polar compounds. Elemental analysis results listed in Table 12 indicate the highest oxygen content among all polar subfractions of the three base oils. The carbon hydrogen ratio has decreased from 8:1 to 7:1. The molecular weight distribution of P-6 subfraction as shown in Figure 25 suggests that the P-6 subfraction contains the lowest amount of high molecular weight compounds among the 600N polar subfractions, but still contains molecules of up to 2000 MW. It should be noted that materials of high polarity, like P-6, could have interacted with the polystyrene packing material in the gel permeation column resulting in artificially low molecular weight distribution profile. Infrared spectrum in Figure 26 suggest the presence of oxygen-hydrogen bond at 3400 cm^{-1}, carbon oxygen bond at 1775 cm^{-1} as γ-lactone or chloride structures, and esters at 1735 cm^{-1}, aromatic carbons at 1600 cm^{-1}, and sulfur-oxygen bond at 1030 cm^{-1}. High resolution mass spectroscopic data suggest the presence of phenols, carboxylic acids, thiophenes, and esters.

3.3.9 COMPARISON OF 600N POLAR SUBFRACTIONS

Elemental analysis data of the four polar subfractions (Table 12) suggest that more sulfur compounds are in P-2 and P-5 subfractions but nitrogen compounds are evenly distributed among the subfractions. However, oxygen compounds are concentrated in the P-6 subfraction as high as 17%. Molecular weight distribution of the subfractions shown in

Figure 25 suggest that the P-6 subfraction has the lowest amount of high molecular weight molecules among the subfractions. Infrared spectra (Figure 26) suggest that the carbon-oxygen bond at 1775 cm^{-1} in P-3 and P-6 may be due to the presence of cyclic structures (such as δ-lactones) anhydrides or chlorides. The oxygen-hydrogen band at 3300 cm^{-1} is observed in P-3, P-5, and P-6, but is absent in P-2. The carbonyl bond attributable to ester linkage at 1735 cm^{-1} is observed in all subfractions. Sulfur-oxygen bond at 1030 cm^{-1} is observed in P-3, P-5, and P-6. High resolution mass spectroscopy results (Appendix D) suggest the presence of possibly the following structures.

1. P-2, aromatic hydrocarbons, phthalates, quinolines, carbazoles, and thiophenes.

2. P-3, phthalates, quinolines, carbazoles, indoles, and thiophenes.

3. P-5, phthalates, phenols, carboxylic acids, indoles, quinolines, and carbazoles.

4. P-6, phenols, carboxylic acids, phthalates, and thiophenes.

3.4 COMPARISON OF FRACTIONS AND SUBFRACTIONS

In the previous sections, detailed analytical characterization of an individual fraction and subfraction has been described and compared within each base oil. The effectiveness and the extent of the separation of the base oils into narrow compound classes have been demonstrated. The data are summarized in Table 13 for easy comparison of the separated compound classes from the three base oils. The 150N and the 600N are refined from the same crude source. The 300N is refined from another crude source in Middle East. Overall, there are similarities among the separated fractions from these three oils indicating the effectiveness of the separation method. There are also differences among the fractions suggesting different initial compositions, hence different compounds.

Table 13 lists the most probable molecular structures present in each fraction and subfractions. There are the best estimates from infrared, elemental analysis, high resolution mass spectroscopy. Molecular information in C_{20} plus compounds is usually diffused and complex. Definitive structural determination will require further separations.

Overall, the separation of the base oils into saturates, aromatics, and polars is very clean. The separation of the polars into molecular compounds classes of varying polarity necessitates overlapping molecular structures (but different polarity). One of the key pieces of information is the molecular weight distribution since ofentimes the alkyl chain length, or the molecular weight affects the polarity of a macromolecule. Figures 27 to 33 compares molecular weight distributions of each fraction from the

Table 13

Comparison of Base Oil Fractions in Terms of
Elemental Analysis and Molecular Structures

	N	S	O	Most Probable Molecular Structures
Saturate				
150N	< 0.01	0.01	< 0.3	paraffins, naphthenes
300N	< 0.01	0.01	< 0.3	paraffins, naphthenes
600N	< 0.01	0.09	< 0.3	paraffins, naphthenes, alkyl sulfides
Aromatic				
150N	< 0.01	1.54	< 0.3	mono-, di-aromatics, thiophenes
300N	< 0.01	2.26	< 0.3	mono-, di-aromatics, thiophenes
600N	< 0.01	1.24	< 0.3	alkylated aromatics, thiophenes
Polar				
150N	1.8	2.83	1.6	heteroatom compounds
300N	1.4	1.68	1.5	heteroatom compounds
600N	1.2	2.19	0.8	heteroatom compounds
P-2				
150N	1.6	2.71	0.7	thiophenes, amides, polynuclear aromatics
300N	< 0.01	1.60	0.4	phthalates, indoles, mono- and polynuclear aromatics
600N	1.1	2.53	0.6	phthalates, carbazoles, thiophenes, polyaromatics
P-3				
150N	1.6	2.66	2.1	quinolines, amides, sulfoxides, thiophenes
300N	1.9	2.28	1.2	quinolines, carbazoles, carboxylic acids, thiophenes
600N	1.3	1.78	1.1	phthalates, carbazoles, thiophenes, polyaromatics

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Table 13 (Con't)

Comparison of Base Oil Fractions in Terms of
Elemental Analysis and Molecular Strucutres

	N	S	O	Most Probable Molecular Structures
P-5				
150N	1.2	3.52	3.2	phenols, carboxylic acids, quinolines, indoles, thiophenes
300N	1.3	1.65	1.8	phthalates, carboxylic acids, phenols
600N	0.8	2.53	2.9	esters, indoles, carboxylic acids
P-6				
150N	1.0	3.11	7.3	phenolic, alcohols, sulfoxides, thiophenes
300N	0.2	0.47	4.3	phenols, carboxylic acids
600N	0.8	1.21	17.0	esters, acids, sulfoxides (lactone or chloride)

three base oils. Generally, the molecular weight increases from
150N fractions to 600N fractions, but there are a few exceptions
in the polar subfractions.

In the polar subfraction separation, the data in Table 13 suggest
that P-2 and P-6 are the most different. P-2 fractions are generally
mostly polynuclear aromatics but contain little or no oxygenated
compounds. P-6 fractions are mostly oxygenated compounds with few
aromatics. The P-3 and P-5 fractions have overlapping structures
between these two extremes.
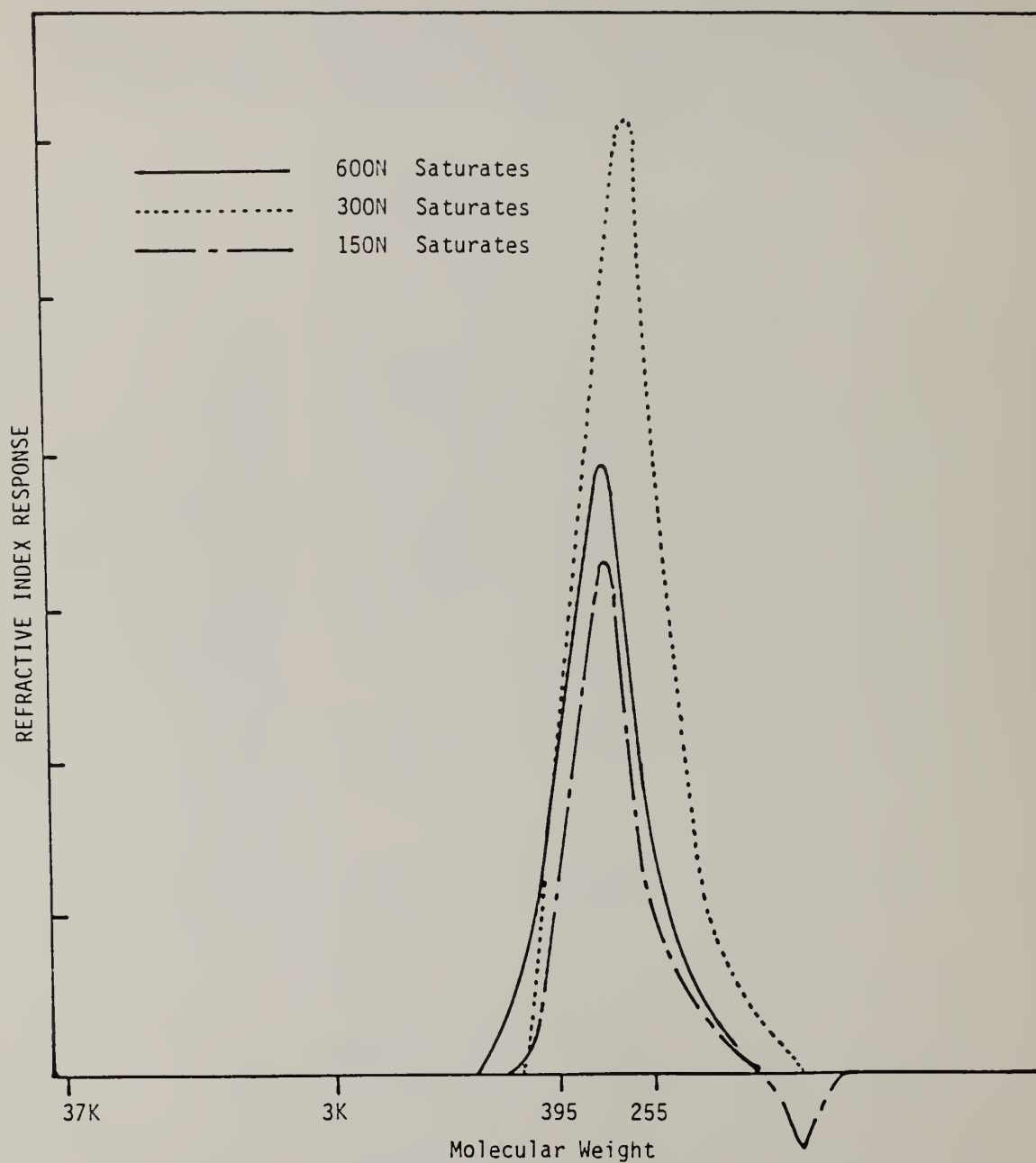
FIGURE 27. COMPARISON OF THE MOLECULAR WEIGHT PROFILES
OF THE SATURATE FRACTIONS FROM BASE OILS
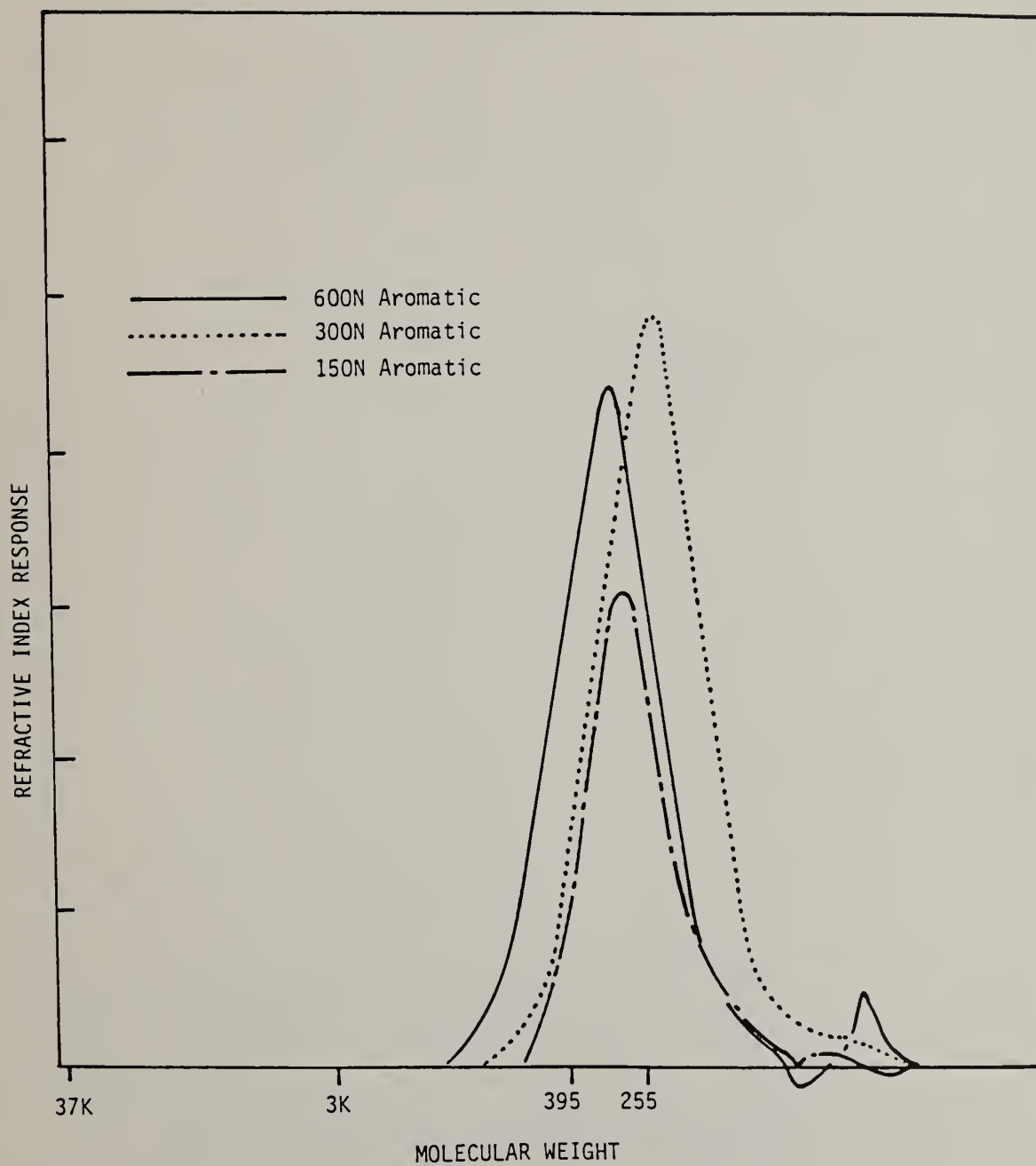
FIGURE 28. COMPARISON OF THE MOLECULAR WEIGHT PROFILES OF
AROMATIC FRACTIONS OF BASE OILS
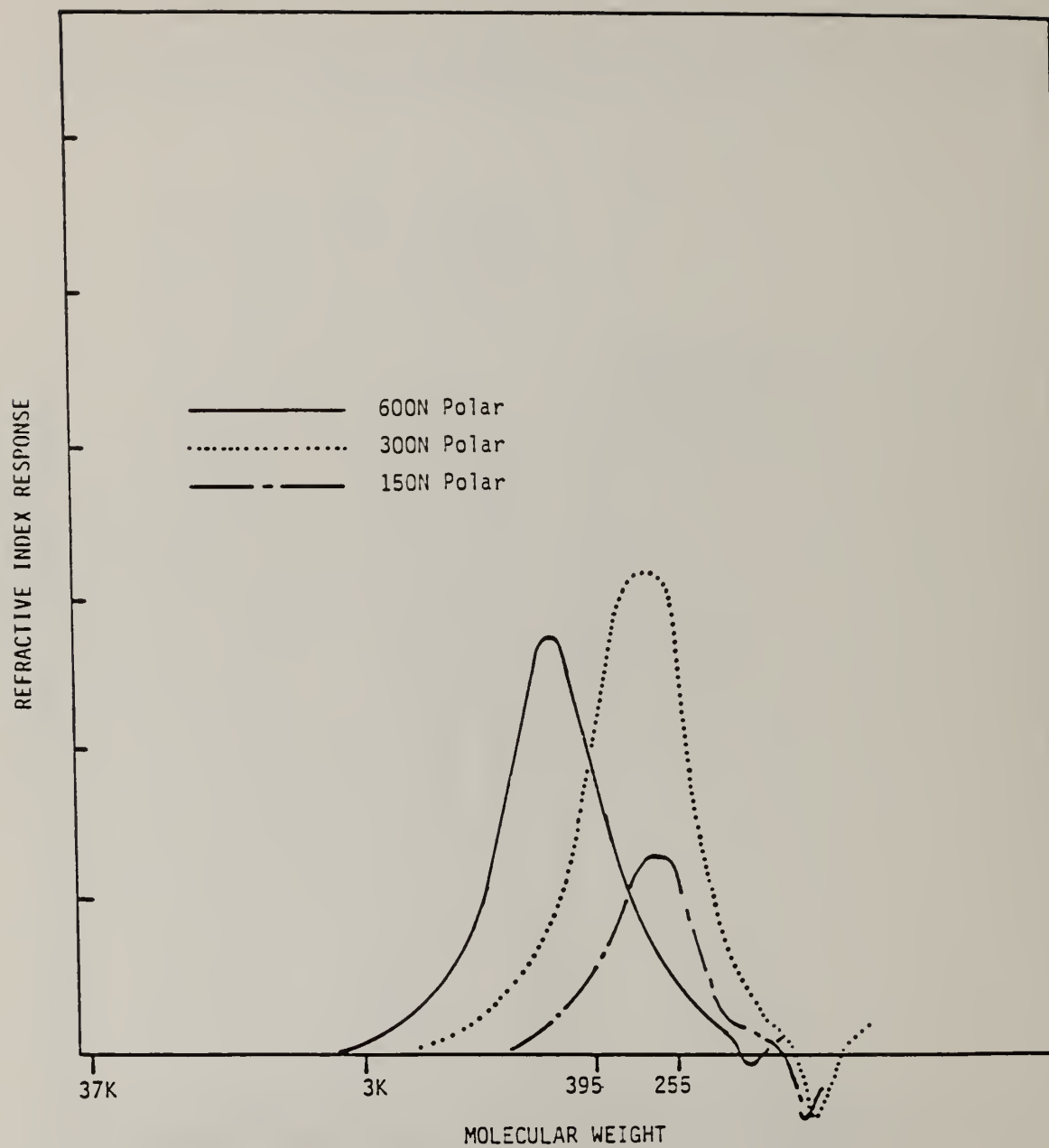
FIGURE 29. COMPARISON OF THE MOLECULAR WEIGHT PROFILES OF THE
POLAR FRACTIONS FROM THE THREE BASE OILS

68
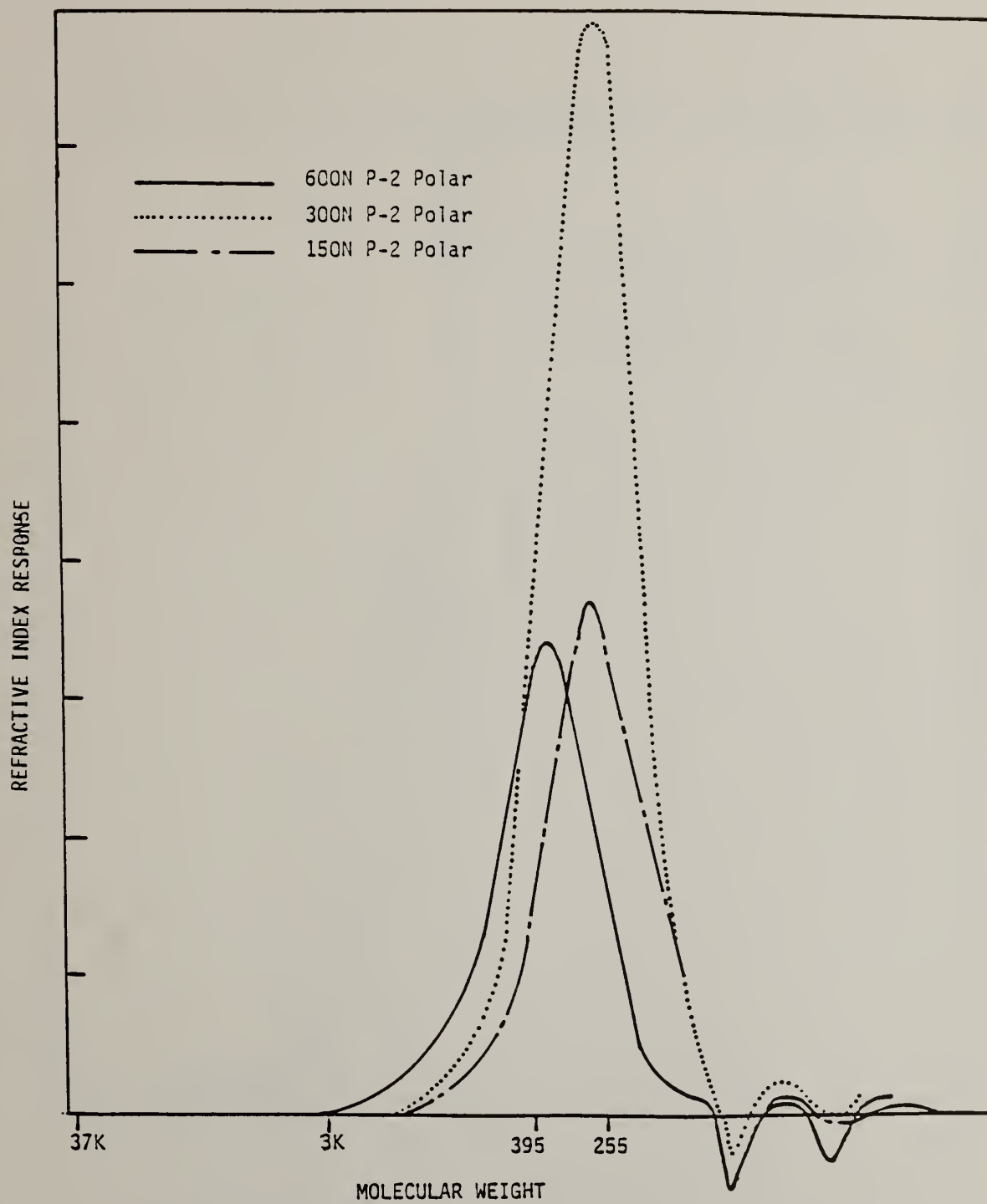
FIGURE 30. COMPARISON OF THE MOLECULAR WEIGHT PROFILES OF
P-2 SUBFRACTIONS FROM THE THREE BASE OILS

69
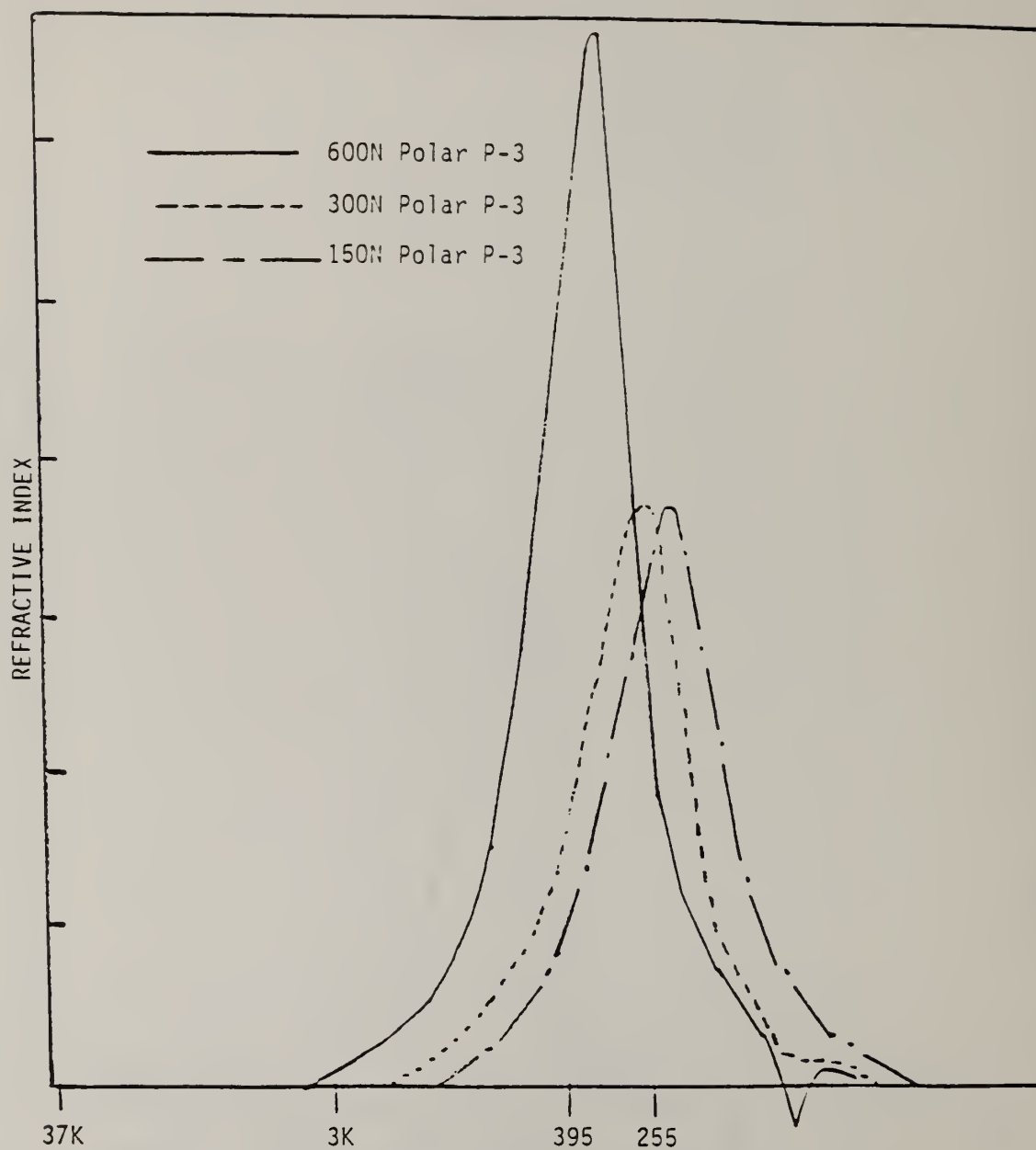
FIGURE 31. COMPARISON OF THE MOLECULAR WEIGHT PROFILES
OF P-3 SUBFRACTIONS OF BASE OILS
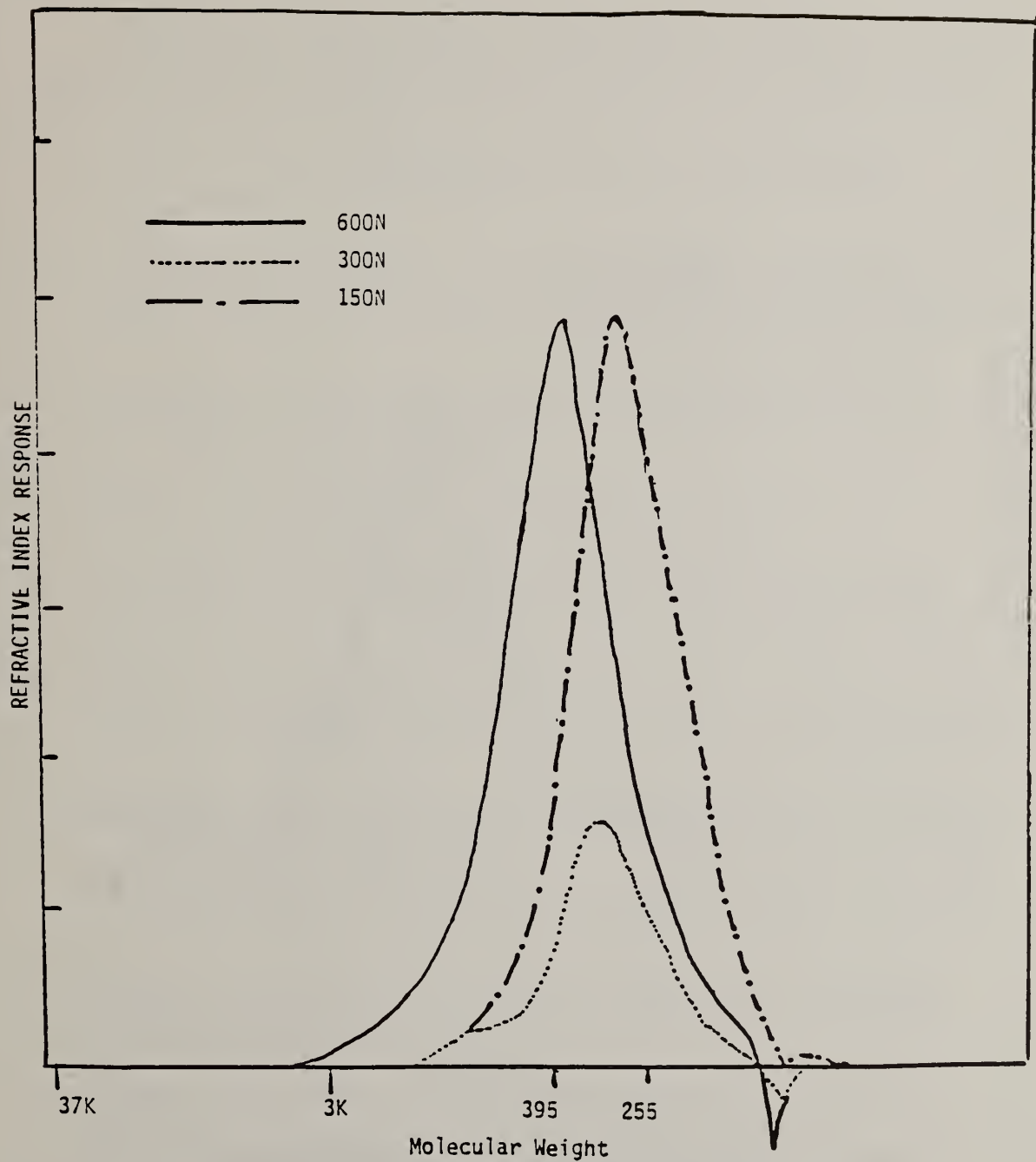
FIGURE 32. COMPARISON OF THE MOLECULAR WEIGHT PROFILES OF
P-5 SUBFRACTIONS P-5 OF BASE OILS
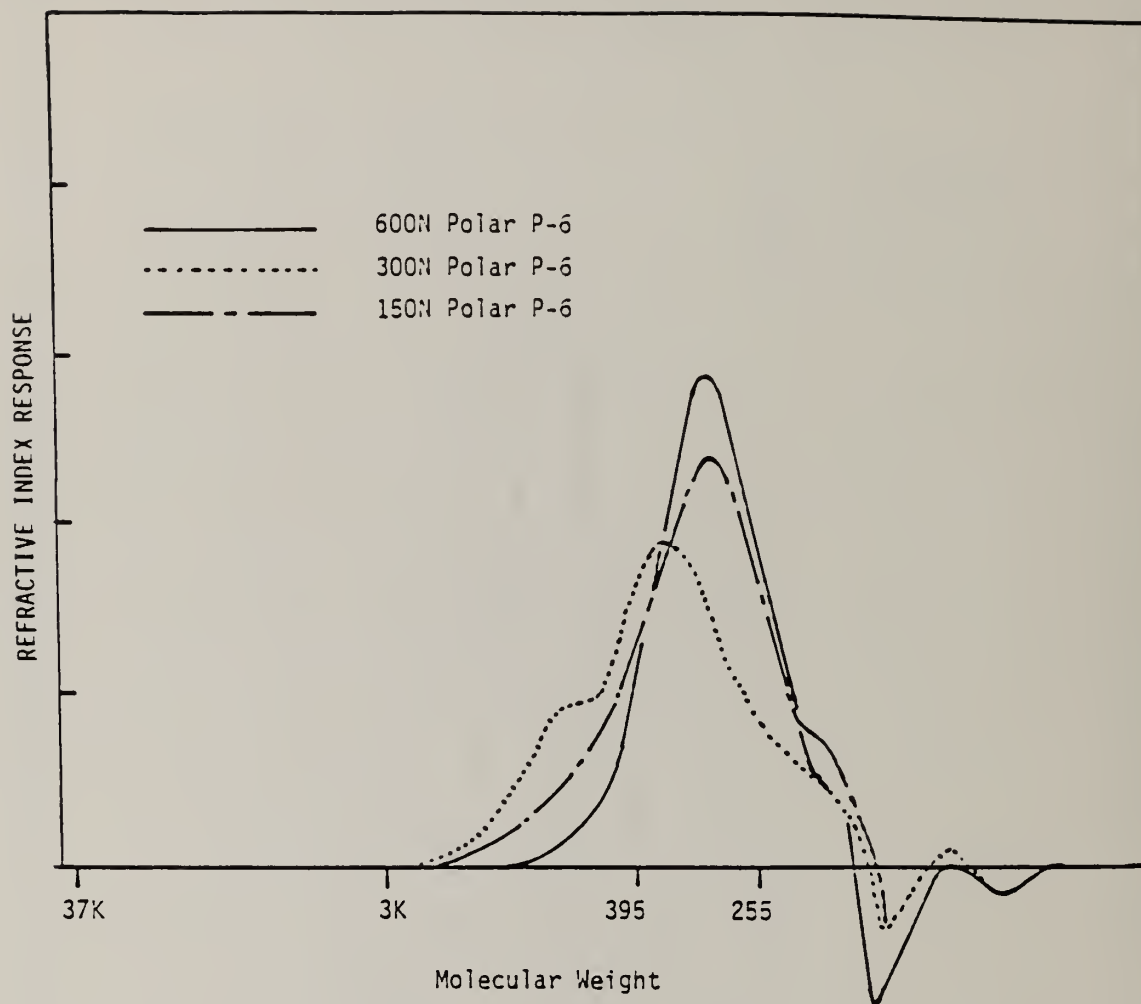
FIGURE 33. COMPARISON OF THE MOLECULAR WEIGHT PROFILES OF
P-6 SUBFRACTIONS OF BASE OILS

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APPENDIX A

CHARACTERIZATION OF FRACTIONS FROM

LARGE SCALE ALUMINA COLUMN CHROMATOGRAPHY

Table A1

Activated Alumina
Wt. % Distribution of Base Oils

	Pure Fraction	Pentane Eluted Oil Fraction	Acetone Eluted Fraction
Mid-East (150N)	49	48	2
Mid-East (600N)	35	61	3
Re-refined (350N)	58	39	3

Table A2

Physical and Chemical Properties
of a 350N Re-refined Base Oil

Property	Units	Method	350N Re-refined Base Oil				
			Base Oil	Pure Oil	Pentane Eluted Oil	Acetone Eluted Fraction	
Refractive Index		D 1218	1.4850	1.4798	1.4864	1.5682	
Density	g/cm³	Vibrating tube Densimeter	0.8780	0.8696	0.8797	1.0071	
Viscosity @ 40 °C	cSt	D 445	73.	65.	73.	560.	
Viscosity @ 100 °C	cSt	D 445	9.4	8.8	9.0	20.	
Viscosity Index		D 2270	104	108	97	< 0	
Avg. Mol. Wt. from Visc. Data	g/mol	D 2502	502	498	481	438	
Color	ASTM Color Units	D 1500	L6.5	L1.0	L2.0	> 8.0 est.	
Sulfur	Wt. %	D 1552	0.20	< 0.01	0.27	2.75	
Total Acid #	MgKOH/gOil	D 664	0.18	0.03	0.10	0.74	

Table A3

Physical and Chemical Properties of a 150N Virgin Base Oil

Property	Units	Method	150N Virgin Base Oil (Mid-East)			
			Base Oil	Pure Fraction	Pentane Eluted Fraction	Acetone Eluted Fraction
Refractive Index		D 1218	1.4803	1.4754	1.4819	1.5608
Density	g/cm³	Vibrating Tube Densimeter	0.8686	-	-	-
Viscosity @ 40 °C	cSt	D 445	30.06	28.63	31.83	150.17
Viscosity @ 100 °C	Cst	D 445	5.23	5.15	5.37	8.52
Viscosity Index		D 2270	104	109	102	<0
Avg. Mol. Wt. from Visc. Data	g/mol	D 2502	404	-	-	-
Color	ASTM Color Units	D 1500	0.5	0.0	L0.5	-
Sulfur	Wt. %	D 1552	0.35	0.08	0.47	-
Total Acid #	MgKOH/g oil	D 664	-	-	-	-

Table A4

Physical and Chemical Properties of a 600N Virgin Base Oil

Property	Units	Method	600N Virgin Base Oil (Mid-East)			
			Base Oil	Pure Fraction	Pentane Eluted Fraction	Acetone Eluted Fraction
Refractive Index		D 1218	1.4904	1.4828	1.4909	1.5538
Density	g/cm^3	Vibrating Tube Densimeter	0.8874	-	-	-
Viscosity @ 40 °C	cSt	D 445	107.49	85.56	106.65	22.30
Viscosity @ 100 °C	Cst	D 445	11.52	10.44	11.42	26.28
Viscosity Index		D 2270	93	104	93	< 0
Avg. Mol. Wt. from Visc. Data	g/mol	D 2502	521	-	-	-
Color	ASTM Color Units	D 1500	L2.5	L0.5	L1.0	-
Sulfur	Wt. %	D 1552	0.65	0.17	0.71	-
Total Acid #	MgKOH/gOil	D 664	-	-	-	-
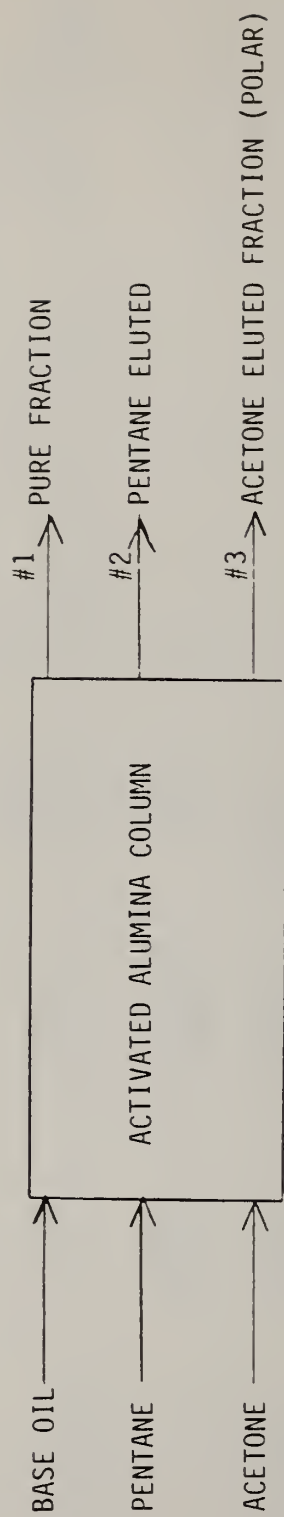
FIGURE A1. GRADIENT ELUTION SEPARATION SCHEME FOR ACTIVATED PREPARATIVE ALUMINA COLUMN

80
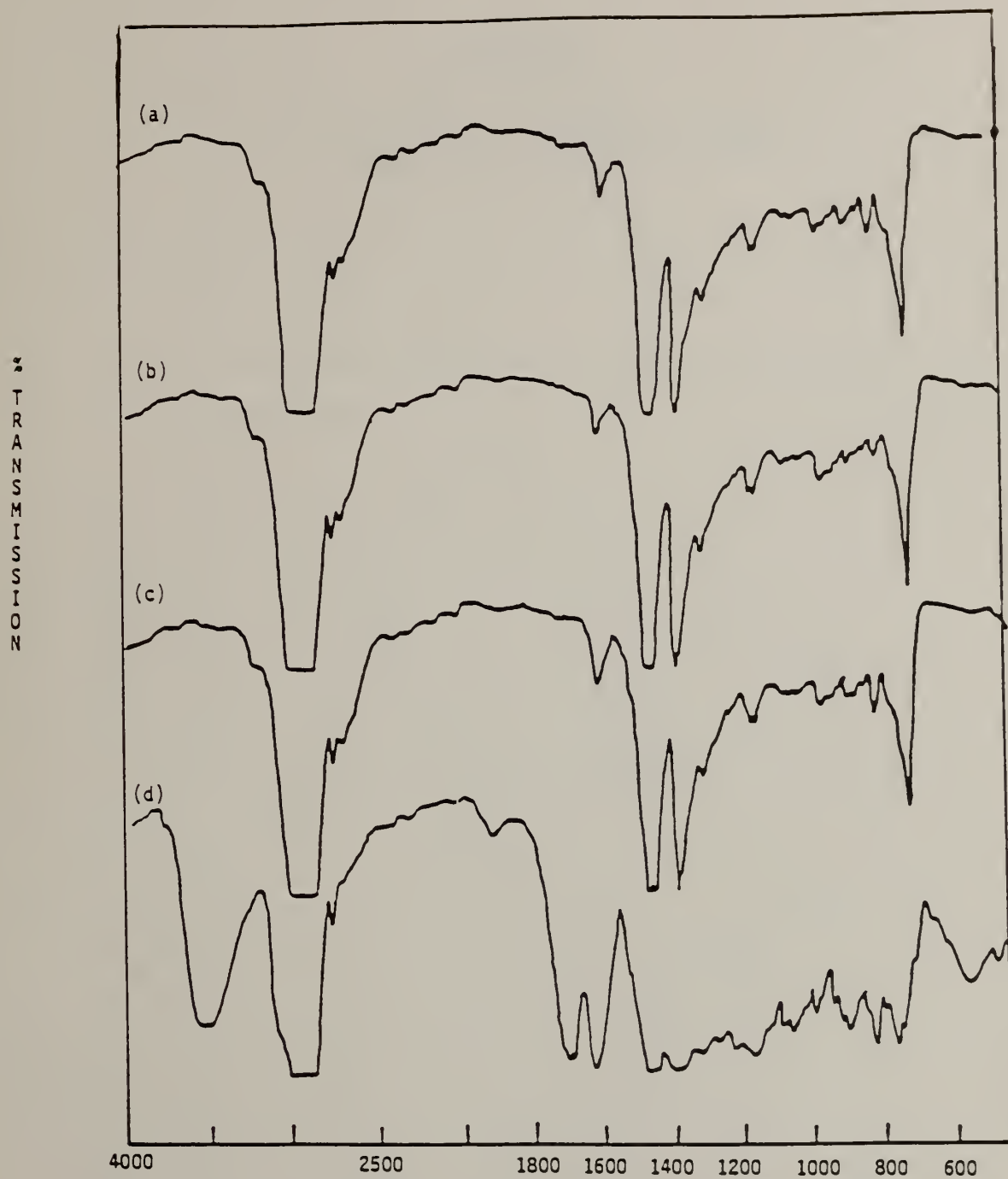
FIGURE A2. IR SPECTRA OF FRACTIONS FROM ACTIVATED ALUMINA COLUMN

(a) Original Oil
(b) Pure Fraction
(c) Pentane Eluted Fraction
(d) Acetone Eluted Fraction

Appendix B

CHARACTERIZATION OF SEPARATED FRACTION
FROM ASTM D-2007 METHOD
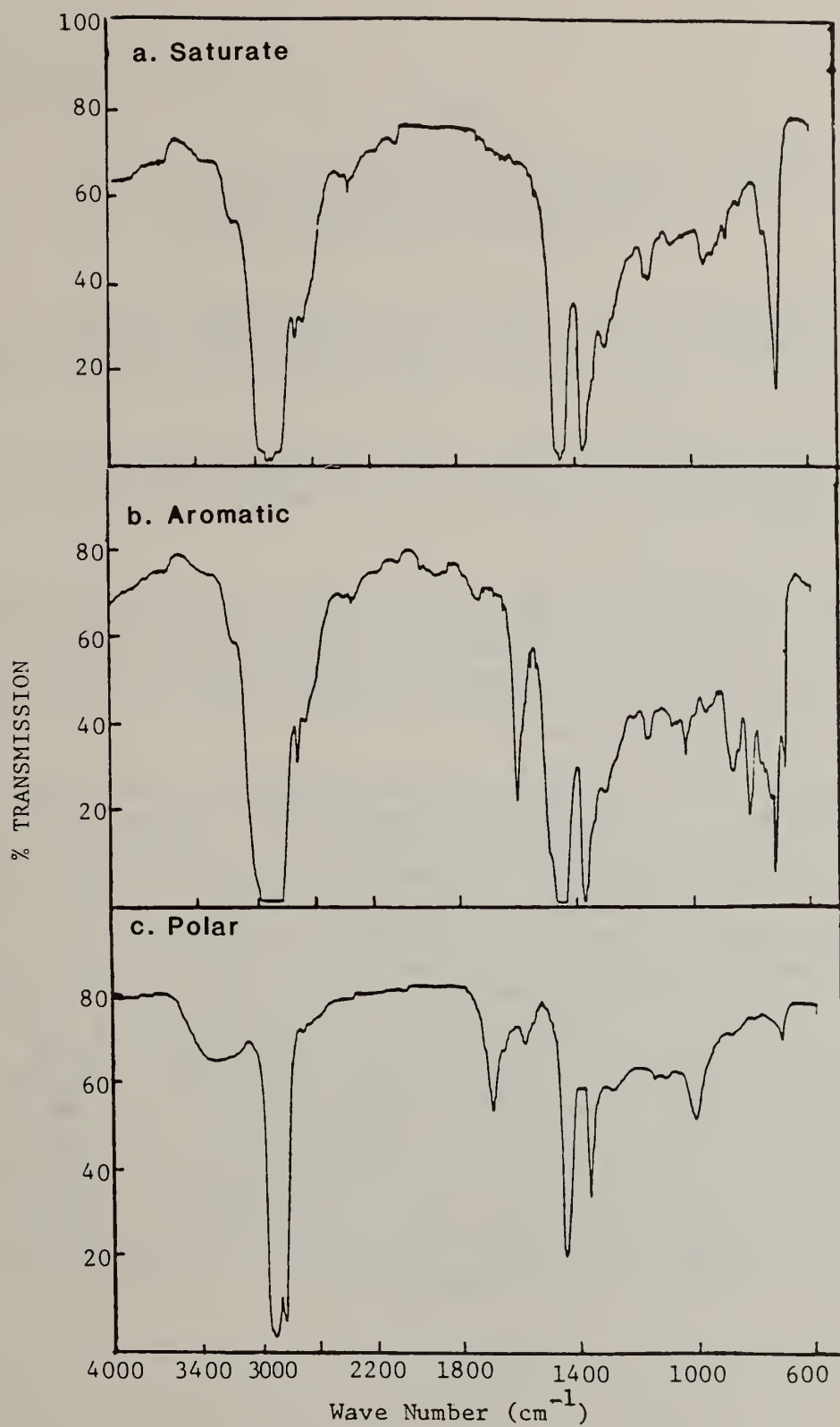
FIGURE B1. INFRARED SPECTRA OF FRACTIONS OF
OIL D BY ASTM D2007 METHOD

Appendix C

CHARACTERIZATION OF FRACTIONS FROM
ION-EXCHANGE COLUMN CHROMATOGRAPHY

IR spectra of these isolated fractions are illustrated in Figures C1
and C2. Molecular weight profiles of the polar subfractions are shown
in Figures C3, C4, and C5 obtained by Gel Permeation Chromatograms (GPC).

IR spectra of the polar subfractions from the ion-exchange column do show
similar IR bands except the neutral fraction (POLB-1) which does not have
the NH/OH⁻ band. This is expected as POLB-1 should not contain any phenols,
acids, and amines.

The molecular weight profile for the POLB-1, neutral fraction is similar
to the polar fraction. Both GPC curves of basic fractions POLB-2 and
B-3 are very uniform with even Gaussian distribution with peaks at
300 and 500 molecular weight. However, for the acidic fractions, the apparent
molecular weight profile is very broad covering a range of high molecular
weight from 100 to 100,000 mw.

Two performance evaluation tests have been applied on these neutral acid
and base fractions. The tests are the antioxidant titration method
developed by Mahoney [C1] and the micro-sample step loading seizure test
developed by Gates and Hsu [C2]. The antioxidant test is intended to
determine the oxidation stability of the base oils and the micro-
sample step loading seizure test is designed to measure an oil's antiwear
behavior under boundary lubricating conditions. The result of both
tests are listed in Tables C1 and C2. The antioxidant value of a 350N
base oil is 0.009×10^{-3} mole/g but the polar fraction has a value
of 0.305×10^{-3} mole/g. This value indicates that the neutral and acidic
polar subfractions have very high antioxidant capacities. Phenols in
POLA-2 and POLA-3 and the amides in the neutral, POLB-1 are suspected
of being responsible for the high antioxidant values. In the case of the
micro-sample step loading seizure test, the test results indicate that the
neutral fraction (POLB-1) can effectively increase the seizure load
from 180 kg to 300 kg with the addition of 1.9% of POLB-1. However,
the wear scar diameter measurements do not show any difference among
the polar subfractions by ion-exchange resins.

Appendix C - References

C1.   Mahoney, L.R., Korcek, S., Hoffman, S., and Willermet, P.A.,
      "Determination of the Antioxidant Capacity of New and Used
      Lubricants; Method and Applications," Ind. Eng. Chem. Prod.
      Res. Dev., Vol. 17, No. 3, pp. 250-255, 1978.

C2.   Gates, R.S., and Hsu, S.M. "Development of an Oxidation-Wear
      Coupled Test for the Evaluation of Lubricants," ASLE Preprint
      No. 82-LL-1D-2

Table C1

The Anti-Oxidant Values from the Polar Subfraction
by Ion-Exchange Resin Columns

		Anti-Oxidant Value
Re-refined Base Oil		0.009×10^{-3}
Polar Fraction		0.305×10^{-3}
POLB-1	Neutral	1.3×10^{-3}
POLB-2		0.59×10^{-3}
POLB-3	Basic	0.085×10^{-3}
POLB-4		Not determined
POLA-2		1.06×10^{-3}
POLA-3	Acidic	1.70×10^{-3}
POLA-4		Not determined

Table C2

Micro Sample Loading Seizure Test Results on
the Polar Subfractions by Ion-Exchange Column

	Seizure Load kg	Wear Scar Diameter mm
RB0033	> 300	0.69
RB0033 Sat.	180	0.61
RB0033 Sat. + 1.9% Neutral (POLB-1)	> 300	0.69
RB0033 Sat. + 1.9% Acid (POLA-2)	> 270	0.655
RB0033 Sat. + 1.(% Basic B2)	225	0.69
RB0033 Sat. B3	165	0.61

Conditions

Apparatus: NBS Modified Four-Ball Wear Tester

Speed: 400 rpm

Load: 15 mg increments

Duration: 30 second intervals

Atmosphere: 0.25 ℓ/min dry Air

Lubricant: 6 μl samples
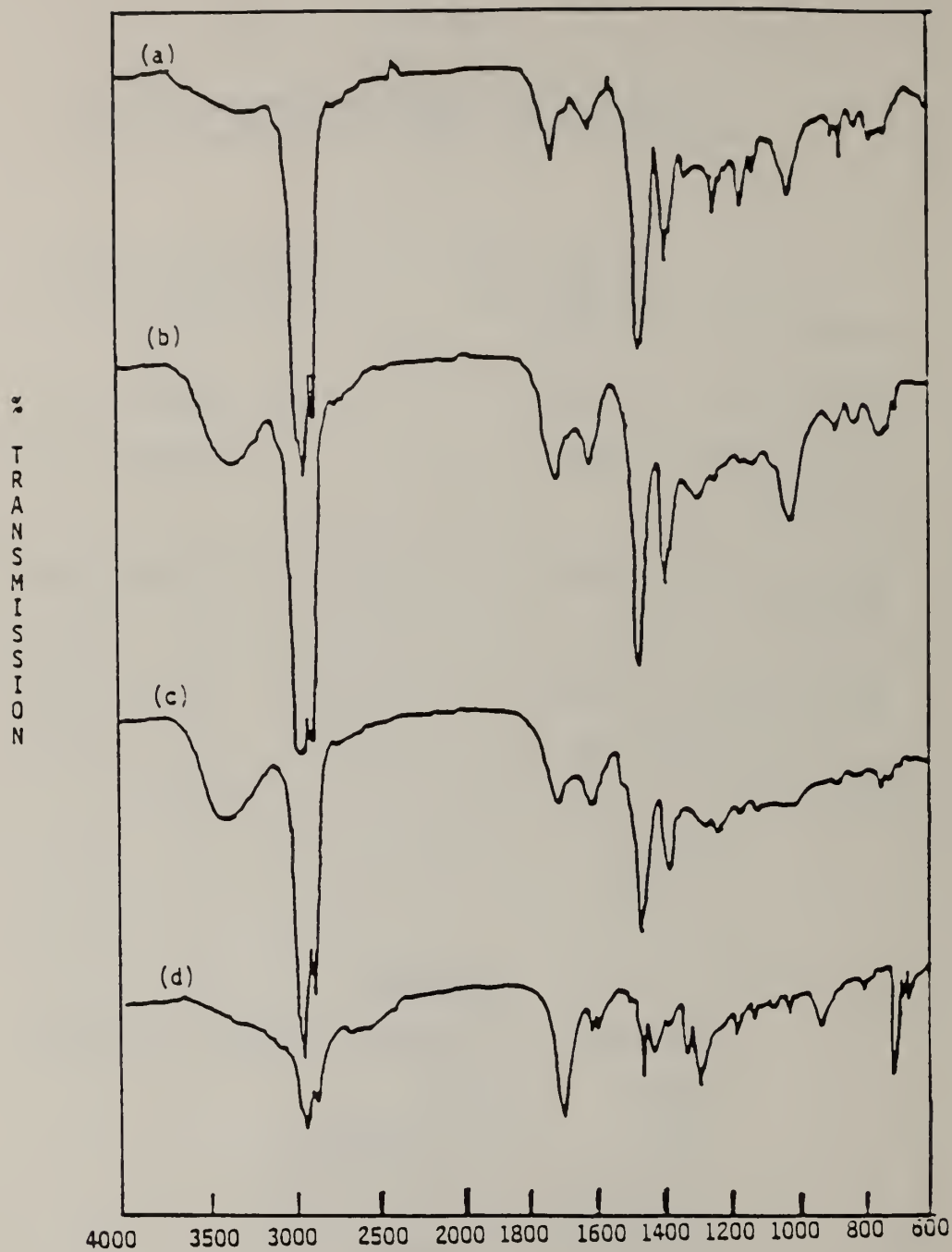
FIGURE C1.   IR SPECTRA OF POLAR ACIDIC SUBFRACTIONS
FROM ION-EXCHANGE COLUMNS

(a)   Polar Fraction
(b)   Polar A-2 Sub-Fraction
(c)   Polar A-3 Sub-Fraction
(d)   Polar A-4 Sub-Fraction

FIGURE C2. IR SPECTRA OF POLAR BASIC SUBFRACTIONS FROM
ION-EXCHANGE COLUMNS

(a) Neutral Subfraction POLB-1
(b) Basic Subfraction POLB-2
(c) Basic Subfraction POLB-3

89
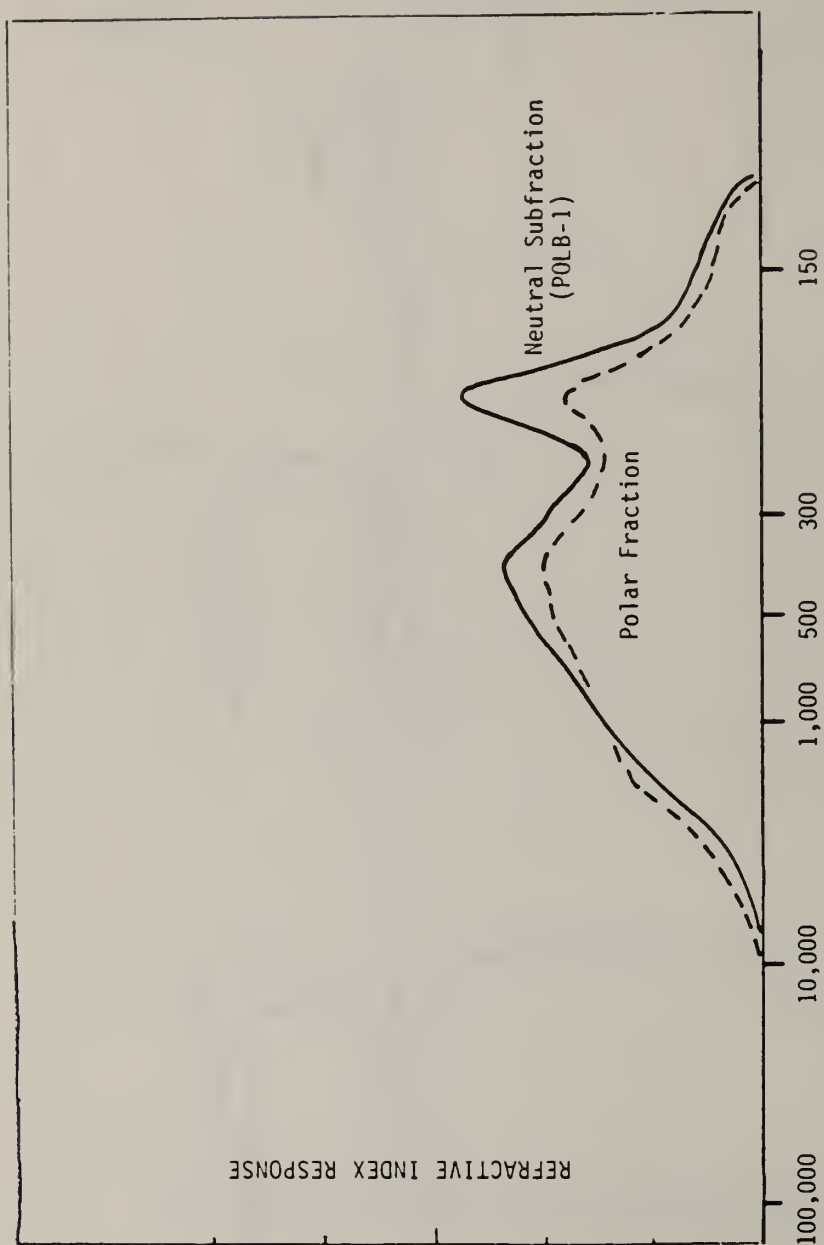
FIGURE C3. MOLECULAR WEIGHT PROFILE OF POLAR FRACTIONS AND ITS
NEUTRAL SUBFRACTION BY ION-EXCHANGE COLUMNS

90
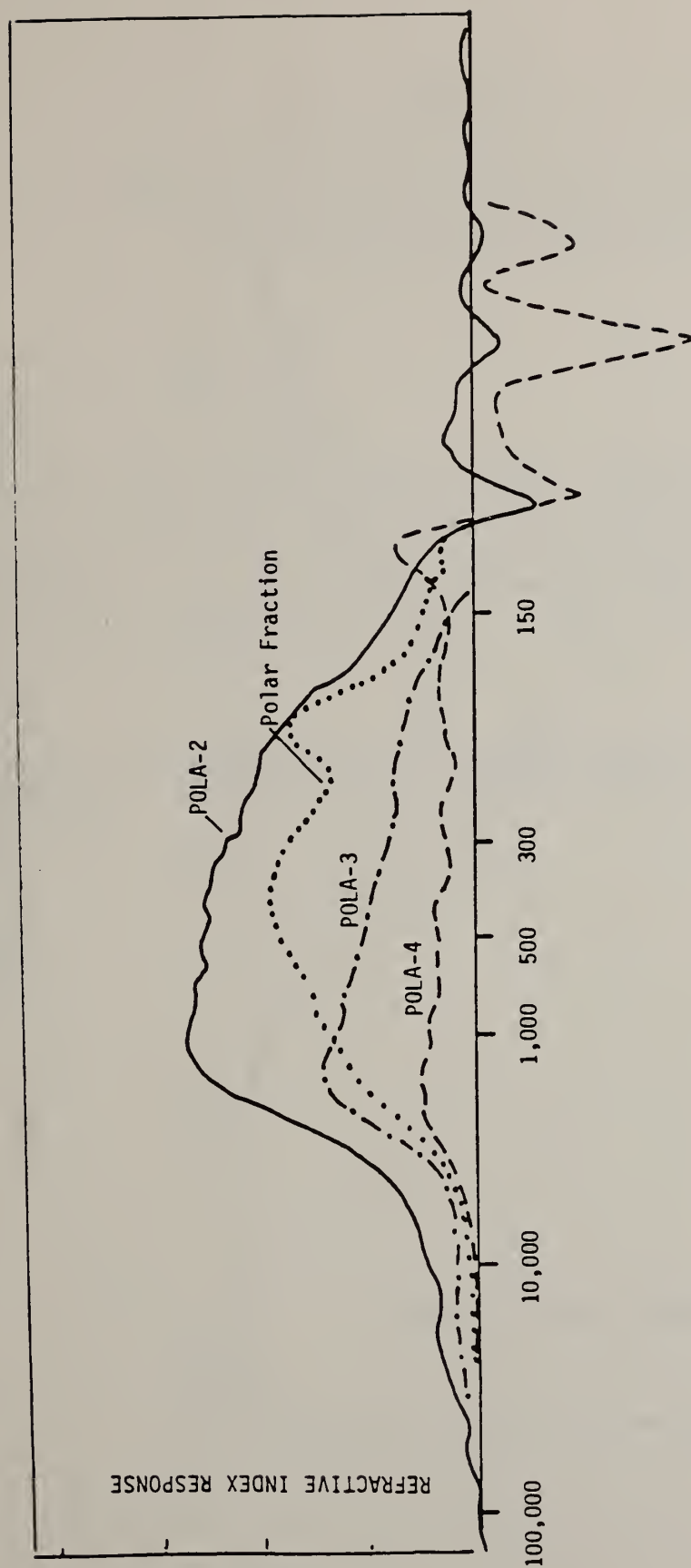
FIGURE C4. MOLECULAR WEIGHT PROFILE OF THE ACIDIC SUBFRACTION BY
ION-EXCHANGE COLUMN IN COMPARISON TO POLAR FRACTION
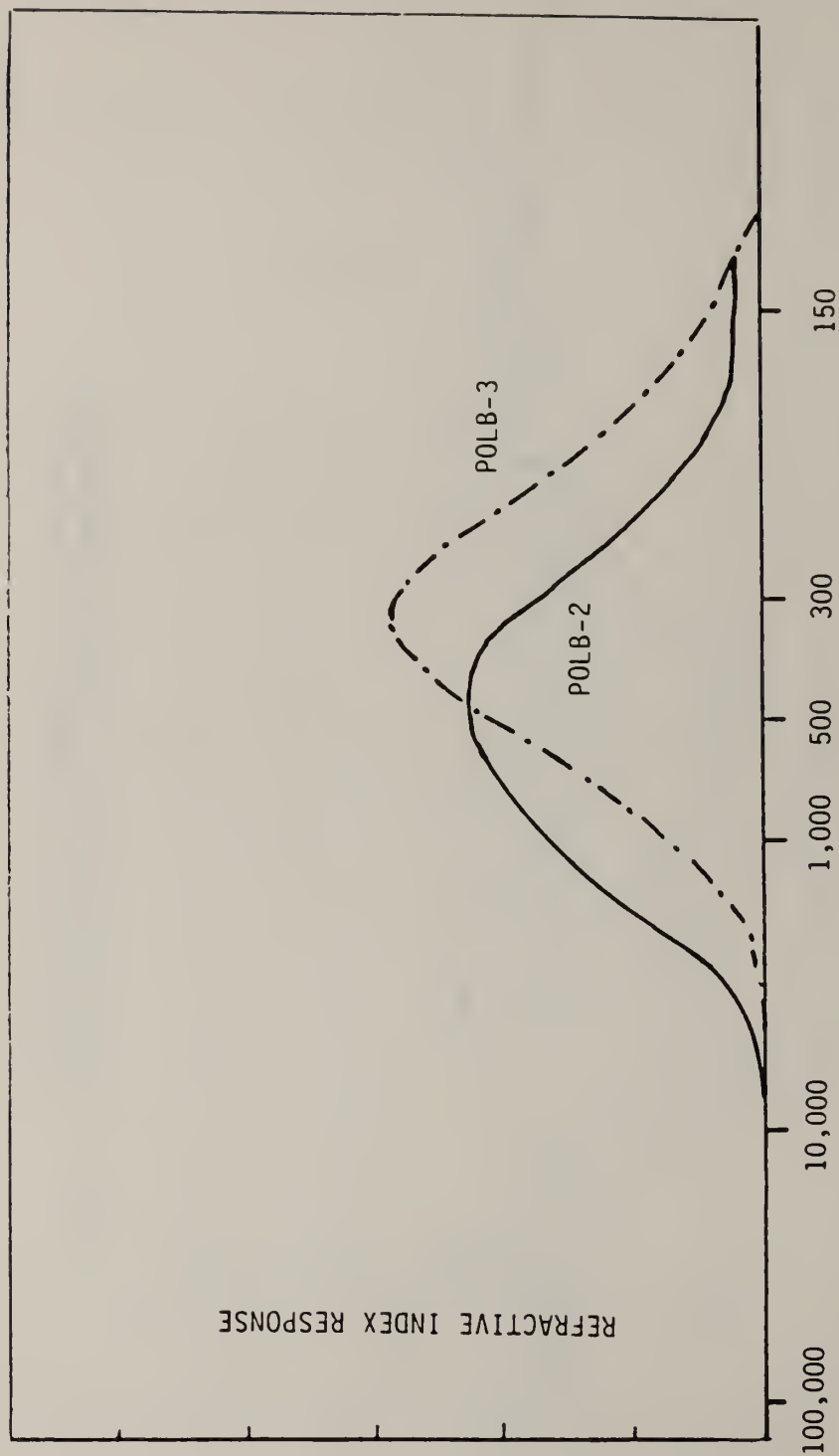
FIGURE C5. MOLECULAR WEIGHT PROFILE OF BASIC SUBFRACTIONS (POLB-2 AND POLB-3) OF THE POLAR FRACTION SEPARATED BY ION-EXCHANGE COLUMN

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APPENDIX D

CHARACTERIZATION OF POLAR FRACTION AND SUBFRACTIONS
FROM NEUTRAL ALUMINA COLUMN CHROMATOGRAPHY BY
HIGH RESOLUTION MASS SPECTROMETRY

ANALYTICAL PROCEDURES:

Mass spectra were recorded at a resolution of approximately 10,000 using
direct probe introduction and electron impact ionization. A relatively
stable ion current could be maintained for several minutes at a probe
temperature of 100 $^{\circ}$C, thereby allowing several spectra of each sample
to be recorded. The spectra were then averaged by the computer. In
order for an ion to appear in the final report, it must have appeared
in at least two of the scans.

RESULTS:

The summary report format gives the summed intensities of all the ions
of a particular heteroatom content, distributed by the degree of
unsaturation.

TABLE D1

ELEMENTAL DISTRIBUTION OF THE 150N POLAR FRACTION BY
HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	52					
-2	213			63		
-4	242			83		34
-6	255			40	10	23
-8	228			16	89	14
-10	83			16	488	11
-12	141			28	894	
-14	123	17			1035	
-16	14				1059	
-18	101	15			876	
-20	41				494	
-22	34				216	
TOTAL	1527	32		246	5161	82

TOTAL INTENSITY OF UNASSIGNED IONS: 90

TABLE D2

ELEMENTAL DISTRIBUTION OF THE 150N P-2 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	136			4	78	
-2	343			30		4
-4	276			60		5
-6	175			40	10	12
-8	132		6	48	150	
-10	79			24	164	3
-12	73			46	272	4
-14	82				303	
-16	28				267	
-18	40			9	264	4
-20	18				174	
-22					89	
-24	3				38	
-26	4				36	
-28	4				36	
-30					4	
TOTAL	1393		6	261	1885	32

TOTAL INTENSITY OF UNASSIGNED IONS: 405

95

TABLE D3

ELEMENTAL DISTRIBUTION OF THE 150N P-3 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	48			6		6
-2	211			102		18
-4	228			62		
-6	158			24	11	
-8	176			15	183	4
-10	53	5		10	303	5
-12	92				615	
-14	90				638	
-16	31				590	
-18	39	4			519	
-20	26				236	
-22	8				71	
-24	6					
-26	6				8	
-46	6					
TOTAL	1178	9		219	3174	33

TOTAL INTENSITY OF UNASSIGNED IONS: 289

TABLE D4

ELEMENTAL DISTRIBUTION OF THE 150N P-5 POLAR FRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	61			8		
-2	239			18		25
-4	326			32		24
-6	329				10	23
-8	349	30		31	22	15
-10	98	27			148	
-12	169		12		304	
-14	124				304	
-16	58				325	
-18	113	13			157	
-20	18				43	
-22					9	
-24	9					
-26	12					
TOTAL	1905	70	12	89	1322	87

TOTAL INTENSITY OF UNASSIGNED IONS: 117

97

TABLE D5

ELEMENTAL DISTRIBUTION OF THE 150N P-6 POLAR FRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	49			7		
-2	250	100	19	15		21
-4	310	14	13	22		24
-6	284			40		20
-8	342	97				
-10	129	57			78	
-12	226	40		19	279	
-14	163				342	
-16	95	50			298	
-18	219	169			148	
-20	106	86			53	
-22	36				13	
-24	12					
-26	5					
-42				13		
-44				7		
TOTAL	2226	613	32	123	1211	65

TOTAL INTENSITY OF UNASSIGNED IONS: 155

TABLE D6

ELEMENTAL DISTRIBUTION OF THE 300N POLAR FRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	84			5		20
-2	269		11	35		26
-4	252			18		42
-6	214			43	33	18
-8	219	35		62	16	15
-10	61			83	77	
-12	138	9		37	240	
-14	74		9	6	216	
-16	19			11	183	
-18	19	13			204	
-20	16	13			101	
-22		21		13	37	15
-24	11				15	
-26				7		
-28					13	
-30					12	
-32	6		23			
-34				5		50
-36		9	26			21
-38		10	34			
-40	41	34				
TOTAL	1423	144	103	325	1147	207

TOTAL INTENSITY OF UNASSIGNED IONS: 387

TABLE D7

ELEMENTAL DISTRIBUTION OF THE 300N P-2 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	160			17		
-2	461			29		
-4	465			155		
-6	296			194		
-8	258			205	32	
-10	82			129	181	
-12	109			112	524	
-14	80			66	910	
-16				18	1068	
-18	26	43			1038	
-20					685	
-22					429	
-24					112	
TOTAL	1937	43		925	4979	

TOTAL INTENSITY OF UNASSIGNED IONS: 138

TABLE D8

ELEMENTAL DISTRIBUTION OF THE 300N P-3 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	32					
-2	177			82		
-4	146			247		
-6	82			130		
-8	145		27	202	23	
-10	18			181	114	
-12	43			110	994	
-14				27	1300	
-16	34			50	1589	
-18					1633	
-20					1172	
-22					801	
-24					190	
-26					73	
-30	23			32		
TOTAL	700		27	1061	7889	

TOTAL INTENSITY OF UNASSIGNED IONS: 289

TABLE D9

ELEMENTAL DISTRIBUTION OF THE 300N POLAR P-5 SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	62					
-2	253	8		56		38
-4	275			81		
-6	212			115	8	
-8	162	51	13	48	40	
-10	51	3		25	205	
-12	58			18	418	
-14	67	7		3	342	
-16		31			420	
-18	17				326	
-20	6				155	
-22					64	
-24					11	
TOTAL	1163	100	13	346	1989	38

TOTAL INTENSITY OF UNASSIGNED IONS: 167

102

TABLE D10

ELEMENTAL DISTRIBUTION OF THE 300N P-6 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	5					
-2	21	18	4	1		
-4	10	3	3			
-6	5					
-8	4	1				
-22	1					
TOTAL	46	22	7	1		

TOTAL INTENSITY OF UNASSIGNED IONS: 136

TABLE D11

ELEMENTAL DISTRIBUTION OF THE 600N POLAR FRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	51					6
-2	215			8		
-4	205			19		38
-6	89			25		21
-8	146		10	18	14	
-10	49			37	24	
-12	53			11	88	4
-14	15			5	153	7
-16	29				180	
-18	12				149	
-20	4			7	84	
-22					59	
-24					5	
-26	6				12	
-28	4					
TOTAL	878		10	130	768	76

TOTAL INTENSITY OF UNASSIGNED IONS: 259

TABLE D12

ELEMENTAL DISTRIBUTION OF THE 600N P-2 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	330			16		15
-2	473	47	8	30	6	16
-4	322			42		
-6	173			8		5
-8	249	15				
-10	150			6		12
-12	87		37	71		8
-14	80				6	
-16	23		10		34	
-18	22	20			63	
-20		15			31	
-22		21			4	
-24				9	11	
-30	8					
TOTAL	1917	118	55	182	155	56

TOTAL INTENSITY OF UNASSIGNED IONS: 267

TABLE D13

ELEMENTAL DISTRIBUTION OF THE 600N P-3 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	62			36		
-2	283		9	58		21
-4	306			283		23
-6	348			245	11	25
-8	311		15	112	93	36
-10	84		17	288	358	50
-12	136	11		199	525	39
-14	111	15	15	133	590	
-16	69	13	11	56	798	
-18	175		9	65	564	
-20	21	32			545	
-22	107	13			282	
-24	26				147	
-26	95	24			91	
-28	9				39	
-30	52					
-32	15					
TOTAL	2210	108	76	1475	4043	194

TOTAL INTENSITY OF UNASSIGNED IONS: 266

TABLE D14

ELEMENTAL DISTRIBUTION OF THE 600N P-5 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	89		10			
-2	283	45	45	34		25
-4	350	31	16	38		27
-6	363		14	37		12
-8	323	58		25	23	
-10	143	20		11	116	12
-12	146		11		199	
-14	120				155	
-16	69	19			143	8
-18	83	14			131	
-20	18	18			49	
-22		16				
-24				16	7	
-26	22					
-28				18		
-30	12					
-36			10			
-42						11
-44		11				10
-46				24		
TOTAL	2021	232	106	203	823	105

TOTAL INTENSITY OF UNASSIGNED IONS: 436

TABLE D15

ELEMENTAL DISTRIBUTION OF THE 600N P-6 POLAR SUBFRACTION
BY HIGH RESOLUTION MASS SPECTROMETRY
(ION-INTENSITY UNITS)

UNSAT.	CH	CHO1	CHO2	CHO3	CHN1	CHS1
0	7		1			1
-2	21	105	19	3		1
-4	19	16	14	4		
-6	12	1	1	1		
-8	11	1				
-10	4				2	
-12	2		4	1		
-14	1	1				
-16			1			
-18		1			1	
-20		1				
-22		1				
-24				1		
-26	2					
-28	1			1		
-30	1		1			
-36			1			
-42						1
-44						1
-46		11	7	1		1
TOTAL	81	138	49	12	3	5

TOTAL INTENSITY OF UNASSIGNED IONS: 45

108

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5. AUTHOR(S)

S. M. Hsu, P. Pei, and R. S. Gates

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

A high performance liquid chromatography separation scheme which subdivides three lubricating base oils into molecular compound classes has been developed. These compound classes were characterized analytically and also with regard to oxidation, friction, and wear characteristics. In part 1 of this report, the separation scheme and chemical characterization of the fractions are described.
The separation scheme is subdivided into two stages. During the first stage, the lubricating base oil is separated into three major fractions-- saturates, aromatics, and polars using clay-silica gel liquid chromatography. The saturate fraction consists mainly of paraffinic and cyclic paraffinic compounds. The aromatic fraction is composed of mono-, di-, and tri-aromatic compounds. Both polynuclear aromatic compounds and hetroatoms such as nitrogen, sulfur, halogen, and oxygen are present in the polar fraction. The polar fraction is found to have the most influence on performance. The polar fraction is further separated into narrow molecular compounds classes having different polarities and functional structures via neutral alumina column chromatography. Analytical methods such as elemental analyses, infrared and high resolution mass spectrometry were used to elucidate the functional structures of the compounds in each fraction.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

HPLC; hydrocarbon separation; liquid-solid chromatography; lubricating base oils; molecular structural influence; polar molecules; structural characterization; tribology

13. AVAILABILITY ☒ Unlimited ☐ For Official Distribution. Do Not Release to NTIS ☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. ☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161	14. NO. OF PRINTED PAGES 114
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