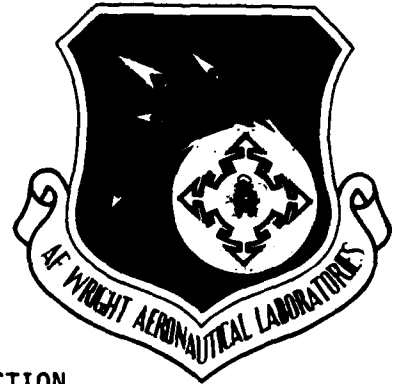


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QUANTITATIVE DETERMINATION OF HYDROCARBON
GROUP-TYPES VIA HIGH PERFORMANCE
LIQUID CHROMATOGRAPHY WITH DIELECTRIC CONSTANT DETECTION

P. C. Hayes Jr.
S. D. Anderson

Fuels Branch
Fuels and Lubrication Division

July 1985

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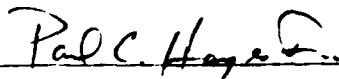
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This technical report has been reviewed and is approved for publication.



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FOREWORD

This technical report describes work performed under the In-House Work Unit 30480591 administered by the Fuels Branch (POSF), Fuels and Lubrication Division (POS), Aero Propulsion Laboratory (AFWAL/PO), Air Force Wright Aeronautical Laboratories. Project scientists for this program were Paul C. Hayes Jr. and Steven D. Anderson, both of whom also prepared this report.

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SECTION I
INTRODUCTION

The abundance of high quality, low cost petroleum crudes and feedstocks is rapidly diminishing. Current feedstocks are incorporating lower grade crudes and off-streams as well as processed liquids from alternate sources of energy, e.g., shale oil, tar sands, coal liquids, and biomass materials. The petrochemical engineer needs timely and accurate analytical results to optimize refinery operations and monitor product character. Consequently, the analytical chemist must respond faster with more pertinent and accurate compositional detail on samples of a continuously variable nature.

Liquid chromatography has helped to characterize the group composition of crude oils and petroleum products since the beginning of this century. The fluorescent indicator adsorption (FIA) method, ASTM D 1319 (Reference 1), has served for over 30 years as the official method of the petroleum industry for measuring the paraffinic, olefinic, and aromatic content of gasolines and jet fuels. Despite its widespread use, the FIA has numerous limitations as detailed by Suatoni and co-workers (Reference 2), Ettore, et al. (Reference 3), and recently by Norris and Rawdon (Reference 4).

However, a severe shortcoming of most high performance liquid chromatographic (HPLC) approaches to a hydrocarbon group-type analysis is the difficulty in obtaining accurate response factors applicable to different distillate products. Unfortunately, accuracy can be compromised when these response factors are used to analyze hydrotreated and hydrocracked materials having the same boiling range. As Drushel (Reference 5) observed, given

significant changes in the hydrocarbon distribution within a certain group-type, analytical results will be misleading for such samples because of the variation in response with carbon number exhibited by most routinely used HPLC detectors. Thus the ideal detector for a truly versatile and accurate hydrocarbon group-type analysis is one that is sensitive to hydrocarbons, of course, but demonstrates a response that is independent of carbon number.

Two recent HPLC separation schemes are particularly interesting since they also incorporate detectors not usually associated with conventional hydrocarbon group-type analyses. Matsushita, et al. (Reference 6) employed dual column chromatography with carbon tetrachloride as the mobile phase and infrared detection. Ettre, et al. (Reference 3) also investigated the infrared detector but instead used only a single column and Fluorinert FC-72 (perfluoroheptane) as the mobile phase. However, in both cases, the relative response factors spanned a wide range, thus limiting the methods to a particular distillate product (References 3,4). Norris and Rawdon (References 4,7) reported on a hydrocarbon type analysis that employed the same kind of column packings as Matsushita but utilized supercritical carbon dioxide as the mobile phase with flame ionization detection. This method holds great promise owing to the sensitivity and uniformity of response to hydrocarbons that is characteristic of the flame ionization detector.

Alfredson and Tallman (Reference 8) suggested that a dielectric constant (DC) detector, marketed specifically for HPLC (References 9-14), may offer a viable means of quantitation in a hydrocarbon type analysis of petroleum products. Presented herein is an HPLC scheme that incorporates a dielectric constant detector for the accurate determination of hydrocarbon group-types in a myriad of hydrocarbon matrices.

SECTION II

EXPERIMENTAL

A Varian Model 4200 Liquid Chromatograph was used to perform all the analyses in this study. It is equipped with a Varian Model 8000 autosampler, a Valco six port injection valve with 10 μ L sample loop, and an Optichrom Model 430 Dielectric Constant Detector (Applied Automation, Inc.). Two Partisil PAC columns (Whatman), 25 x 4.6 mm i.d., 5 μ m particle size, and one TENF (Tetranitrofluorenimino) column (ES Industries), 30 x 4.6 mm i.d., 10 μ m particle size, were used for the separations. A guard column (Upchurch Scientific, Inc.) packed with 30-40 μ m pellicular silica preceded the analytical columns. Quantitation was accomplished on the Hewlett Packard 3357 Laboratory Automation System. Perpendicular baseline drops displayed in the chromatograms were automatically determined by the computer without outside manipulation.

HPLC grade n-butyl chloride (Burdick + Jackson) was used for the mobile phase. It was dried by adding 4A molecular sieves directly into the solvent bottle, agitating the bottle, and allowing it to sit overnight. The mobile phase was filtered to remove any particulates above 0.45 μ m in size.

Calibration of the detector was accomplished by selecting one compound to represent each hydrocarbon group and calculating response factors relative to the saturate component. The calibration mix was prepared by accurately pipetting 1 mL each of iso-octane, ethyl benzene, and 3,3-dimethyldiphenyl into a 100 mL volumetric flask and diluting with n-butyl chloride to the mark. Relative response factors of 1.00 for the saturates, 1.10 for the alkyl benzenes and 1.20 for the alkyl naphthalenes were obtained.

Samples were prepared for analysis by diluting them ~1:30 in n-butyl

chloride. This was accomplished by using a micropipetter to deliver ~50 uL of sample into an HPLC autosampler vial and diluting with mobile phase (~1500 uL total solution). This dilution factor ensured that we remained well within the linear dynamic range of the detector.

The liquid chromatographic separations were completed in 24 minutes using a 0.5 mL/min sample cell flow rate. The analysis time could be significantly reduced by raising the sample cell flow rate with minimal deterioration to the separations.

The PAC columns were primarily responsible for separating the saturates from the aromatics, but some selectivity was observed for the aromatic group itself. The addition of the TENF column improved the resolution between the alkyl benzene and alkyl naphthalene groups. A summary of the experimental operating conditions is shown in Table 1. (NOTE: both the sample cell and the reference cell require flowing environments, however, the flow rates need not be matched.)

TABLE 1
HPLC OPERATING CONDITIONS

SYSTEM PARAMETERS	OPTION/VALUE
DETECTOR TYPE ELECTROMETER	DIELECTRIC CONSTANT (DC) AMP RANGE = X1; ATTN = 1000 mvFS
INJECTOR TYPE SAMPLE	AUTOSAMPLER W/ 10 uL LOOP DILUTED ~1:30 W/ MOBILE PHASE
MOBILE PHASE	n-BUTYL CHLORIDE
DC CELL FLOW RATES	SAMPLE CELL = 0.5 mL/min REFERENCE CELL ~ 0.1 mL/min
DC CELL TEMPERATURE	AMBIENT (INSULATED)
BACK PRESSURE	~1000 psig for 3 COLUMNS
COLUMN TYPES	ALKYL AMINO-NITRILE (PAC) TETRANITROFLUORENIMINO (TENF)

SECTION III

RESULTS AND DISCUSSION

1. THE DETECTOR

The characteristics and applications of a commercially available dielectric constant detector for HPLC have been exhaustively investigated and reported by Benningfield, et al. (References 9-14). In general, the DC detector measures small changes in the dielectric constant of the liquid stream eluting from an HPLC column, i.e., the sample stream. To minimize detector drift and noise caused by fluctuations in the dielectric constant of the sample stream, the difference in capacitance of two nearly identical parallel-plate capacitors is monitored. One capacitor (reference cell) has simply pure mobile phase flowing through it. The other capacitor (sample cell) has the HPLC column eluants passing through it. The difference in capacitance is converted to an analog output signal for data collection and reduction.

Basically, the DC detector is a universal detector that responds to a change in a bulk property (dielectric constant) of the mobile phase. But what is the "right" mobile phase to use with this detector for a hydrocarbon group-type analysis? The mobile phase must have a relatively low solvent strength to enable conventional HPLC columns to resolve hydrocarbon groups that characteristically display low capacity factors. Concurrently, the mobile phase must have a relatively high dielectric constant to provide uniformity of response as indicated in previous applications of the detector (References 9-14). Since all hydrocarbons have approximately the same dielectric constant (DC ~ 2.0), the selection of a mobile phase with a significantly higher dielectric constant offers a two-fold pay-off. The sensitivity of detection

for hydrocarbons is markedly amplified. The small differences in dielectric constants among the hydrocarbons is mitigated and their relative response factors converge on unity. This paper deals with optimizing mobile phase polarity and dielectric constant with column selection to effect adequate resolution in a hydrocarbon group-type analysis.

The minimum dielectric constant required of the mobile phase to ensure uniformity of response of the detector for hydrocarbons was found experimentally. Steric exclusion chromatography permitted the use of a binary mobile phase offering a wide range of dielectric constants and solvent strengths while still providing good separation of a series of normal paraffins. The mobile phase was a volumetrically accurate blend of p-dioxane (DC = 2.21) and methylene chloride (DC = 8.93). The resultant dielectric constant of each mobile phase mixture was calculated, but not measured. It was assumed that the dielectric constant of a binary mixture was linearly dependent on the volume fraction of each component, which is not necessarily true. However, the dielectric constant of an 80% p-dioxane/20% methylene chloride blend was determined by a modified ASTM D 924 (Reference 1) procedure to be 3.30 while calculated to be 3.55, the relative error being less than 8%.

Figure 1 illustrates the variation in the response of normal octane (n-C8) relative to normal docosane (n-C22) with increasing dielectric constant of the mobile phase. Normal paraffins with carbon numbers between these two compounds were also analyzed and showed intermediate values of relative response factors. According to Figure 1, a threshold of uniform response appears to occur at the knee in the curve corresponding to a mobile phase dielectric constant of roughly 4.5 to 5.0. For mobile phases with dielectric constants above that threshold value, the relative response factors of the normal paraffins varied by less than 2-3% from normal docosane. A perusal of the most commonly used

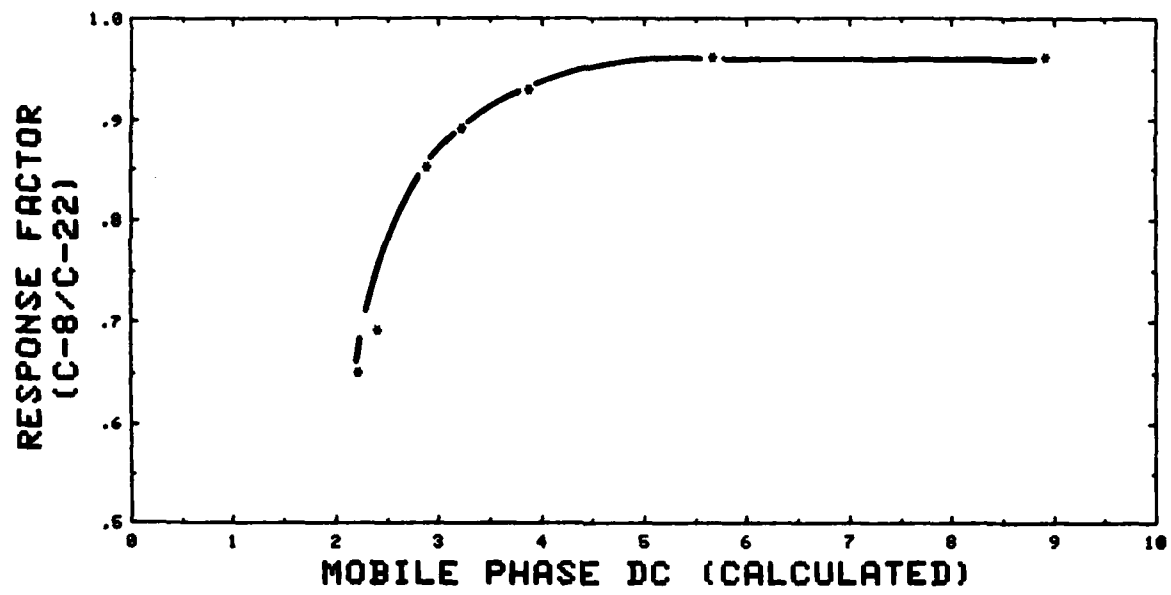


Figure 1. Response Factor Variation with Mobile Phase DC

HPLC solvents indicates n-butyl chloride has a sufficiently high dielectric constant ($\epsilon = 7.39$) but a relatively low solvent strength ($\epsilon = 0.26$).

Tables 2-7 list the relative response factors (RRF*), relative to n-C22, of over 100 hydrocarbons determined in triplicate on a single Whatman PAC column with n-butyl chloride as the mobile phase. These compounds have a high probability of occurring in jet fuels and cover a wide range of carbon numbers and structural complexity. In all cases, the relative standard deviation for a hydrocarbon group or sub-group was less than 2.6%. This uniformity of response is rivaled only by that of the flame ionization detector of gas chromatography.

Obviously, calibration of the analysis was extremely simple. Iso-octane was selected to represent all the saturates, ethylbenzene, all the alkyl benzenes, and 3,3-dimethylbiphenyl, all the polynuclear aromatic hydrocarbons. This three-component calibration mix was used to quantitate the separations of simple and complex standard solutions as well as real world fuel samples.

Another characteristic of the DC detector that is crucial for a successful hydrocarbon group-type analysis is the magnitude of the linear dynamic range with the above mobile phase (n-butyl chloride). Given a dilute solution, i.e., a solute injected into a flowing mobile phase, the dielectric constant of the mix when inside the sample cell of the DC detector should be a linear function of the volume fraction of that solute. Figure 2 is a plot of the linear dynamic range of the DC detector based on dilute solutions of iso-octane in n-butyl chloride. Since the other hydrocarbon group-types displayed nearly identical response as iso-octane, it was assumed that the linear dynamic range and the minimum detectability of the detector would be approximately the same for all other hydrocarbons.

The linear portion of Figure 2, i.e., between the two dashed vertical lines, indicates a linear dynamic range of approximately four (4) orders of

TABLE 2
DC RELATIVE RESPONSE FACTORS* (RRF): n-ALKANES

<u>HC GROUP-TYPE</u>	<u>COMPOUND NAME</u>	<u>CARBON #</u>	<u>RRF(VOL)</u>
n-alkanes	hexane	6	1.00
	heptane	7	1.04
	octane	8	1.03
	nonane	9	1.03
	decane	10	1.03
	undecane	11	1.05
	dodecane	12	1.01
	tridecane	13	1.02
	tetradecane	14	1.04
	pentadecane	15	1.03
	hexadecane	16	0.99
	heptadecane	17	1.01
	octadecane	18	1.01
	nonadecane	19	0.99
icosane	20	0.99	
heneicosane	21	0.99	
docosane	22	1.00	

AVERAGE RRF = 1.01
 S.D. = 0.02
 R.S.D. = 1.90%

TABLE 3
DC RELATIVE RESPONSE FACTORS* (RRF): BRANCHED PARAFFINS

HC GROUP-TYPE	COMPOUND NAME	CARBON #	RRF(VOL)
branched paraffins	2-methyl pentane	6	1.01
	2,2,3-trimethylbutane	7	1.03
	3-methylhexane	7	1.07
	2,2,4-trimethylpentane	8	1.04
	2-methylheptane	8	1.06
	2,2,4-trimethylhexane	9	1.05
	3-methyloctane	9	1.02
	2,3,4-trimethylhexane	9	1.07
	3,4,5-trimethylheptane	10	1.07
	2-methylnonane	10	1.06
	2-methyldecane	11	1.05
	3-methyl-4-ethyloctane	11	1.07
	2-methylundecane	12	1.03
	2,2,4,6,6-pentamethylheptane	12	1.03
	4,4-dipropylheptane	13	1.04
	3-methyldodecane	13	1.03
	3-methyltridecane	14	1.07
	2,6,11-trimethyldodecane	15	1.03
	3-methyltetradecane	15	1.05
	2,2,4,4,6,8,8-heptamethylnonane	16	1.07
2-methylpentadecane	16	0.99	
2-methylhexadecane	17	1.03	
5,5-dibutylnonane	17	1.00	

AVERAGE RRF = 1.04
S.D. = 0.02
R.S.D. = 2.20%

TABLE 4
DC RELATIVE RESPONSE FACTORS* (RRF): CYCLOPARAFFINS

HC GROUP-TYPE	COMPOUND NAME	CARBON #	RRF (VOL)
naphthenes	cyclohexane	6	1.04
	methylcyclopentane	6	1.01
	cycloheptane	7	1.01
	bicyclo(2.2.1)heptane	7	1.00
	c-1,2-dimethylcyclopentane	7	1.00
	methylcyclohexane	7	1.04
	t-1,2-dimethylcyclohexane	8	1.06
	i-propylcyclopentane	8	0.99
	methylcycloheptane	8	1.03
	butylcyclopentane	9	1.00
	c-bicyclo(4.3.0)nonane	9	1.07
	c-1-ethyl-2-methylcyclohexane	9	1.05
	c,t,t-1,2,4-trimethylcyclohexane	9	1.03
	c-decalin	10	1.07
	t-decalin	10	1.05
	t-1-methyl-4-i-propylcyclohexane	10	1.08
	i-camphane	10	1.00
	pentylcyclopentane	10	1.02
	pinane	10	1.04
	2-methylbutylcyclohexane	11	1.04
	1-butyl-1-2,5-dimethylcyclohexane	12	1.06
	heptylcyclohexane	13	1.06
	octylcyclohexane	14	1.04
nonylcyclohexane	15	1.06	
decylcyclohexane	16	0.99	
dodecylcyclohexane	18	1.03	

AVERAGE RRF = 1.04

S.D. = 0.03

R.S.D. = 2.57

TABLE 5
DC RELATIVE RESPONSE FACTORS* (RRF): 1-OLEFINS

HC GROUP-TYPE	COMPOUND NAME	CARBON #	RRF(VOL)
1-olefins	1-heptene	7	1.04
	1-octene	8	1.06
	1-decene	10	1.08
	1-undecene	11	1.07
	1-dodecene	12	1.04
	1-tridecene	13	1.04
	1-tetradecene	14	1.03
	1-hexadecene	16	1.03
	1-octadecene	18	1.05
	1-eicosene	20	1.03

AVERAGE RRF = 1.05
 S.D. = 0.02
 R.S.D. = 1.89%

TABLE 6
DC RELATIVE RESPONSE FACTORS* (RRF): ALKYL BENZENES

HC GROUP-TYPE	COMPOUND NAME	CARBON #	RRF(VOL)
alkyl benzenes	benzene	6	1.09
	toluene	7	1.08
	o-xylene	8	1.13
	m-xylene	8	1.11
	p-xylene	8	1.09
	ethylbenzene	8	1.11
	propylbenzene	9	1.10
	1,2,4-trimethylbenzene	9	1.11
	indan	9	1.13
	tetralin	10	1.13
	butylbenzene	10	1.15
	pentylbenzene	11	1.15
	1-tert-butyl-3-methylbenzene	11	1.15
	hexylbenzene	12	1.14
	1-tert-butyl-4-ethylbenzene	12	1.17
	heptylbenzene	13	1.10
	1-tert-butyl-3,4,5-trimethylbenzene	13	1.10
octylbenzene	14	1.10	
nonylbenzene	15	1.15	
tridecylbenzene	19	1.10	

AVERAGE RRF = 1.12

S.D. = 0.03

R.S.D. = 2.46%

TABLE 7
DC RELATIVE RESPONSE FACTORS* (RRF): POLYCYCLIC AROMATIC HYDROCARBONS

HC GROUP-TYPE	COMPOUND NAME	CARBON #	RRF(VOL)
pah's	naphthalene	10	1.20
	2-methylnaphthalene	11	1.17
	2,3-dimethylnaphthalene	12	1.22
	biphenyl	12	1.22
	bibenzyl	14	1.16
	3,3-dimethylbiphenyl	14	1.18
	anthracene	14	1.19

AVERAGE RRF = 1.19
S.D. = 0.02
R.S.D. = 2.08%

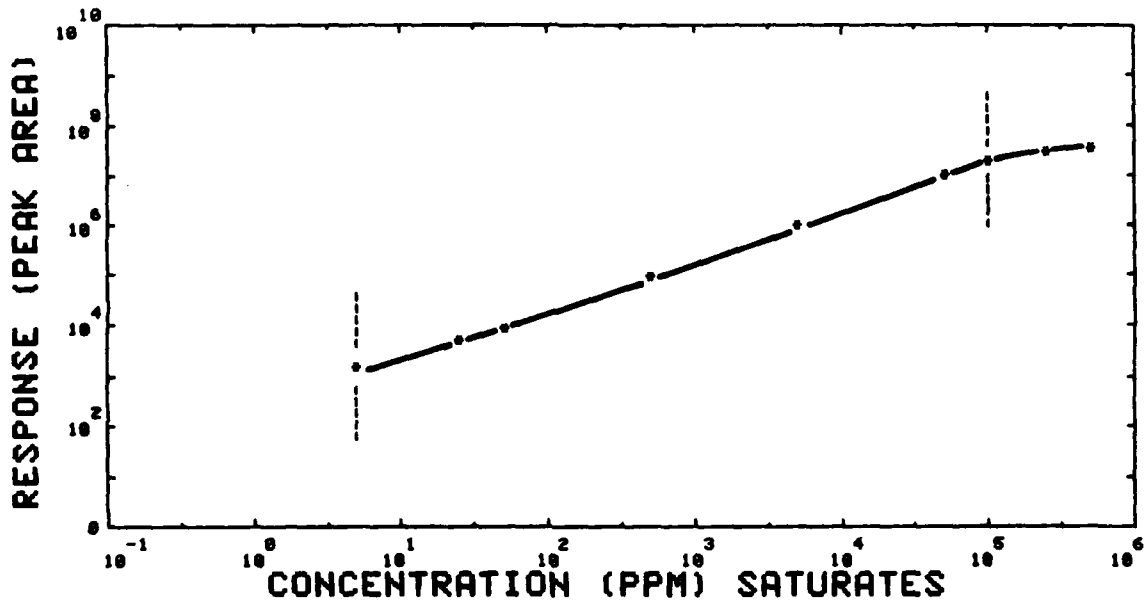


Figure 2. DC Detector Linear Dynamic Range

magnitude with a correlation coefficient of 0.9989. Given a signal-to-noise ratio of 2:1, the minimum detectability of the detector (with one HPLC column) is approximately 1 ppm for iso-octane. This value compares favorably with previously reported data (Reference 11). The minimum detectability of the detector should not be confused with the limit of chromatographic detection of the system which incorporates the band broadening contributions of the sample injection loop (10 uL), the guard column, three analytical columns, all the interconnecting tubing, and the dead volume of the detector (~23 uL). For a late eluting solute, i.e., biphenyl, the chromatographic limit of detection was found to be approximately 150 ng, given a signal-to-noise ratio of ~ 2:1.

2. THE ANALYSIS

In order to identify the different hydrocarbon groups, the elution window for each group had to be mapped. Chromatographic runs of hydrocarbon standards indicated that a molecular sizing phenomena was occurring within each hydrocarbon group. The largest compounds eluted first and the smallest compounds eluted last. With this in mind, compounds found in jet fuel were selected that represented the high and low molecular size extremes of each group (See Figure 3). Retention times were measured for these compounds assuming that all other hydrocarbons in that group-type would elute within that specific time window. Incomplete resolution of hydrocarbon groups was observed in several of the standard mixtures and jet fuel samples. When the larger alkyl benzenes (phenyloctane and above) were present, overlap occurred between the saturate and alkyl benzene groups. Overlap was also observed between large alkyl naphthalenes, i.e., 5,6-dimethyl-1-(4-methylpentyl)naphthalene, and small alkyl benzenes. This overlap did not pose any serious problem for two reasons: a) the relative response factors for each hydrocarbon group are similar and thus quantitative errors are minimized, b) the large compounds causing such overlaps between hydrocarbon groups are usually not found in significant concentrations in fuel distillates.

Standard mixtures were initially analyzed in which the volume percent of each hydrocarbon group was accurately known. The HPLC results were compared to the FIA (ASTM D1319) and mass spectrometric (ASTM D2789) methods (References 1,15). The quantitative results were directly determined in volume percent for each method. All results used in the comparison were calculated from single sample runs affording no advantage to any one method. (NOTE: the mass

HYDROCARBON ELUTION WINDOWS

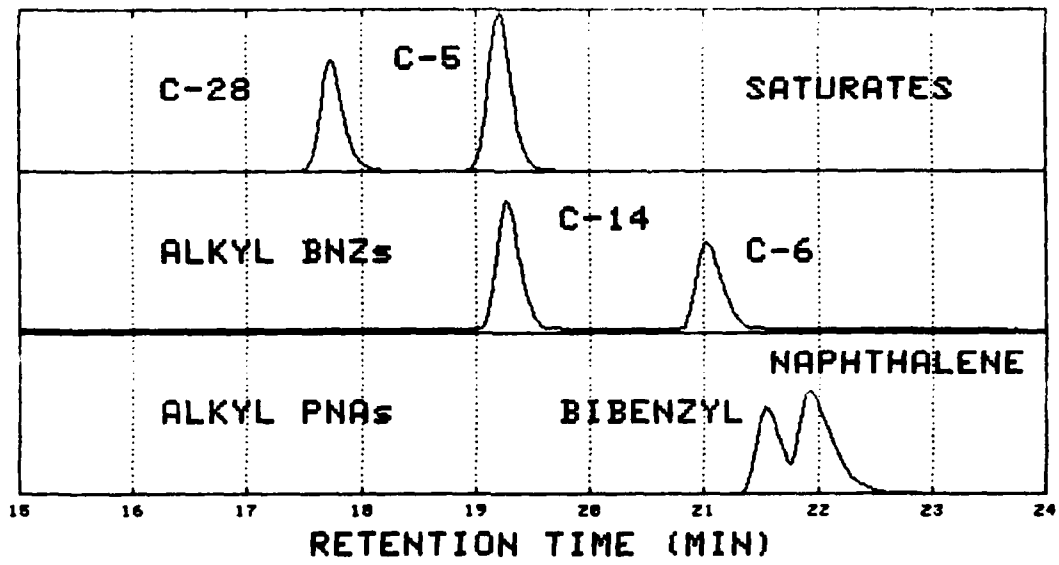


Figure 3. Hydrocarbon Group-Type Elution Windows

spectrometric method was developed to analyze complex hydrocarbon matrices, therefore, the results calculated by this method for the simpler standard mixtures are suspect.)

Tables 8-12 list the individual components, the amount of each component, and the carbon number range of the hydrocarbon groups in each standard mixture analyzed. Figures 4-8 compare the quantitative results of these standard mixes as determined by the three methods. The results for the HPLC method compare most favorably with the known volume percentages in each hydrocarbon group.

The composition of the "Grand Mix" is displayed in Table 13. This is an extremely complex standard mixture with over 400 compounds detected by capillary GC-FID (Figure 9). The quantitative results determined for the three methods are shown in Figure 10. Coelution of the olefins with the saturates account for the high results reported for the saturate group in the HPLC analysis.

A comparison of the absolute error for total aromatics in several standard mixtures, as determined by the different methods, is shown in Table 14. Each mixture varies greatly as to the number of components in a particular hydrocarbon group and the carbon number range represented.

Figures 11-19 demonstrate the ability of the HPLC method to analyze actual fuel distillates with vastly different hydrocarbon distributions. Note that in spite of incomplete resolution between the saturate and alkyl benzene groups, the HPLC method compares quite favorably with the mass spectrometric results. In Figure 20 and Table 15, the hydrogenation of a light pyrolysis fuel oil was monitored and quantitated. The top chromatogram, Figure 20a, represents the highly aromatic fuel oil before hydrogenation. The chromatogram indicates that there is a significant amount of alkyl naphthalenes present. The middle and bottom chromatograms, Figure 20b and 20c respectively, reflect the decrease in the naphthalenes and the dramatic increase in the saturates after hydrogenation.

TABLE 8
PREPARATION OF STANDARD MIX: VN-82-221

<u>HC CLASS</u>	<u>CARBON #</u>	<u>COMPONENT NAME</u>	<u>VOL %</u>
SATURATES	---	-----	87.5
	6	CYCLOHEXANE	25.0
	7	METHYLCYCLOHEXANE	25.0
	12	DODECANE	12.5
	16	HEXADECANE	25.0
ALKYL BNZs	---	-----	12.5
	12	CYCLOHEXYLBENZENE	12.5

TABLE 9
 PREPARATION OF STANDARD MIX: VN-82-214

HC CLASS	CARBON #	COMPONENT NAME	VOL %
SATURATES	---	-----	71.4
	7	METHYLCYCLOHEXANE	14.3
	8	ISOCTANE	28.5
	10	DECANE	14.3
	12	DODECANE	14.3
ALKYL BNZs	---	-----	28.6
	7	TOLUENE	14.3
	8	p-XYLENE	14.3

TABLE 10
 PREPARATION OF STANDARD MIX: VN-82-215

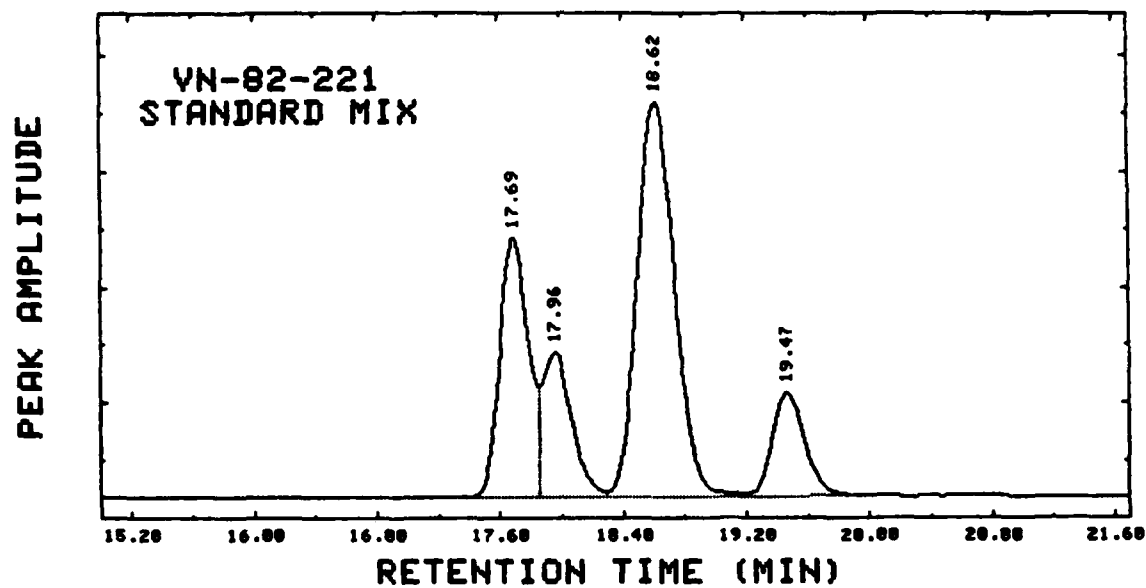
HC CLASS	CARBON #	COMPONENT NAME	VOL %
SATURATES			53.5
	7	METHYLCYCLOHEXANE	3.9
	7	2-METHYLHEXANE	2.2
	7	2,2,3-TRIMETHYLBUTANE	6.5
	8	ISOOCTANE	5.2
	9	NONANE	5.2
	9	4-METHYLOCTANE	1.2
	9	2,5-DIMETHYLHEPTANE	0.8
	9	2,2,5-TRIMETHYLHEXANE	3.9
	10	DECANE	5.2
	11	HENDECANE	5.2
	11	2-METHYLDECANE	1.2
	12	DODECANE	5.2
	15	PENTADECANE	3.9
	16	HEXADECANE	3.9
ALKYL BNZs			46.5
	7	TOLUENE	5.2
	8	m-XYLENE	5.2
	8	p-XYLENE	6.5
	9	1,3,5-TRIMETHYLBENZENE	3.8
	9	1-ETHYL-4-METHYLBENZENE	5.2
	9	ISOPROPYLBENZENE	3.8
	10	TETRAHYDRONAPHTHALENE	2.5
	12	CYCLOHEXYLBENZENE	7.8
	14	PHENYLOCTANE	6.5

TABLE 11
PREPARATION OF STANDARD MIX: VN-82-210

HC CLASS	CARBON #	COMPONENT NAME	VOL %
SATURATES	---	-----	71.4
	6	CYCLOHEXANE	9.2
	7	2-METHYLHEXANE	1.6
	7	3-METHYLHEXANE	2.0
	7	METHYLCYCLOHEXANE	7.0
	8	OCTANE	2.9
	8	ISOOCTANE	4.0
	9	NONANE	4.7
	9	3-METHYLOCTANE	1.2
	9	2,5-DIMETHYLHEPTANE	2.4
	10	DECANE	4.7
	10	3,6-DIMETHYLOCTANE	1.6
	10	4-PROPYLHEPTANE	0.8
	10	DECALINS (c,t)	1.8
	10	JP-10	10.6
	11	HENDECANE	1.9
	11	2-METHYLDECANE	0.7
	12	DODECANE	9.5
	15	PENTADECANE	1.9
	16	HEXADECANE	2.9
ALKYL BNZs	---	-----	16.8
	7	TOLUENE	6.5
	8	m-XYLENE	10.3
ALKYL PNAs	---	-----	11.8
	10	NAPHTHALENE	2.3
	11	2-METHYLNAPHTHALENE	3.4
	12	2-ETHYLNAPHTHALENE	1.6
	12	2,3-DIMETHYLNAPHTHALENE	1.2
	12	2,6-DIMETHYLNAPHTHALENE	0.6
	12	BIPHENYL	1.6
	14	BIBENZYL	1.1

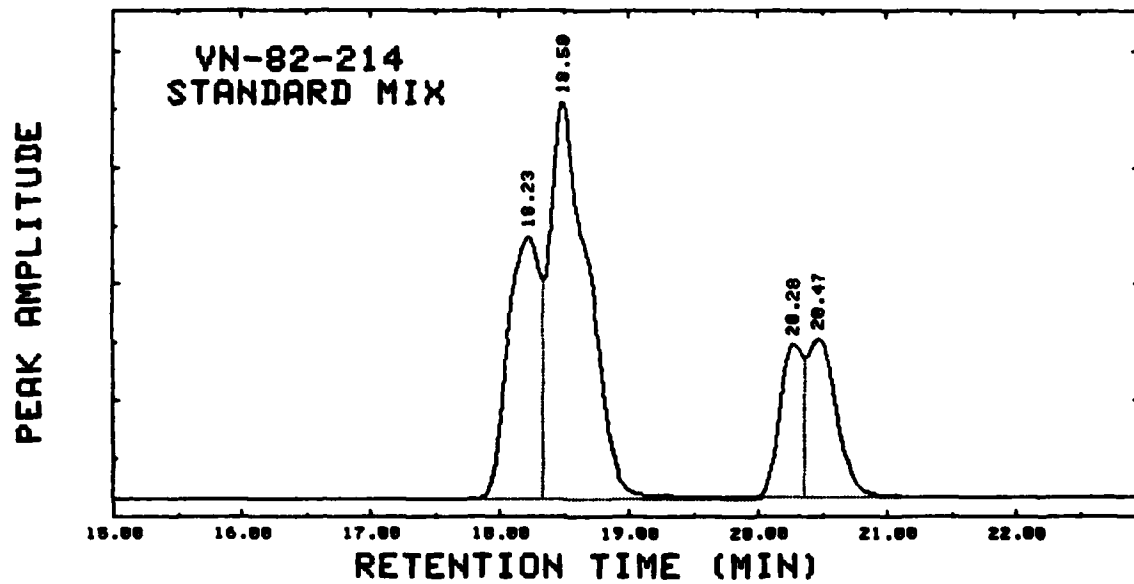
TABLE 12
 PREPARATION OF STANDARD MIX: VN-82-216

HC CLASS	CARBON #	COMPONENT NAME	VOL %
SATURATES			51.1
	6	CYCLOHEXANE	7.3
	7	2-METHYLHEXANE	2.6
	7	3-METHYLHEXANE	3.3
	7	METHYLCYCLOHEXANE	5.5
	8	OCTANE	0.2
	8	ISOOCTANE	6.6
	9	NONANE	0.4
	9	3-METHYLOCTANE	2.1
	9	2,5-DIMETHYLHEPTANE	4.2
	10	DECANE	0.4
	10	3,6-DIMETHYLOCTANE	2.9
	10	4-PROPYLHEPTANE	1.4
	10	DECALINS (c,t)	1.6
	10	JP-10	10.1
	11	HENDECANE	0.1
	11	2-METHYLDECANE	1.3
	12	DODECANE	0.6
	15	PENTADECANE	0.2
	16	HEXADECANE	0.2
ALKYL BNZs			38.9
	7	TOLUENE	7.3
	8	m-XYLENE	10.5
	8	p-XYLENE	2.8
	9	ISOPROPYLBENZENE	1.4
	9	1,2,4-TRIMETHYLBENZENE	2.8
	9	1,3,4-TRIMETHYLBENZENE	1.7
	10	BUTYLBENZENE	1.1
	10	TETRALIN	1.6
	12	2-METHYLPENTYLBENZENE	0.8
	12	CYCLOHEXYLBENZENE	6.1
	14	PHENYLOCTANE	2.8
ALKYL PNAs			10.0
	10	NAPHTHALENE	2.0
	11	2-METHYLNAPHTHALENE	2.8
	12	2-ETHYLNAPHTHALENE	1.4
	12	2,3-DIMETHYLNAPHTHALENE	1.0
	12	2,6-DIMETHYLNAPHTHALENE	0.5
	12	BIPHENYL	1.4
	14	BIBENZYL	0.9



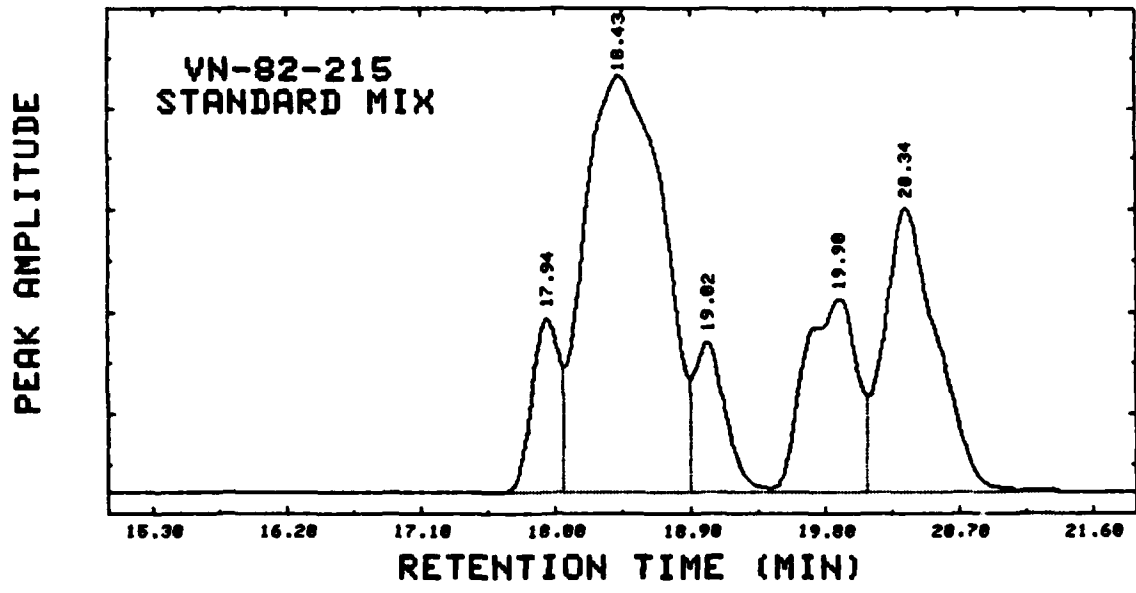
HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)				
SAMPLE: VN-82-221		STANDARD MIX		
	HPLC	FIA	MS	KNOWN
SATURATES	87.7	87.8	84.2	87.5
OLEFINS	----	0.7	----	0.0
ALKYL BNZs	12.3	----	15.0	12.5
ALKYL PNA _s	0.0	----	0.0	0.0
TOTAL AROMATICS	12.3	12.3	15.0	12.5

Figure 4. Comparative Analysis of VN-82-221 Standard Mix



HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)				
SAMPLE: VN-82-214		STANDARD MIX		
	MPLC	FIA	MS	KNOWN
SATURATES	72.4	71.9	73.0	71.4
OLEFINS	----	0.7	----	0.0
ALKYL BNZs	27.6	----	26.2	20.6
ALKYL PHAs	0.0	----	0.0	0.0
TOTAL AROMATICS	27.6	20.0	26.2	20.6

Figure 5. Comparative Analysis of VN-82-214 Standard Mix

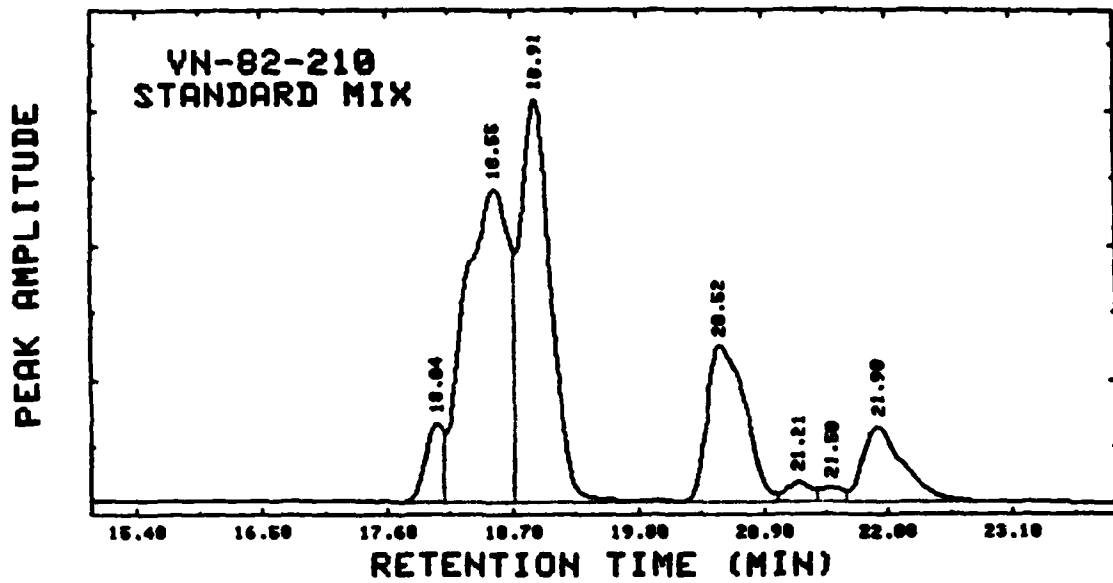


HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)

SAMPLE: VN-82-215 STANDARD MIX

	MPLC	FIA	MS	KNOWN
SATURATES	53.5	52.0	56.1	53.5
OLEFINS	----	0.0	----	0.0
ALKYL BNZs	46.5	----	43.9	46.5
ALKYL PNA _s	0.0	----	0.0	0.0
TOTAL AROMATICS	46.5	47.2	43.9	46.5

Figure 6. Comparative Analysis of VN-82-215 Standard Mix

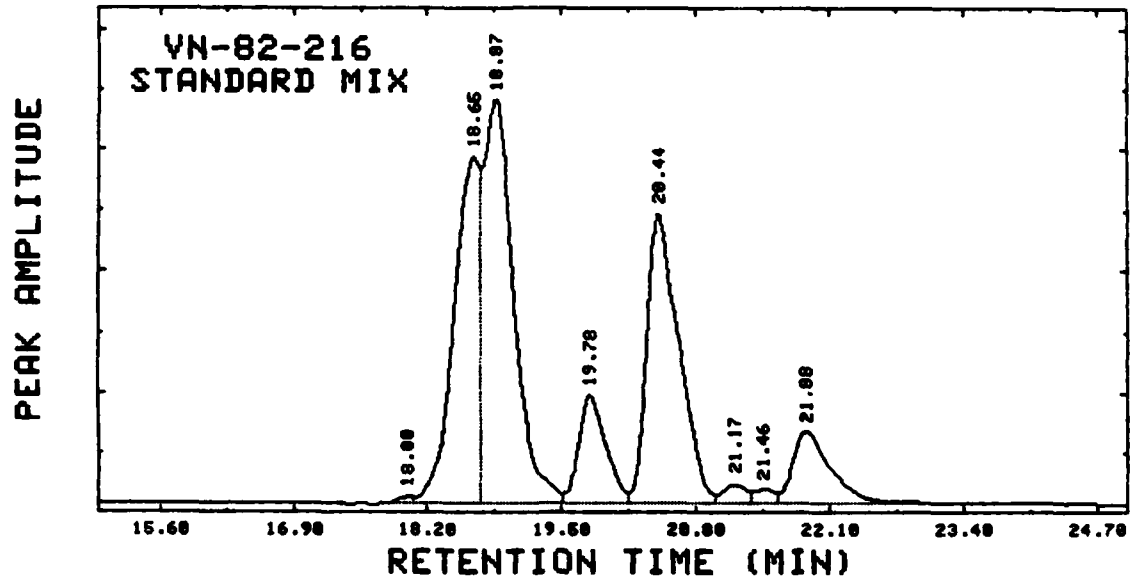


HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)

SAMPLE: VN-82-210 STANDARD MIX

	HPLC	FIA	MS	KNOWN
SATURATES	71.4	70.0	67.0	71.4
OLEFINS	----	0.0	----	0.0
ALKYL BNCs	16.0	----	20.0	16.0
ALKYL PHAs	11.0	----	12.2	11.0
TOTAL AROMATICS	20.6	29.2	32.2	20.6

Figure 7. Comparative Analysis of VN-82-210 Standard Mix



HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)				
	HPLC	FIR	MS	KNOWN
SATURATES	59.1	48.8	46.9	51.1
OLEFINS	----	1.5	----	0.0
ALKYL BNZs	36.7	----	42.2	38.9
ALKYL PNAs	10.2	----	10.9	10.0
TOTAL AROMATICS	46.9	50.5	53.1	48.9

SAMPLE: VN-82-216 STANDARD MIX

Figure 8. Comparative Analysis of VN-82-216 Standard Mix

TABLE 13
PREPARATION OF STANDARD MIX: GRAND MIX

<u>HC GROUP-TYPE</u>	<u>BLENDING STOCK/ PURE COMPONENT</u>	<u>VOL %</u>
saturates	-----	70.0
	hydrocracked n-C16 (C6-C16 isomers)	40.0
	methylcyclohexane	10.0
	JP-10 (dicycloparaffin)	20.0
alkyl benzenes	-----	20.0
	xylylene bottoms blending stock	19.0
	toluene	1.0
alkyl naphthalenes	-----	5.0
	2-Methylnaphthalene	3.0
	1-Ethylnaphthalene	1.0
	1,4-Dimethylnaphthalene	1.0
olefins	-----	5.0
	2-Heptenes (c,t)	2.0
	1-Octene	2.0
	1-Decene	1.0

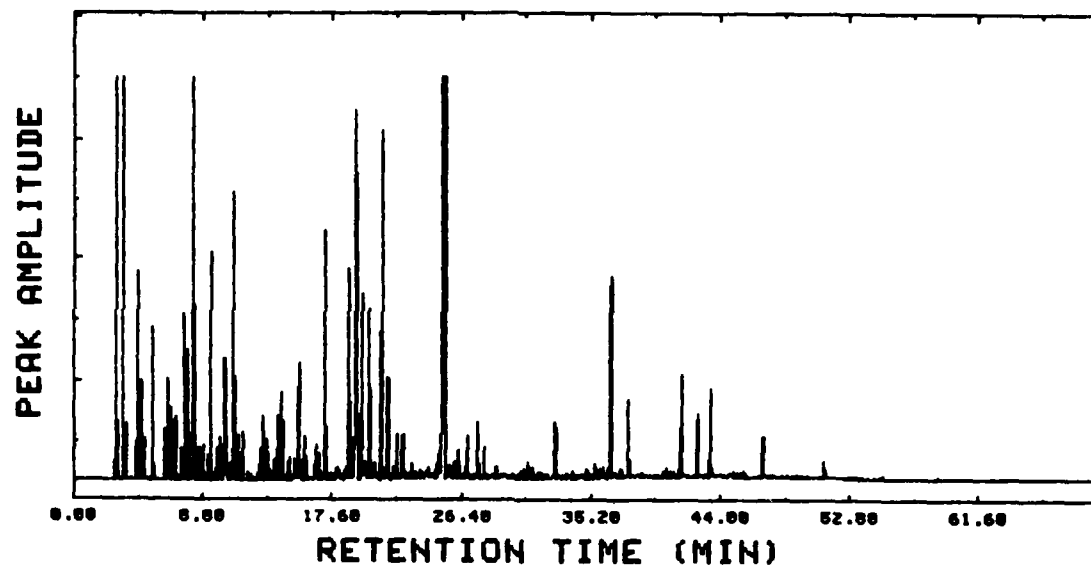
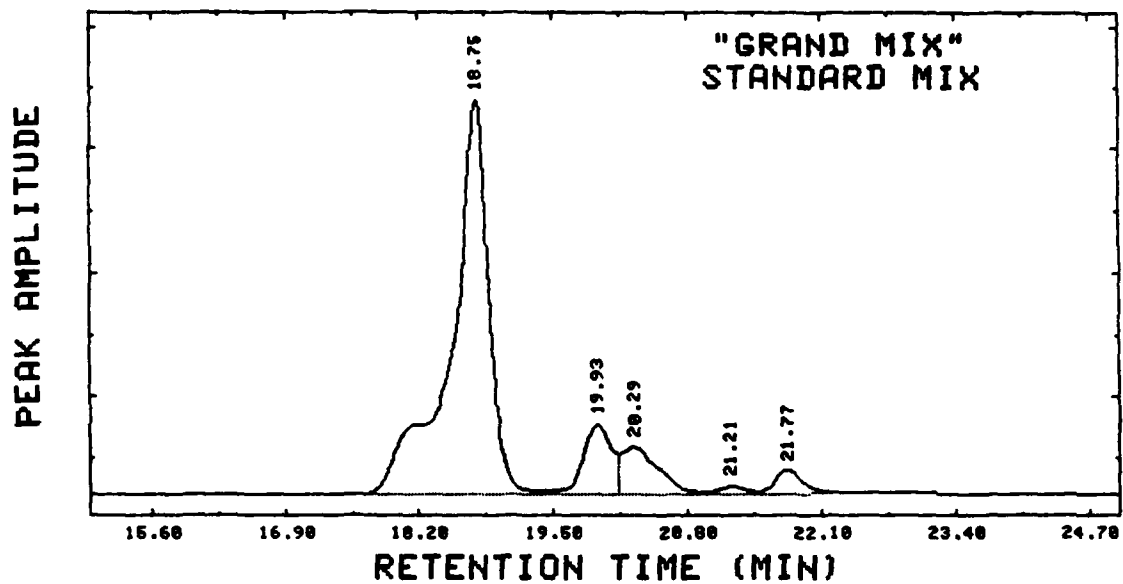


Figure 9. Capillary GC Chromatogram of "Grand Mix"
Operating Conditions: 60 m x 0.20 mm ID methyl-silicone bonded
phase fused silica column, 3°C/min directly from 35°C to 245°C,
 \bar{u} = 25 cm/sec (He), make-up = 30 ml/min (He)

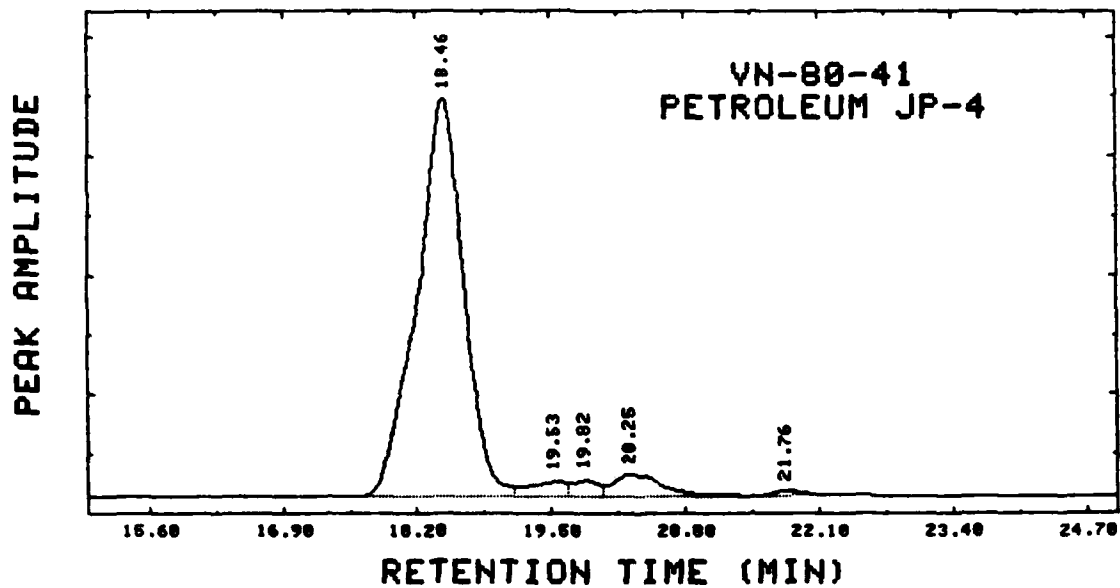


HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)				
SAMPLE:	GRAND MIX	STANDARD MIX		
	MPLC	FIA	MS	KNOWN
SATURATES	74.9	60.0	69.3	70.0
OLEFINS	----	3.7	----	5.0
ALKYL BNZs	20.1	----	24.0	20.0
ALKYL PNRs	5.0	----	5.0	5.0
TOTAL AROMATICS	25.1	27.5	30.7	25.0

Figure 10. Comparative Analysis of "Grand Mix"

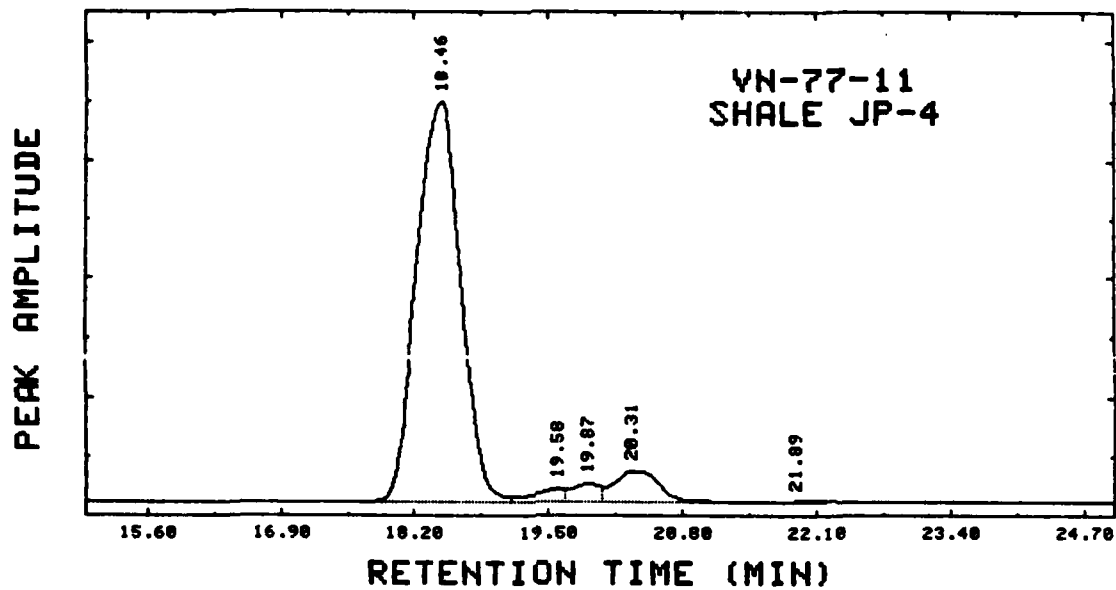
TABLE 14. COMPARISON OF ABSOLUTE ERROR FOR
TOTAL AROMATICS IN THE STANDARD MIXTURES (VOL%)

	KNOWN	HPLC	FIA	MS
VN-82-221	12.5	0.2	0.2	-3.3
VN-82-214	28.6	1.0	0.6	2.4
VN-82-215	46.5	0.0	-0.7	2.6
VN-82-210	28.6	0.0	-0.6	-3.6
VN-82-216	48.9	2.0	-1.6	-4.2
GRAND MIX	25.0	-0.2	-2.5	-5.7



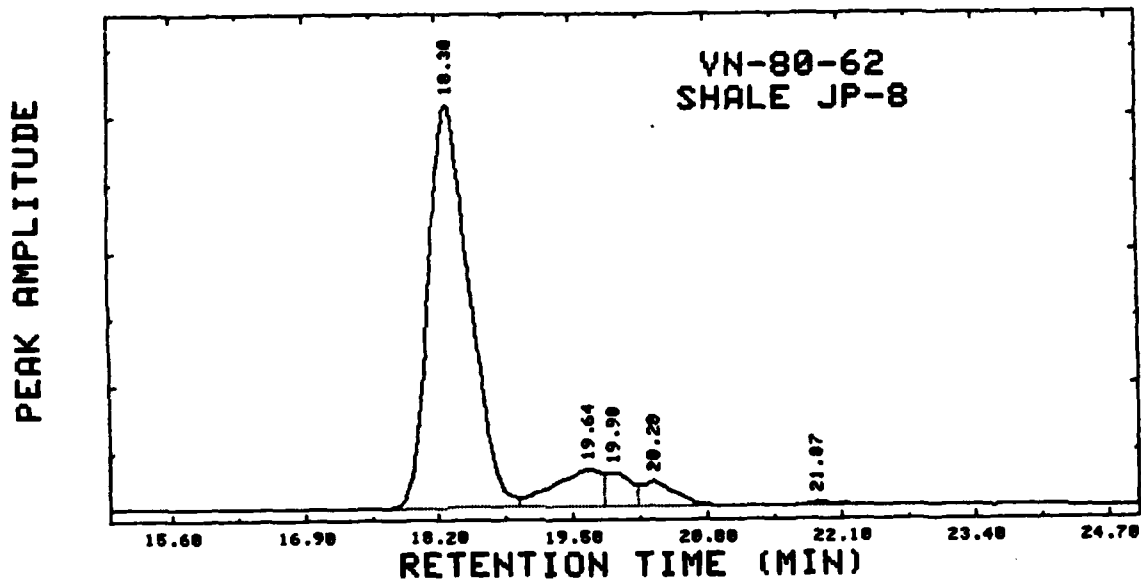
HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: VN-80-41		PETROLEUM JP-4	
	HPLC	FIA	MS
SATURATES	89.0	86.2	90.0
OLEFINS	----	1.5	----
ALKYL BNZs	10.3	----	9.5
ALKYL PNA's	0.7	----	0.5
TOTAL AROMATICS	11.0	12.3	10.0

Figure 11. Comparative Analysis of Petroleum-derived JP-4



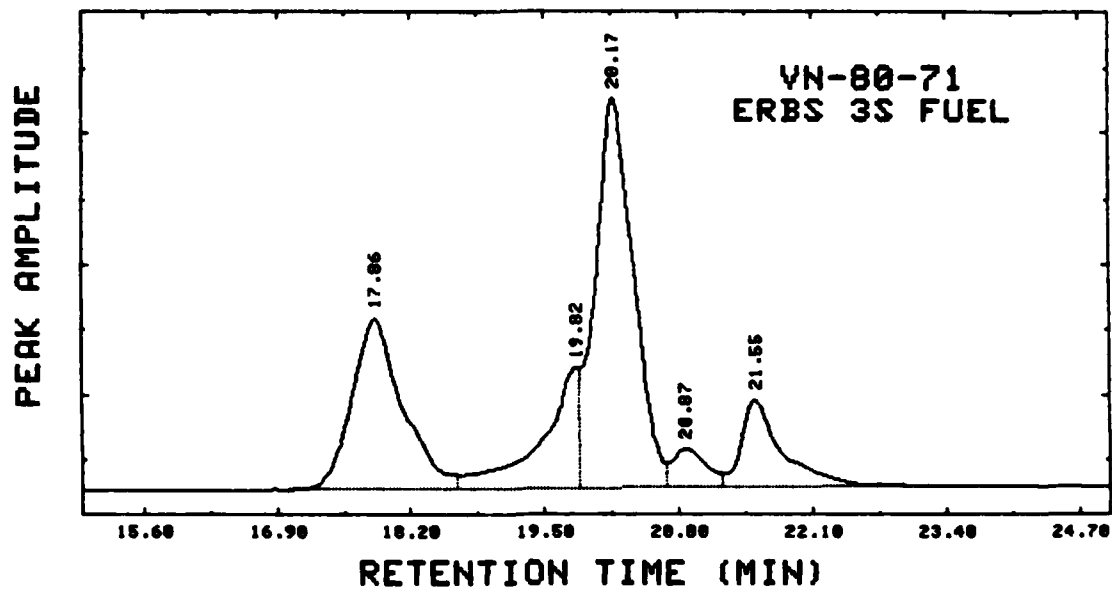
HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: VN-77-11		SHALE JP-4	
	NPLC	FIA	MS
SATURATES	87.6	86.8	89.9
OLEFINS	----	1.5	----
ALKYL BMZs	12.3	----	10.1
ALKYL PNAs	0.1	----	0.0
TOTAL AROMATICS	12.4	11.7	10.1

Figure 12. Comparative Analysis of Shale-derived JP-4



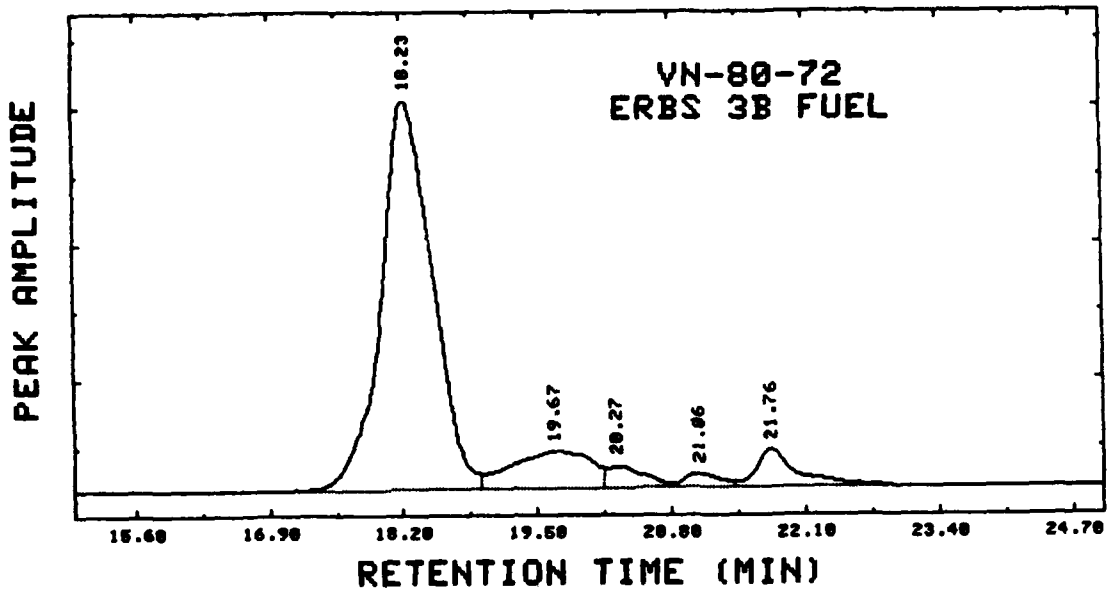
HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: VN-80-62		SHALE JP-8	
	HPLC	FIA	MS
SATURATES	88.7	76.2	79.5
OLEFINS	----	1.6	----
ALKYL BNZs	18.9	----	19.7
ALKYL PHAs	8.4	----	8.8
TOTAL AROMATICS	19.3	22.2	28.5

Figure 13. Comparative Analysis of Shale-derived JP-8



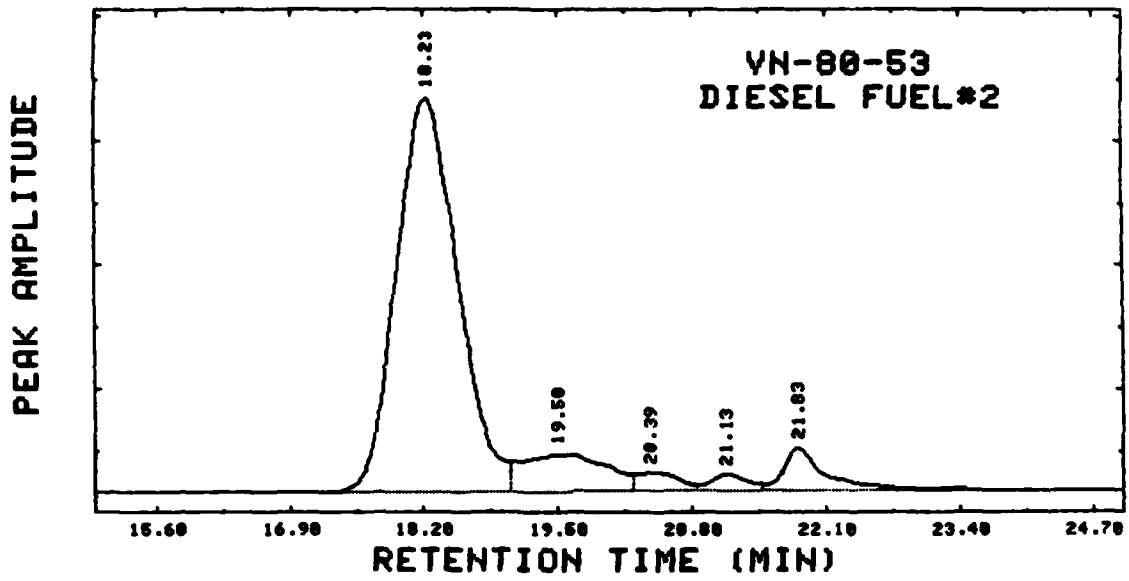
HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: VN-80-71		ERBS 3S FUEL	
	MPLC	FIA	MS
SATURATES	25.2	13.6	27.1
OLEFINS	----	0.6	----
ALKYL BNZs	60.4	----	50.0
ALKYL PNA _s	14.4	----	14.1
TOTAL AROMATICS	74.8	85.8	72.9

Figure 14. Comparative Analysis of Experimental Referee Broad Spec (ERBS)
Fuel: ERBS 3S



HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE:	VN-80-72 ERBS 3B FUEL		
	MPLC	FIR	MS
SATURATES	76.4	69.9	77.2
OLEFINS	----	0.6	----
ALKYL BNZs	15.3	----	15.6
ALKYL PNs	0.3	----	7.2
TOTAL AROMATICS	29.6	29.6	22.8

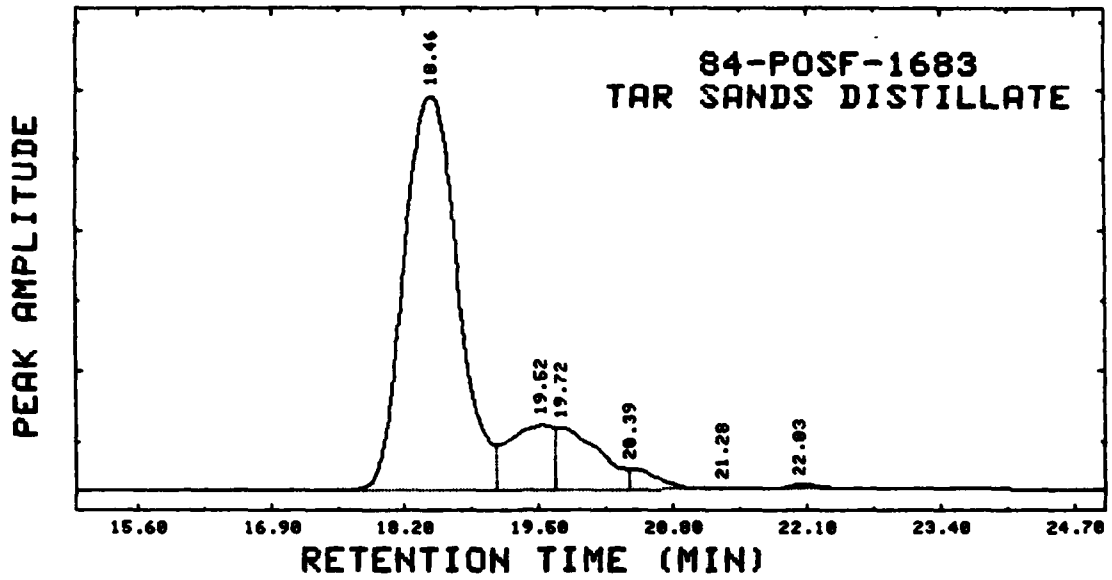
Figure 15. Comparative Analysis of Experimental Referee Broad Spec (ERBS)
Fuel: ERBS 3B



HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)
SAMPLE: VY-80-53 DIESEL FUEL (DF-2)

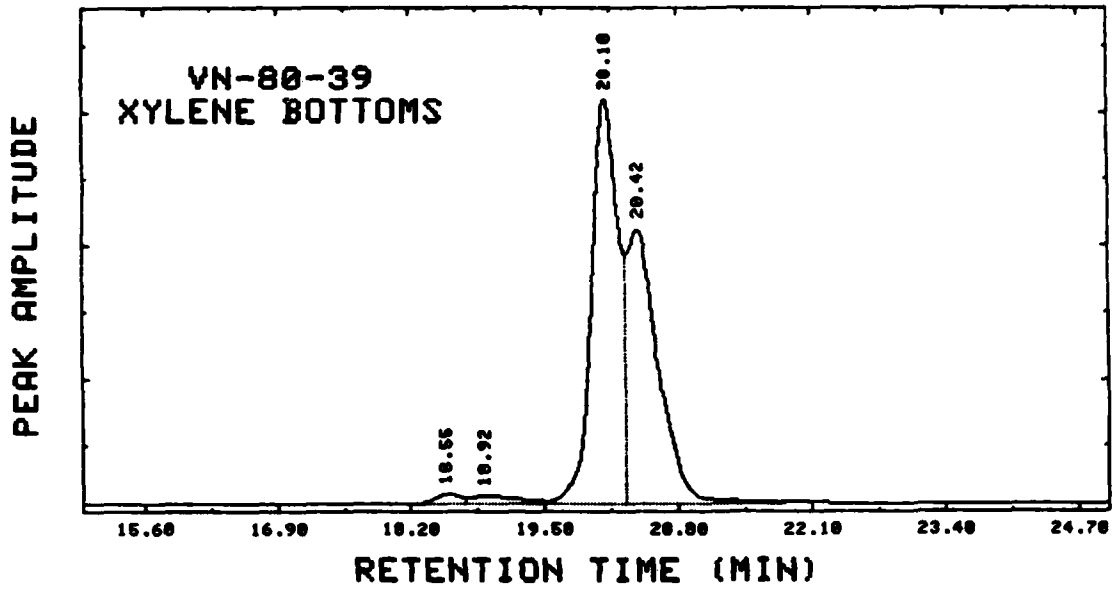
	MPLC	FIR	MS
SATURATES	76.4	65.0	78.4
OLEFINS	----	2.9	----
ALKYL BNZs	14.3	----	14.1
ALKYL PNAs	9.3	----	7.5
TOTAL AROMATICS	23.6	32.1	21.6

Figure 16. Comparative Analysis of Petroleum-derived Diesel Fuel No. 2



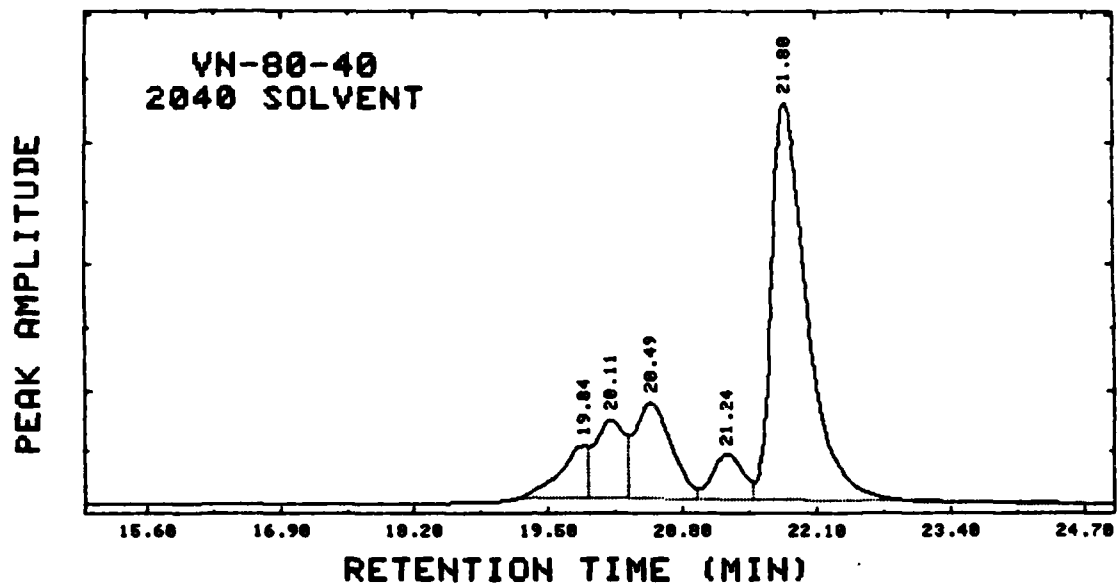
HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: 84-POSF-1683 TAR SANDS FUEL			
	MPLC	FIR	MS
SATURATES	74.9	61.0	70.0
OLEFINS	----	1.0	----
ALKYL BNZs	24.5	----	20.6
ALKYL PHAs	0.6	----	1.4
TOTAL AROMATICS	25.1	37.2	22.0

Figure 17. Comparative Analysis of Tar Sands Distillate



HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: VN-80-39 XYLENE BOTTOMS			
	MPLC	FIA	MS
SATURATES	2.9	1.0	1.3
OLEFINS	----	0.0	----
ALKYL BNZs	97.1	----	98.7
ALKYL PNAs	0.0	----	0.0
TOTAL AROMATICS	97.1	99.0	98.7

Figure 18. Comparative Analysis of Xylene Bottoms



HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)

SAMPLE: VN-80-40 2040 SOLVENT

	HPLC	FIR	MS
SATURATES	0.0	1.0	4.4
OLEFINS	----	0.0	----
ALKYL BNZs	30.7	----	29.2
ALKYL PNArs	69.3	----	66.4
TOTAL AROMATICS	100.0	99.0	95.6

Figure 19. Comparative Analysis of 204U Solvent

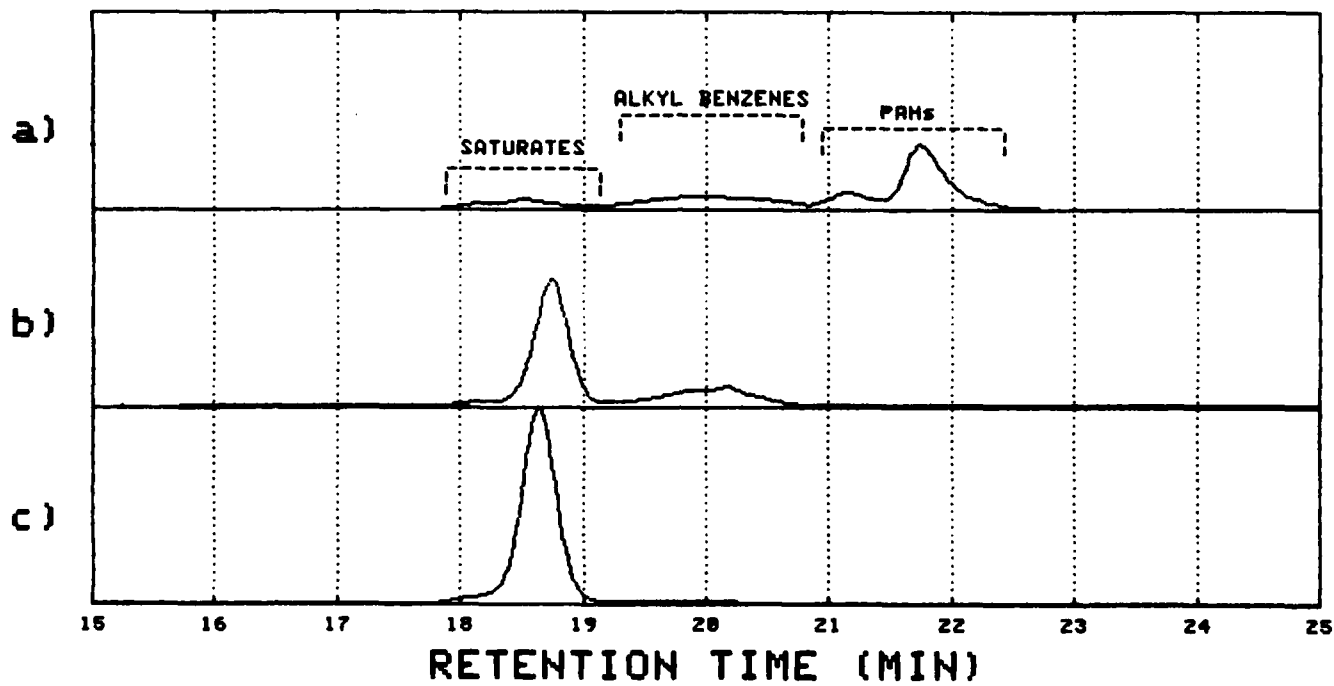


Figure 20. Monitoring the Hydrogenation of a Light Pyrolysis Fuel Oil
 a) pyrolysis fuel oil charge; b) intermediate product; c) fully hydrogenated

TABLE 15
COMPARATIVE ANALYSES OF HYDROGENATED PRODUCTS

HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: 83-POSF-0994 FUEL OIL (HDS)			
	HPLC	FIA	MS
SATURATES	10.0	0.0	14.2
OLEFINS	----	0.0	----
ALKYL BNZs	27.9	----	30.2
ALKYL PNAs	62.1	----	55.6
TOTAL AROMATICS	90.0	100.0	85.8

HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: 83-POSF-0800 FUEL OIL (IHD)			
	HPLC	FIA	MS
SATURATES	70.98	60.0	72.9
OLEFINS	----	0.0	----
ALKYL BNZs	29.0	----	26.2
ALKYL PNAs	0.02	----	1.0
TOTAL AROMATICS	29.02	32.0	27.2

HYDROCARBON GROUP-TYPE ANALYSIS (VOL%)			
SAMPLE: 83-POSF-0161 FUEL OIL (CHD)			
	HPLC	FIA	MS
SATURATES	96.0	96.0	97.9
OLEFINS	----	0.0	----
ALKYL BNZs	3.2	----	1.9
ALKYL PNAs	0.0	----	0.2
TOTAL AROMATICS	3.2	4.0	2.1

This type of application should be extremely advantageous to hydroprocessing facilities.

The repeatability of relative response factors and sample analysis was determined for the HPLC method over a five-day period (see Table 16). The response factors were evaluated using the calibration mix previously described and exhibited a RSD of less than 1% (see Table 16a). A sample similar to ERBS 3S (see Table 16b), i.e., ERBS 3S-RP, was used to determine the repeatability of the analysis of a given fuel sample. ERBS 3S-RP was selected because of its complexity and the lack of complete resolution between hydrocarbon groups. The quantitative repeatability for this sample was excellent. The assumption is then made that this repeatability is typical of samples having similar and less complex hydrocarbon matrices.

TABLE 16
HPLC REPEATABILITY STUDY (5 DAYS)

a) RRF*: CALIBRATION MIX

<u>GROUP-TYPE</u>	<u>MEAN RRF*</u>	<u>n</u>	<u>S.D.</u>	<u>% RSD</u>	<u>RANGE</u>
SATURATES	1.00	--	----	---	----
ALKYL BNZs	1.11	15	0.01	0.5	0.01
PAHs	1.20	15	0.01	0.5	0.02

b) SAMPLE: ERBS 3S-RP

<u>GROUP-TYPE</u>	<u>MEAN VOL%</u>	<u>n</u>	<u>S.D.</u>	<u>% RSD</u>	<u>RANGE</u>
SATURATES	26.3	15	0.2	0.6	0.6
ALKYL BNZs	58.6	15	0.2	0.3	0.6
PAHs	15.0	15	0.2	1.2	0.7

NOTE: * = relative to saturates peak

SECTION IV

CONCLUSIONS AND FUTURE WORK

The HPLC method described in this paper is ideal for the simple, accurate and rapid determination of saturates (+ olefins), alkyl benzenes, and polynuclear aromatics in fuel distillates. The quantitative results are directly determined in volume percent. Response factors are easily calculated using a three-component calibration blend containing one compound from each hydrocarbon group. These response factors can be applied to sample types with significantly different boiling ranges. The presence of light hydrocarbons (C4's and C5's), highly colored species, and/or polar heteroatomic compounds do not affect quantitation. The dielectric constants of the polar compounds are similar to the mobile phase and thus have reduced, if any, response. Other polar species are either irreversibly adsorbed on the silica guard column or elute outside the retention windows of the hydrocarbon groups.

Any inexpensive HPLC system can perform this analysis without modification. Total automation can be achieved with the use of an automatic sampler and a computing integrator. The mobile phase required for this application is moderately priced, but it can be reused to significantly reduce that cost. The use of very stable bonded phase columns reduces equilibration time and negates the need for repeated column activation. The adaptability of this method to on-line analysis makes it very attractive to facilities involved in the hydroprocessing of petroleum and synthetic feedstocks.

This HPLC method opens the door to many important applications which need to be researched. Preliminary work has demonstrated the capability to quantitate the polar species, i.e., additives and impurities, found in jet fuels. By simply

applying absolute response factors to the hydrocarbon groups, the polar compounds can be estimated by difference. Statistical programs will determine the confidence limits for the determination of the polar components.

The Air Force is presently investigating the feasibility of using high density fuel distillates in its aircraft. The compositional detail of these samples must be determined and monitored. By selecting the appropriate analytical columns and mobile phase, an HPLC method incorporating the DC detector could be devised to report additional hydrocarbon sub-groups, e.g., cycloparaffins.

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