

The Analysis of Hydrocarbon Distillates for Group Types Using HPLC With Dielectric Constant Detection: A Review*

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Abstract

The hydrocarbon group-type composition of distillate products can be measured with speed and accuracy using high-performance liquid chromatography (HPLC) with a dielectric constant detector (DCD). The DCD ensures a genuine uniformity of response independent of the carbon number distribution of the sample type or the group types resolved by the chromatographic process. As HPLC columns offering distinct selectivities are assembled upstream in configurations with backflushing or switching valves, a variety of hydrocarbon group types can be resolved and ultimately quantified. The kinds of hydrocarbon classes separated include: saturates + olefins, alkylbenzenes, alkylnaphthalenes; saturates, olefins, aromatics; normal + branched paraffins, cycloparaffins, unsaturates; normal + branched paraffins, cycloparaffins, olefins, aromatics; and, previously unreported, saturates, unsaturates. Some of the HPLC separations are accomplished on commercially available bonded phase columns, while others require argentation columns of different activities. Hydrocarbon mixtures of known group-type composition are analyzed to verify the accuracy of a particular HPLC/DCD configuration. The results of the HPLC/DCD analysis schemes are compared, when appropriate, to several other methods for group-type determinations for a range of distillate products. Steps to optimize analysis time, solvent consumption, and minimum detectability are discussed.

Introduction

The application of liquid chromatography (LC) to the analysis of petroleum samples predates the discovery and development of the chromatographic process by Tswett. Before this century, David Talbot Day, chief of the Division of Mineral Resources of the American Geological Survey, was the first to characterize changes in the color and composition of Pennsylvania green petroleum after percolation through a column of powdered limestone. In August of 1900, Day reported these and other data at the First International Petroleum Conference in Paris (1).

Classical liquid displacement chromatography is still an integral part of several American Society of Testing and Materials (ASTM) methods, as Ettre observed (2). Specifically, ASTM D1319, the Fluorescent Indicator Adsorption (FIA) test (3), is the official method for the petroleum industry to determine saturates, olefins, and aromatics in hydrocarbon samples boiling up to 315°C. Nevertheless, the need persists for alternative high-performance liquid chromatographic (HPLC) techniques that are fast, accurate, automated, and applicable to an ever broadening range of product types.

Analytical chemistry in the petrochemical industry must continue to evolve rapidly to address the demands of a changing product market. Feedstocks from alternate and high boiling sources and the recycling of aromatic off-streams are an economic necessity. The more viable chromatographic procedures are those that can quickly analyze a wider range of sample types, providing more pertinent and accurate chemical information. Active research projects include microbore HPLC columns connected to high information detectors, such as a mass spectrometer (MS), a diode-array absorbance detector, or a Fourier transform infrared detector. Even the on-line coupling of a microbore HPLC column to a high resolution capillary gas chromatographic (GC)/MS system has been reported (4).

Hydrocarbon-type analysis has long been recognized as a crucial approach to characterize the chemical composition of feedstocks and hydrocarbon products. In his review on hydrocarbon group-type analysis, Suatoni emphasized the analytical power and time savings that HPLC offers the oil analyst (5). HPLC can easily resolve selected classes of hydrocarbons in samples of different boiling ranges and alternate energy sources. In the preparative mode, HPLC can separate group types virtually free of cross-contamination for more detailed analysis by ancillary techniques.

According to the literature, there are nearly as many HPLC methods for group-type analyses as there are laboratories analyzing them (one HPLC method for each specific distillate fraction for each laboratory). The vast majority of these HPLC separations depend on the refractive index detector for quantitation, though the ultraviolet detector has been used for alkylnaphthalenes. As cited by several researchers (2,6,7), the reliability of the analysis is a direct function of the accuracy of the response factors for a given detector for that particular sample type. Deriving and reproducing these response factors for each hydrocarbon product having a different carbon number distri-

* This paper was presented, in part, at the Pittsburgh Conference, New Orleans, LA March 1988, paper 1225.

bution is tedious. Implementing worldwide HPLC methods for group-type analysis encompassing a broad range of hydrocarbon matrices is severely hampered by the nonuniformity in response of commonly used HPLC detectors.

Only two uniformly responding detectors for group-type analysis have been soundly demonstrated and reported in the literature. Flame ionization detection (FID) of hydrocarbon eluants separated by supercritical fluid (SFC) (8-11), thin layer (TLC) (12,13), and normal phase (14-17) chromatography is quantitatively dependable. The present paper deals with applications of normal phase chromatography with a dielectric constant detector (HPLC/DCD) (18-21). The global community of oil chemists has only these two detectors as tools for fast, accurate, and versatile group-type analyses.

Experimental

Apparatus

A hydrocarbon group-type analyzer system was configured according to the particular group-type separations desired (18-21). A Varian Model 4200 liquid chromatograph equipped with syringe-type pumps was used to perform all the analyses in these studies. Other kinds of pumps delivering low pulsations can be used as well. Detection was performed via an Optichrom Model 430 dielectric constant detector (Applied Automation, Inc., Bartlesville, OK). The electrometer of the DCD was set at an amplification range of 1.0 or 2.0 and at an attenuation of 1,000 mV full scale. Both the sample cell and the reference cell require flowing environments; however, the flow rates need not be matched. The reference cell flow rate was measured as approximately 0.1 mL/min. The column flow rate was usually 1.0 mL/min. A silica guard column preceded the analytical columns to adsorb polar heteroatomic compounds present in the injected samples. All analyses were performed under ambient conditions.

DCD

The DCD monitors a bulk property (dielectric constant) of the mobile phase. The capacitance of two nearly identical parallel-plate capacitors is tracked with time. Pure mobile phase flows through one capacitor (reference cell) while HPLC column eluants pass through the other (sample cell). Any difference in capacitance between the cells is converted to an analog output signal for data collection and reduction.

When the DCD is used in unison with a mobile phase having a dielectric constant at least twice that of hydrocarbons, the detector performs as a universal hydrocarbon analyzer. In this mode, the detector has a high sensitivity for hydrocarbon species. More importantly, the DCD responds on a volume fraction basis independent of the carbon number distribution of the sample type or the hydrocarbon group type. Relative response factors were calculated for more than 100 hydrocarbons ranging in carbon number from C_6 to C_{22} , including linear and highly branched isomers of all the major group types (22). The uniformity of response for each subgroup was as narrow in variance as that demonstrated for the FID of GC. The DCD is commercially available as a laboratory unit (Laitec, Inc., Bartlesville, OK).

Reagents

Envron 123 (2,2-dichloro-1,1,1-trifluoroethane, Halocarbon Products Corp.) and *n*-butyl chloride (Burdick & Jackson) were used as the mobile phases in different group-type separations

because they both have a relatively low solvent strength and a sufficiently high dielectric constant. Samples were prepared for analysis by diluting them ~1:10 to 1:30 in the mobile phase, again depending on the configuration of the system. Dilution ensured that sample concentrations were still within the linear dynamic range of the detector (18,22).

Ring-number-selective columns

In an application with *n*-butyl chloride, two Partisil PAC columns (Whatman), 250 mm × 4.6 mm i.d., 5- μ m particle size, and one TENF (tetranitrofluorenimino) column (ES Industries), 300 mm × 4.6 mm i.d., 10- μ m particle size, were used (18). A TENF column, highly loaded with stationary phase, is recommended. The PAC columns resolved the saturates from the aromatics and expanded the aromatic envelope, but the TENF column improved on the separation of the alkylbenzenes from the alkylnaphthalenes.

Argentation columns

In applications with Envron 123, experimental olefin-selective and unsaturate-selective HPLC columns, as detailed previously (19-21), were used for separating the olefins and the aromatics from the saturates. These columns were 100 mm × 4.6 mm i.d. and contained 5- μ m silica particles that had been bonded to a strong cation exchange stationary phase. The silver form of the ion exchange column was prepared in situ by flushing with aqueous silver nitrate. The olefin-selective column is a deactivated version of the unsaturate-selective column. The lifetimes of these columns are as yet undetermined under actual industrial workloads, but they are certainly longer than the three-month investigative period reported here. Versions of these silver-modified columns are now under evaluation by an HPLC column manufacturer (Whatman).

Naphthene-selective columns

Varian MicroPak PONA analysis columns were custom packed in Envron 123 (Varian). These columns have a micro-particulate organic gel that demonstrates a unique selectivity to saturated hydrocarbons providing separation into normal + branched or acyclic paraffins and naphthenes (20,21). The PONA columns are of preparative size (300 mm × 7.5 mm i.d.), and larger injection volumes are required for adequate sensitivity. For use with Envron 123, at least three columns in tandem are recommended.

Qualitative analysis

The elution windows for each hydrocarbon group type were mapped for each configuration of the analyzer system based on the retention behavior of pertinent reference hydrocarbons. To confirm group-type purity, HPLC fractions were collected and subsequently analyzed by on-column, high resolution capillary GC/MS. At least three dozen major and several minor, randomly selected peaks from each fraction were scanned. Their spectra were compared to the resident National Bureau of Standards library and to a local in-house library on the data station. The comparisons confirmed that all the prominent components were members of the appropriate hydrocarbon group type.

Quantitative analysis

To establish the quantitative accuracy of the hydrocarbon group-type analyzer system, a series of complex solutions of known group-type composition were chromatographed. Blending solvents were used wherever applicable to increase sample

complexity and more closely imitate different product types. Interestingly, experience with *n*-butyl chloride as the mobile phase dictated that group-type response factors were required. As detailed previously, a three-component calibration mix proved valid for a wide range of distillate products (18,22). With Environ 123 as the mobile phase, however, unity response factors were sufficient (19–21). In both cases, the response within a chromatographically resolved group type was independent of its carbon number distribution. It is suggested that the necessity for group-type response factors be first examined for different mobile phases.

Quantitation was accomplished on a Hewlett-Packard 3357 laboratory automation system. Perpendicular baseline drops displayed in the chromatograms were automatically determined by the computer without operator intervention.

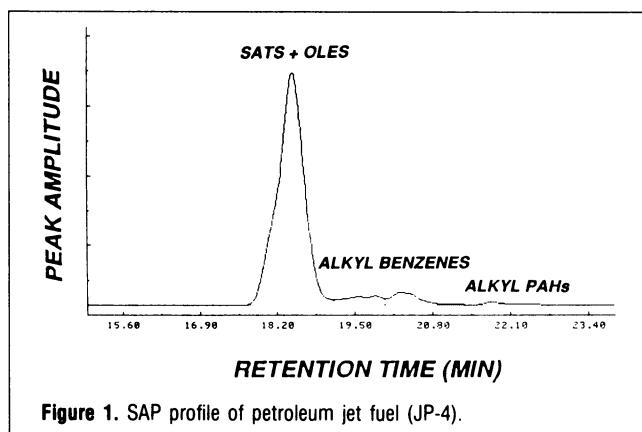


Figure 1. SAP profile of petroleum jet fuel (JP-4).

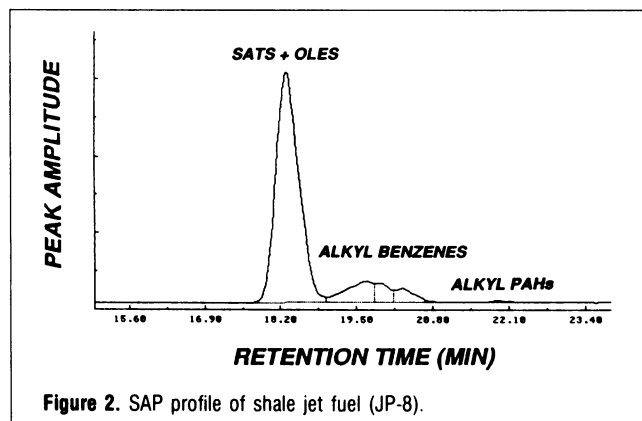


Figure 2. SAP profile of shale jet fuel (JP-8).

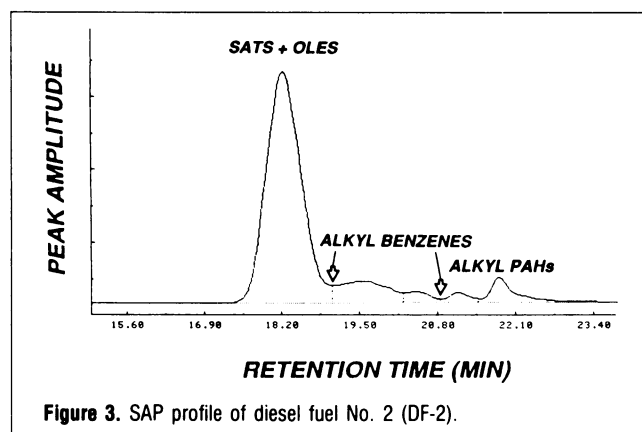


Figure 3. SAP profile of diesel fuel No. 2 (DF-2).

Results and Discussion

Resolving the aromatic envelope

A recurring task posed by petroleum engineers is to provide rapid response information on the classes of aromatics present in process feeds and intermediates. To resolve the types of aromatic hydrocarbons in matrices distilling below 400°C, the configuration reported earlier was developed (18,22). The separation of aromatics was by ring number, alkylbenzenes, and alkylnaphthalenes (including biphenyls and bibenzyls). The saturates elute first, then the alkylbenzenes, and finally the polycyclic aromatic hydrocarbons (PAHs) (by ring number). For illustrative purposes, the separation will be referred to as SAP. Typical applications are shown in Figures 1 through 3 with the corresponding comparative analyses listed in Tables I through III. In Tables I through III, SAP refers to the current HPLC/DCD configuration, while FIA and MS refer to the liquid displacement and mass spectrometric ASTM procedures, D1319 and D789, respectively. The agreement among the methods for total aromatics is generally close for the jet fuel range products, but is poorer for diesel fuels. In the SAP

Table I. Comparative Analyses of Petroleum JP-4 (Vol. %)

Hydrocarbon group type	SAP*	FIA**	MS***
Saturates	89.0	86.2	90.0
Olefins	—	1.5	—
Alkyl benzenes	10.3	—	9.5
Alkyl PAHs	0.7	—	0.5
Total aromatics	11.0	12.3	10.0

* Current HPLC/DCD configuration
 ** ASTM procedure D1319, fluorescent indicator adsorption
 *** ASTM procedure D2789, mass spectrometric

Table II. Comparative Analyses of Shale JP-8 (Vol. %)

Hydrocarbon group type	SAP*	FIA**	MS***
Saturates	80.7	76.2	79.5
Olefins	—	1.6	—
Alkyl benzenes	18.9	—	19.7
Alkyl PAHs	0.4	—	0.8
Total aromatics	19.3	22.2	20.5

* Current HPLC/DCD configuration
 ** ASTM procedure D1319, fluorescent indicator adsorption
 *** ASTM procedure D2789, mass spectrometric

Table III. Comparative Analyses of Diesel Fuel (Vol. %)

Hydrocarbon group type	SAP*	FIA**	MS***
Saturates	76.4	65.0	78.4
Olefins	—	2.9	—
Alkyl benzenes	14.3	—	14.1
Alkyl PAHs	9.3	—	7.5
Total aromatics	23.6	32.1	21.6

* Current HPLC/DCD configuration
 ** ASTM procedure D1319, fluorescent indicator adsorption
 *** ASTM procedure D2789, mass spectrometric

method, the olefins coelute with the saturates. Nevertheless, as olefins and saturates have identical response factors with *n*-butyl chloride, quantitative accuracy is preserved.

Traditionally, the FIA method is not applied to diesel fuels. These products can exhibit distillation end points well beyond the range covered by the FIA. Compounding the problem, highly colored samples often mask the elution zones of the separated group types in the FIA method. Small differences in the volume fraction of the 2-ring aromatics for the SAP and MS methods are reasonable in light of the variance associated with the MS technique.

A limitation of the SAP arrangement is the lack of resolution of small saturated hydrocarbons such as hexanes from large alkyl-benzenes of 15 carbons or greater. For special samples, the addition of another PAC type of HPLC column could be warranted. The total analysis time could be significantly reduced by increasing the flow rate to 1.0 mL/min. The potential also exists for extending the analysis to include the 3- and 4-ring aromatic homologs, although this has not been investigated in detail.

Separating the olefins

Traditionally, splitting out the olefins from the saturates in the HPLC analysis of hydrocarbon products has been accomplished in one of two approaches. Suatoni, for example, used highly activated silica gel and a low polarity mobile phase to effect a separation of saturates, olefins, and backflushed aromatics for gasoline range samples. Argentation chromatography, separation techniques in which silver(I) is involved, has also been exploited (23). On the molecular level, a reversible complex is rapidly formed between the pi-electrons of a hydrocarbon containing a double bond and the partially empty d-

orbitals of the Ag(I) ion. The high selectivity for unsaturated hydrocarbons and the fast kinetics make the chromatographic process feasible. Historically, silver salts are impregnated into silica gel packing. Characteristically, however, these mechanically coated phases demonstrate poor efficiencies and short lifetimes.

More recently, strong cation exchange (SCX) columns in the silver ion mode have separated olefins in a hydrocarbon group-type analysis (11,19-21). The elution order on the olefin-selective columns is different from that of the silica gel columns mechanically coated with silver nitrate. On the SCX columns, the saturates are closely followed by the aromatics while the olefins are backflushed. For illustrative purposes, the separation will be called SAO, and chromatograms are shown in Figures 4 through 6. The corresponding quantitative results and comparative analyses by FIA from two different laboratories are listed in Table IV. For aromatics less than 75 vol % and olefins greater than 1%, the comparison is usually quite good, but only as long as the samples are clear fluids. Furthermore, significantly different results can be obtained by the FIA if the samples distill outside the boiling range covered by ASTM D1319.

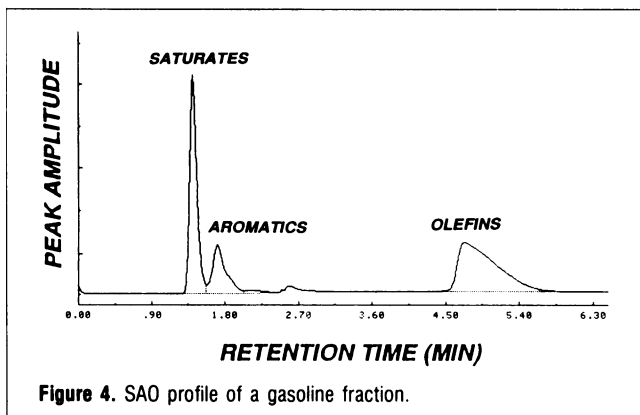


Figure 4. SAO profile of a gasoline fraction.

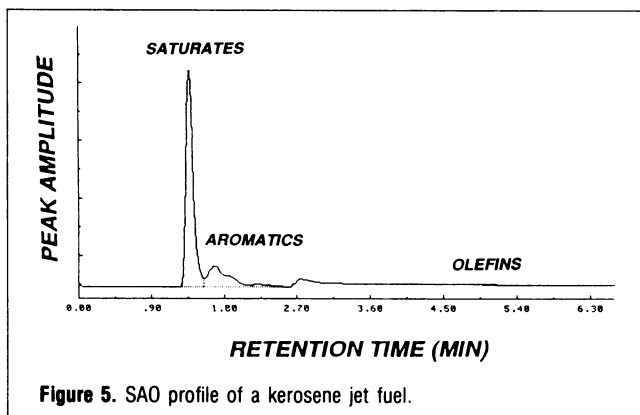


Figure 5. SAO profile of a kerosene jet fuel.

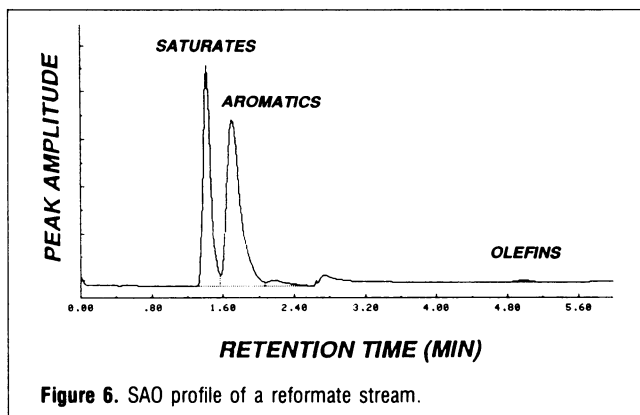


Figure 6. SAO profile of a reformat stream.

Table IV. Comparative Analyses of Distillate Products (Vol. %)

Sample code	Hydrocarbon group type	SAO*	FIA	
			Lab1	Lab2
Gasoline	Saturates	38.7	35.0	36.6
	Olefins	45.2	49.5	48.0
	Aromatics	16.1	15.5	15.4
Kerosene	Saturates	76.4	77.3	75.0
	Olefins	0.4	0.0	0.8
	Aromatics	23.2	22.7	24.2
Naphtha	Saturates	90.2	91.7	92.0
	Olefins	0.5	0.0	0.6
	Aromatics	9.3	8.3	7.4
Reformat	Saturates	40.8	43.0	43.0
	Olefins	0.6	0.8	0.5
	Aromatics	58.6	56.0	56.5
Feedstock	Saturates	85.3	80.2**	86.7
	Olefins	10.6	16.0**	9.6
	Aromatics	4.1	3.8**	3.7

* HPLC/DCD method

** Results were determined by a proprietary HPLC method on this sample only

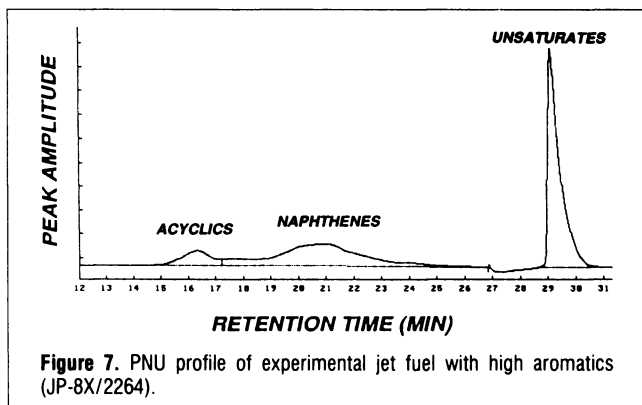


Figure 7. PNU profile of experimental jet fuel with high aromatics (JP-8X/2264).

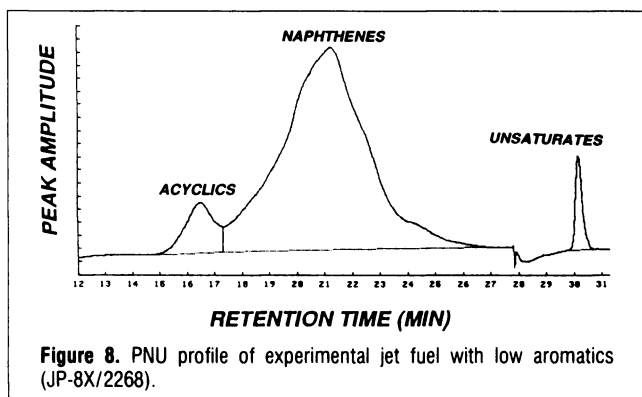


Figure 8. PNU profile of experimental jet fuel with low aromatics (JP-8X/2268).

The SAO configuration can safely be applied to diesel fuels with distillation endpoints below 400°C. Fuels distilling above 400°C could contain 3- and 4-ring PAHs. The olefin-selective HPLC column resolves aromatics by ring number. In the forward flow direction, alkylanthracenes and phenanthrenes elute in a low broad band well beyond the alkyl naphthalenes. The analytical results could suffer in one of several ways if the present system were used indiscriminately on these kinds of samples. If the onslaught of these polycyclics is not detected and the backflush valve activated prematurely, some or all of the 3-ring aromatics would be backflushed along with the olefins. Characteristically, the 3-ring aromatics are in a gradually rising band that could be easily mistaken for a drifting baseline and not integrated at all. Even if detected and integrated, the longer the delay in backflushing the olefins, the more diffused the olefin peak and the more difficult to integrate accurately.

Research in conjunction with Whatman is focusing on the advantages available in narrower bore and shorter olefin-selective columns and in optimizing column activity. If successful, the analytical payoffs would be shorter analysis time, sharper peaks, and a lower chromatographic limit of detection for the olefins. The optimized olefin-selective column will be a disposable cartridge type. The end fittings will be permanent. The cartridge will need to be replaced every two to three months, depending on sample throughput.

Resolving the saturate envelope

The accurate determination of cycloparaffins or naphthenes as a group in hydrocarbon distillate products is a formidable analytical challenge. As the carbon number distribution widens to encompass kerosenes and as olefins are included, fewer analytical approaches are applicable. Two recent HPLC investi-

Table V. Comparative Analyses of High Aromatic Experimental Fuel (Vol. %)

Hydrocarbon group type	PNU*	MS**	SAO***	FIA†
Paraffins (acyclics)	8.8	10.7	—	—
Naphthenes	39.6	44.9	—	—
Saturates	48.4	55.6	49.8	45.9
Olefins	—	(0.6)	0.0	0.6
Aromatics	—	43.8	50.2	53.5
Total aromatics and Olefins	51.6	44.4	50.2	54.1

* Current analyzer configuration
 ** ASTM procedure D2789, mass spectrometric
 *** HPLC/DCD method for olefins
 † ASTM procedure D1319, fluorescent indicator adsorption

Table VI. Comparative Analyses of Low Aromatic Experimental Fuel (Vol. %)

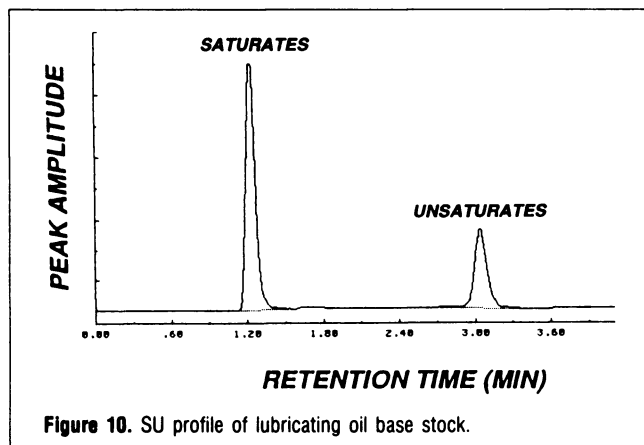
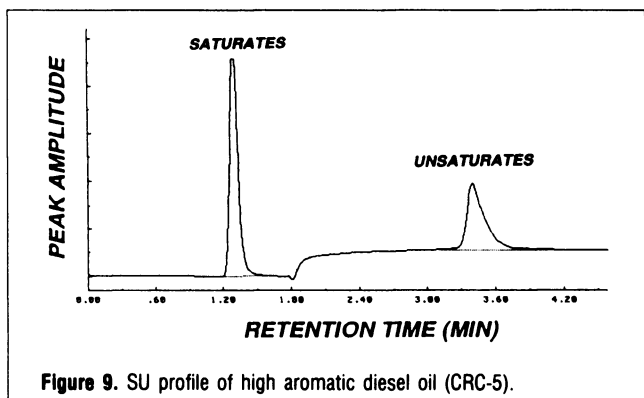
Hydrocarbon group type	PNU*	MS**	SAO***	FIA†
Paraffins (acyclics)	7.7	5.3	—	—
Naphthenes	89.0	92.1	—	—
Saturates	96.7	97.4	97.2	95.1
Olefins	—	(0.0)	0.0	0.0
Aromatics	—	2.6	2.8	4.9
Total aromatics and Olefins	3.3	2.6	2.8	4.9

* Current analyzer configuration
 ** ASTM procedure D2789, mass spectrometric
 *** HPLC/DCD method for olefins
 † ASTM procedure D1319, fluorescent indicator adsorption

gations have both relied on naphthene-selective HPLC columns and, again, argentation chromatography (20,21).

By configuring the hydrocarbon group-type analyzer system with two switching valves, two naphthene-selective columns, and an unsaturate selective column, the separation of the saturates into acyclics (normal + branched paraffins) and naphthenes was accomplished with the unsaturates backflushed as a composite peak. For illustrative purposes, the separation will be called PNU and chromatograms are shown in Figures 7 and 8. The naphthenes peak was broad because of column selectivity and column dimension. The naphthene-selective columns were attempting to resolve single ring cycloparaffins from double ring, but the result was only a broad elution band. Also, the columns were of preparative size, thus dispersing the naphthenes peak in a large elution volume. Subsequent work gave better resolution between the normal + branched and cycloparaffins after a total of three naphthene-selective columns were coupled in series (21).

Comparative analyses are listed in Table V and VI. PNU refers to the current analyzer configuration, MS to D2789, SAO to the previously described HPLC/DCD method for olefins, and FIA to D1319. Most often, when the volume fraction for the naphthenes by MS differs markedly from the PNU analysis, the aromatic content of the fuel as measured by MS is suspect. The SAO method is quite accurate for aromatics. From the history of the samples, the hydrotreated fuels examined here ought to be low in olefins. Thus, the volume fraction for unsaturates, by the PNU method, and that for aromatics, by the SAO, should



be almost identical. The data in Table V show the disparity of the MS results for aromatics. If, for example, the aromatics by MS were increased to approximate that obtained by PNU, the amount of saturates, including the naphthenes, would have to be reduced by a corresponding amount. The naphthenes as measured by MS and PNU would then be much closer.

The above configuration could resolve the unsaturates into olefins and aromatics by incorporation of an olefin-selective HPLC column (21). This separation can be called a paraffins, olefins, naphthenes, and aromatics (PONA) analysis applicable to gasoline and kerosene fuels. Here, three of the naphthene-selective columns were successfully employed.

In both configurations, the substitution of 4.6-mm i.d. naphthene-selective columns for the 7.5 mm versions could yield sharper saturates peaks with significantly reduced retention times. The assumption, of course, is that the columns with the smaller bore could be packed in Environ 123 with the same efficiency, which is not an easy task.

Separating the unsaturates

A logical application of the argentation column is the simplest hydrocarbon group-type separation: saturates from unsaturates. The DCD responds uniformly within hydrocarbon subgroups for mobile phases with high dielectric constants. With *n*-butyl chloride, alkylbenzenes required a slightly different relative response factor than alkylnaphthalenes. With Environ 123, all hydrocarbons had equivalent responses in the DCD, making this fluid the mobile phase of choice for quantitation of saturates and backflushed unsaturates. For this approach, the analyzer system was configured identically to the one for the separation of olefins, but an unsaturate-selective HPLC column was substituted. Complex hydrocarbon matrices with distillation end points in excess of 1000°F can be analyzed on this column. Some of these samples that are solid at room temperature might require ultrasonic agitation to completely dissolve them in Environ 123. PAHs are far more soluble in Environ 123 than in *n*-pentane or *n*-hexane. Use of the unsaturate-selective column can also help confirm the quantitative consistency of the results of several of the aforementioned HPLC/DCD techniques.

For illustrative purposes, the separation of saturates from unsaturates (aromatics + olefins) will be called SU. Figures 9 through 11 show typical chromatograms of heavy hydrocarbon fluids that can be resolved into saturates and unsaturates. Tables VII through X list the comparative analyses on these samples.

As shown in Table VII, the blended diesel fuel sample had a distillation end point outside the specification range, yet posed no problem to the SU method (Figure 9). Several methods were also used to analyze the diesel fuel. ASTM D2549 is a gravimetric

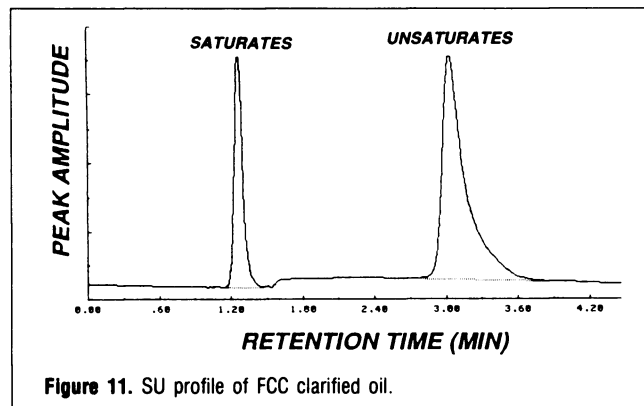


Table VII. Comparative Analyses of Blended Diesel Fuel CRC-5 (Vol. %)

Hydrocarbon group type	SU vol %	ASTM D2549	ASTM D3239	ASTM D1319
Saturates	59.7	(52.0) ^{1,2}	(57.3) ²	58.0
Unsaturates	40.3	(48.0) ^{1,3}	(42.7) ³	42.0

¹ Wt %
² Saturates and olefins
³ Aromatics

procedure for high boiling oils using elution chromatography to separate the saturates from the unsaturates. The conversion from weight fraction aromatics to volume fraction aromatics would lower the D2549 values, bringing the two sets of data closer. ASTM D3239 is a low resolution MS method to quantitate the aromatics of gas oils after prior separation by ASTM D2549. Those data as well as D1319 closely matched the SU results.

Two heavy oil samples (not shown) having distillation end points of approximately 1000°F were analyzed by the SU method and by a preparative HPLC method on silica gel (Table VIII). The aromatics were backflushed after elution of the saturates. Both fractions were collected, the solvent evaporated, and the residues weighed. The conversion of the preparative HPLC data to volume fraction brought the results even closer to the SU results. Polar material, if present, would also be included with the backflushed aromatics in the preparative HPLC method. Nonetheless, as is true of all group-type separations using HPLC/DCD, the polars are ignored.

Sample	Hydrocarbon group type	SU	Prep-HPLC	
			Wt %	Vol %*
Oil 1	Saturates	90.7	88.0	89.9
	Unsaturates	9.3	12.0	10.1
Oil 2	Saturates	69.5	64.0	68.4
	Unsaturates	30.5	36.0	31.6

* Vol % calculated from average relative density: 0.95 for aromatics, 0.78 for saturates.

Sample	Hydrocarbon group type	SU	TLC/FID (area %)
Base stock	Saturates	80.3	81.8*
	Unsaturates	19.7	18.2**
Base/additive	Saturates	79.2	74.1*
	Unsaturates	20.8	25.9**

* Saturates + Olefins
** Aromatics + polars

Hydrocarbon group type	SU	ASTM D2549 ¹	
		Wt %	Vol % ²
Saturates	27.2	20.5 ³	23.9 ³
Unsaturates	72.8	79.5 ⁴	76.1 ⁴

¹ 3.1 Wt % polars, hydrocarbon ratios adjusted accordingly
² Vol % calculated from average relative density: 0.95 for aromatics, 0.78 for saturates
³ Saturates + olefins
⁴ Aromatics only

Two hydrocarbon-based lubricating oil samples were studied and the results are listed in Table IX. The base/additive sample (not shown) was actually the base stock (Figure 10) plus a standard package of polar additives. According to the SU analyses, the two samples were indistinguishable by group-type analysis. A TLC procedure using a glass rod and FID (modified version of references 12,13) included several percent polars along with the aromatics. The relative proportion of unsaturates as determined by the two methods matched reasonably well, considering area percent for FID analysis is nearly equivalent to weight percent.

The data in Table X are the results of an analysis by D2549 of an oil from a fluidized catalytic cracker clarified by settling (Figure 11). After conversion from weight to volume fraction, the D2549 data compared favorably with the SU results. Again, polars, if present, would be measured along with the aromatics by D2549, but not detected by the SU technique.

Conclusions

The abundance of high quality, low cost petroleum crudes and feedstocks is limited. Current feedstocks are incorporating

lower grade crudes and aromatic off-streams as well as processed fluids from alternate sources of energy, such as shale oil, tar sands, coal liquids, and biomass materials. The modern petrochemical engineer needs timely and accurate analytical results to optimize refinery operations and monitor product character. Consequently, the analytical chemist must respond with more pertinent and accurate compositional detail on samples of a continuously variable nature.

During the last decade, a host of HPLC approaches for separating hydrocarbon group types have emerged. Nearly all except those incorporating an FID suffer from a common drawback: the inability to derive accurate response factors, in a timely manner, that are at once applicable to a wide range of hydrocarbon distillate products. The crux of the problem is the variation in response with carbon number of most routinely used HPLC detectors. The DCD, however, responds independently of the carbon number distribution of the sample type.

The hydrocarbon group-type analyzer system is a reliable and versatile approach for analyzing a myriad of hydrocarbon distillate products. The system incorporates an isocratic LC, coupling DCD with novel columns of various selectivities, to guarantee an accurate and precise determination of the hydrocarbon classes in a wide range of conventional and experimental fuels, process intermediates, and feedstocks.

Calibration is simple. For applications with *n*-butyl chloride as the mobile phase, a three-component standard solution gives the relative response factors to handle a wide range of sample types. With Environ 123 as the solvent, the response factors are unity. Quantitative results fall within 1 to 2% absolute of the known values for complex standard solutions. Data is reported directly in volume percent.

Several ASTM methods cannot and should not be applied to just any kind of hydrocarbon product. The analyzer system, in one configuration or another, can supply pertinent compositional information on virtually any distillate sample. Quantitation does not suffer in the presence of significant amounts of light hydrocarbons (C₄ and C₅), highly colored species, or polar heteroatomic compounds. Analyses can be totally automated for unattended operation. In addition, with the proper HPLC columns, fuel samples can be fractionated for more detailed characterization by ancillary techniques.

Acknowledgments

The authors extend their appreciation to the following: E. Butts (Whatman, Inc.) for the continuing development work on the argentation columns; J. Crandall and L. Benningfield, Jr. (Applied Automations, Inc.) for the loan of the DC detector and for technical assistance in its operation; T. Alfredson and R. Simpson (Varian Instrument Group) for custom packing the PONA columns in Environ 123, and E. Steward (U.S.A.F.) for the GC/MS support work.

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Manuscript received March 11, 1988.