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COMPOUND CLASS QUANTITATION OF JP-5 JET FUELS BY HIGH
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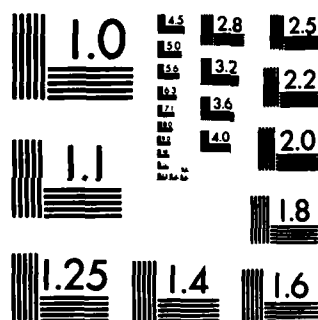
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NRL Memorandum Report 5407

**Compound Class Quantitation of JP-5 Jet Fuels
by High Performance Liquid Chromatography/Differential
Refractive Index Detection**

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<p>➤ Fuel composition effects are known to significantly affect jet turbine engine performance. Currently, one important composition parameter, total aromatics (% v/v), is actually defined in all JP-4 and JP-5 military fuel specifications governing procurement. This report outlines an improved method for defining not only total aromatics but also the two sub-classes, mono-cyclic and di-cyclic aromatics, that make up the total aromatics in JP-5. Special emphasis has been placed on the accurate and precise quantitation of saturates, mono-cyclic and di-cyclic aromatic fractions. This has been accomplished for fuels in the JP-5 distillation range by direct quantitation with a low sensitivity differential refractive index (DRI) detector. The detector is first calibrated by an appropriate standard and the response factors (= weight/area) for each compound class are used by a calculating electronic integrator/recorder to report directly each subsequently analyzed fuel in weight percent for each compound class. The analysis of each fuel is fast and very precise. Accuracy appears to be quite good and is under further investigation. Long term analytical stability has been proven (up to one year).</p> <p style="text-align: right;">(Continues)</p>				
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19. ABSTRACT (Continued)

Quantitative data for thirteen JP-5 fuels have been compared with data from fluorescence indicator absorption, HPLC/GC and gravimetric data. The thirteen fuels include several experimental jet fuel blends and one shale JP-5 fuel.

(High Performance Liquid Chromatography)

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COMPOUND CLASS QUANTITATION OF JP-5 JET FUELS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/DIFFERENTIAL REFRACTIVE INDEX DETECTION

I. INTRODUCTION

The combustion behavior of a jet fuel in a gas turbine engine depends upon physical properties such as viscosity, volatility, and distillation range. The behavior also depends upon the composition of the fuel. For instance, the flame radiation to the combustor walls and the amount of smoke in the exhaust are affected by the constituents of the fuel. An increase in aromatic hydrocarbons in turbine fuel has long been recognized as increasing exhaust smoke and the temperature of combustor walls. Consequently, the turbine fuel specification, MIL-T-5624, has a limit of 25% (v/v) on total aromatics [1]. Total aromatics, however, do not afford a completely reliable indication of combustion behavior.

More recent attempts to relate combustion properties to composition involve measuring the hydrogen content since the value of this property goes down as aromatic content increases. As an example, a reduction of 2.5% in fuel hydrogen content lowered the estimated liner life of a J79 combustor by approximately 65% [2].

Other studies have not observed a direct correlation between percent hydrogen and combustion properties. Rather, the content of dicyclic aromatic compounds in a series of JP-5's and several fuel blends exhibited control over combustor liner temperature [3].

In view of the uncertainty about which components in fuel influence combustion behavior, NRL has undertaken several tasks to develop improved characterization of jet fuels. One of the approaches is to apply liquid chromatography to separation of hydrocarbon classes. By this technique, several classes of hydrocarbons can be separated. For jet fuels, however, only three classes are of interest - saturates, mono-cyclic aromatics, and dicyclic aromatics. Quantitation of separated classes is not routine, however. High performance liquid chromatography (HPLC) combined with gas chromatography (GC) or gravimetric methods are employed for quantitative analyses in this laboratory [4,5,6] but these techniques are time consuming and require complete sample recovery for accurate results. The HPLC and GC combined techniques are referred to as LC/GC in this report. Jet fuel sample total recoveries for HPLC/gravimetry average about 97 weight percent and for LC/GC about 99.9 weight percent.

Thus, we decided to evaluate the potential of direct quantitation during HPLC separations as a possible alternative to these other methods. Concurrently, Seng and Otterson [7] have reported a method for quantitative analysis of hydrocarbon

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classes in jet fuels during HPLC separation but this method appears to be more time consuming and quantifies only the saturates and total aromatics. The method outlined in this report (direct HPLC/DRI) allows quantitation of three compound classes and requires less than 10 minutes for a single analysis once the system is operational. The additional information on dicyclic aromatics may allow more complete specifications to be made regarding the aromatic content of fuels. Such data will also encourage the more extensive evaluation of the effects of fuel composition on combustion behavior.

II. EXPERIMENTAL

The HPLC systems used in this study were modular systems with various detectors and pumps. The following components represent a typical appropriate system for quantitative measurements. Separation into compound classes was accomplished with a Whatman M-9 10/25 Partisil PAC semipreparative column (chemically bonded alkyl amino-alkyl cyano). The pentane or 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) mobile phase was maintained at a flow rate of 6.0 to 8.0 ml per minute with a Beckman 100 A pump operating in the 450 to 600 psi range for the pentane and 800 to 1000 psi range for the Freon 113. The injector was a Waters U6K with a 3 ml fixed loop. The sample size was maintained at 20 to 25 μ l to insure adequate chromatographic resolution while maintaining an acceptable signal to noise ratio to operate the Waters Prep 500 refractive index detector at a relative response setting of 5. As discussed later, it is not critical to inject identical sample volumes for replicate analyses. At these conditions a fuel sample with 70 to 75% saturates would give an off scale deflection on a Rikadenki KA series strip chart recorder operating on the 1.0 v range and still give approximately 3% of full scale deflection on the ten inch chart for a sample of only about 1% dicyclics. These parameters also gave adequate area counts for integration of all three classes on a Hewlett-Packard 3390 A Integrator (in parallel to the strip chart recorder) operating with the following run parameters: attenuator = 128x; chart speed = 0.5 cm/min; peak width = 0.20 sec; threshold = 6; area reject = 50,000. At these integrator settings a 20 μ l fuel sample with 75% saturates typically gave a total area of about 5×10^7 counts. The smallest peak, the dicyclic fraction, would generally represent about 9% of the total area for a fuel that contained about 5% by weight of this class.

Some of the fuel samples generated chromatographic fine structure in the monocyclic and dicyclic fractions. When this occurred the summation of peak areas mode was employed to integrate the total hydrocarbon class rather than the individual peaks. Several samples which did not require this method were also analyzed with the summation function operating and no significant differences in quantitation were observed. Injections of 10 to 40 μ l neat samples gave the same

quantitation with the Prep 500 detector within limits of the electronic integrator precision. Also, several samples were analyzed with this system except for replacing the Waters detector with an Altex Model 156 refractive index detector. Analysis of 10 μ l samples of neat fuels and standards gave identical quantitation of samples within limits of the integrator precision. Recalibration was not necessary. Thus both detectors responded proportionally to the same refractive index change but the Altex is limited to smaller sample sizes as discussed in the next section. The analyses were replicated a year apart with different PAC columns, different lots of pentane, and with the additional mobile phase 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). No significant changes (Table 7) in analytical results were found.

A similar HPLC system was used to separate the JP-5 jet fuel 82-17 into compound classes on a preparative scale. Fractions were collected and used as components in detector calibration standards. About ten mls of this fuel were separated as described below. Since larger samples were used (about 0.2 ml/injection), a Perkin-Elmer Series 2 pump operating at 25 ml per minute and two 25 cm Perkin-Elmer semi-prep silica columns replaced the lower capacity pump and PAC column. The elution was additionally monitored by a Perkin-Elmer 254 nm ultraviolet detector located between the column and the refractive index detector. Fraction collection was started when the refractive index detector first started to respond to the saturate fraction and the first cut was stopped when the ultraviolet detector began to respond to the monocyclic aromatics. The second collection was begun when the refractive index detector began to respond to the monocyclics and stopped after the ultraviolet detector reached the minimum between the monocyclic and the dicyclic peaks. As the refractive index detector began to respond to the dicyclics the third collection was started and continued until this signal returned to the base line. The solvent, pentane, was removed from each fraction with a rotary evaporator until the gas chromatograms showed the sample to be less than 0.5% pentane (w/v). The collected fractions were analyzed on a Hewlett-Packard capillary GC/MS and were found to contain only their respective class of compounds with no cross contamination. The refractive index (RI) of each class was measured on an Abbe refractometer. In earlier work another fuel, 13-15, had been fractionated by atmospheric pressure LC into two groups, saturates and total aromatics. These fractions were also used to prepare other detector calibration standards.

III. METHOD DEVELOPMENT

High performance liquid chromatography (HPLC) is used routinely in this laboratory to separate jet fuels into three compounds classes. Therefore, the focus of the method development is on the quantitation rather than the chromatography.

Three aspects of quantitation must be defined to have a viable technique. One is the choice of a detection method which is reliable and moderate in cost. Another is the method of calibration and third is the definition of the limitations on the technique due to equipment design.

For this quantitative analysis the differential refractive index (DRI) detector was selected because of its universal detection capability and because its difference in sensitivity to various types of compounds is much less than UV or infrared detectors. In addition a review [8] of the refractive indices of representative compounds in each class reveals that the value of this property falls in a narrow range for most common compounds in each class. For example, Table 1 lists the average refractive index (RI) of 55 common normal and branched alkanes (C₁₀ to C₂₀) as well as 24 cyclic saturates. The average RI for each type is 1.431 with a range of approximately ± 0.02 from this average. Substituted benzenes average about 1.50 and substituted naphthalenes average approximately 1.60. These considerations support the choice of DRI as the best possible detector for the quantitation. The difference between the refractive index of the hydrocarbon class and that of the solvent, i.e. n-pentane, would define the sensitivity of that class. Quantitation should be possible by electronic integration of the peak areas for each class in the chromatograms, after suitable calibration response factors are determined.

The validity of this approach was confirmed by preparing a series of mixtures of pure hydrocarbons ranging from 45% to 80% by weight saturates, 18% to 35% by weight mono-cyclic aromatics, and 2% to 20% by weight dicyclic aromatics. These mixtures were prepared by mixing weighed amounts of dodecane, ethyl benzene and 2-methyl naphthalene. These compounds have refractive indices representative of each compound class (Table 1). A typical chromatogram was obtained for one of the 3-component mixtures, designated Calibration Standard 1. The actual weights of each compound in Calibration Standard 1 were entered into the calibration table of the integrator which then calculated relative response factors for each compound class (response factor = weight/area). The chromatograms of all four pure hydrocarbon mixtures were then quantitatively determined using these response factors. Table 2 shows the results of the analyses for the four different pure hydrocarbon mixtures and compares the measured values to the actual weight percent values used to prepare each mixture. The data confirm the reliability of the technique when the detector response factors for each fuel component are matched to the components to be analyzed by similar RI values. The measured values show a random distribution of $\pm 0.7\%$ for the saturates about the actual values. Thus, calibration of the detector with a pure hydrocarbon mixture can give accurate results, within the limits of the electronic integrator precision ($\pm 1\%$ relative standard deviation (RSD)), for a broad range of sample compositions.

**Table 1 - Refractive Indices of Some Typical Fuel Components
and Fuel Fractions**

Fraction	NRL Measured 22°C	Literature 25°C
Saturates		
A. Compounds		
1. n-dodecane	1.422	1.420
2. n-hexylcyclohexane	1.446	1.445
3. 55 normal and branched alkanes	-	(1.431)*
4. 24 cyclic alkanes	-	(1.431)*
B. Fuel Components		
1. JP-5 (82-17-1)	1.436	-
2. JP-5 (J-1-1 Shale II)	1.431	-
3. JP-5 (Pax River)	1.441	-
4. JP-5 (13-15)	1.441	-
Monocyclic Aromatics		
A. Compounds		
1. toluene	1.497	1.494
2. n-butyl benzene	1.488	1.490
3. 1,2,4 trimethyl benzene	-	1.505
4. ethyl benzene	1.496	1.490
B. Fuel Components		
1. JP-5 (82-17-2)	1.503	-
2. toluene bottoms	1.500	-
Dicyclic Aromatics		
A. Compounds		
1. 2-methyl naphthalene	1.611	1.602
B. Fuel Components		
1. JP-5 (82-17-3)	1.598	-
Mobile Phase		
A. n-pentane	-	1.358
B. Freon 113	-	1.356
C. Fluorinert (FC-72)	-	1.251

* Numerical average of the refractive indices.

**Table 2 - Weight Percent of Model Hydrocarbon Mixtures
by Direct Quantitation During HPLC Separation**

Sample	Wt% Dodecane	Wt% Ethyl Benzene	Wt% 2-methyl naphthalene
Mixture 1			
Actual Value	45.32	35.48	19.20
Measured Value	45.28	35.43	19.29
Mixture 2			
Actual Value	59.75	29.72	10.54
Measured Value	60.55	29.54	9.91
Mixture 3			
Actual Value	75.56	19.95	4.49
Measured Value	75.89	19.61	4.50
Mixture 4			
Actual Value	79.71	17.76	2.53
Measured Value	79.13	18.30	2.58

Measured values are averages for 3 determinations; relative Standard Deviations were less than $\pm 1\%$ in all cases. Mixture 1 was the Calibration Standard 1 used to determine detector response factors.

During the analysis of these pure hydrocarbon mixtures with different detectors, it was noticed that the relative peak areas of the three components changed when the sample size was varied. This indicated that the detector was being overloaded. Therefore the four different commercial refractive index detectors available in this laboratory were evaluated for the effect of sample size on the quantitative results. Two of the detectors were easily overloaded by the injection of 3 μ l or less of neat fuel and were not used further to obtain quantitative data. Two others were observed to give constant results for larger size samples. One had a linearity cut off of 15 μ l and the other exhibited linearity of response to around 100 μ l of neat fuel.

All of the detectors, with the exception of the one most easily overloaded, were also checked for linearity of their response to a given change in refractive index. This was done by rotating the optical zero glass through constant angle increments to give test signals covering their entire response range on different attenuation settings. One detector was observed to give reasonably linear response only for small changes in refractive index. Thus most of its dynamic range was not linear and consequently of limited value for quantitative determinations of neat fuel samples. The other three detectors gave linear responses for a given change in refractive index over their entire dynamic range on the attenuation ranges suitable for this study. These detectors included the two which accepted the larger samples without overloading. Because of the greater range on sample signal, all of the quantitative data reported here were obtained with the detector having a linear response up to a sample size of 100 μ l.

At this point the precision of the HPLC/DRI technique was examined using one of the JP-5 jet fuel (82-17) calibration standards. Table 3 lists the results of 11 replicates for this calibration standard. The actual values in Table 3 are the weight percent values of each fraction when recombined to give the calibration standard. The detector response factor was obtained with this calibration standard, hence the good accuracy. The precision for eleven replicate determinations is excellent both in terms of absolute values and of percent relative deviation.

Several jet fuels were then analyzed. The integrator response factors generated from Calibration Standard 1 (the calibration mixture of pure component hydrocarbons), were used to convert area percent to weight percent. Only three of the fuels gave results that were reasonably close to the results obtained from gravimetric, LC/GC, or FIA analysis of these fuels. It was decided that a better calibration (response factor) might be achieved by a calibration standard that more nearly modeled a real fuel. This can be achieved by either making a more complex model mixture from pure compounds or by separating a typical fuel into its component fractions by HPLC and then recombining these components in known weight ratios. We

Table 3 - Repeatability for HPLC/DRI Quantitative
Analysis of Calibration Standard 2

Analysis	Saturates	Monocyclic Aromatics	Dicyclic Aromatics
1	74.791	17.450	7.759
2	74.308	17.570	8.123
3	74.601	17.492	7.906
4	74.169	17.849	7.982
5	74.350	17.846	7.804
6	74.834	17.491	7.675
7	73.571	18.272	8.153
8	74.309	17.932	7.759
9	73.546	18.132	8.322
10	74.313	17.773	7.915
11	<u>74.468</u>	<u>17.730</u>	<u>7.802</u>
Average Value	74.296	17.776	7.927
Actual Value	74.722	17.495	7.783
Standard deviation	±0.401	±0.256	±0.191
Relative deviation(%)	±0.5	±1.4	±2.4

(a) Calibration Standard 2: Made by recombining fractions of JP-5 jet fuel 82-17; details in the text.

chose the latter method because the refractive indices of the classes were not already known. (The main advantage of a pure compound mixture is the ability to adjust the refractive index of a given class.) Since the RI values required are not known, a recently acquired JP-5 fuel (82-17) was separated into compound class fractions by semi-preparative HPLC as described in the Experimental Section. The fractions were stripped of their solvent and recombined in known weight ratios to provide a standard calibration mixture designated as Calibration Standard 2. The refractive index for each class was measured so that a model fuel might be made in the future from pure hydrocarbon components. The refractive indices of these classes are reported in Table 1 (82-17-1, 82-17-2, and 82-17-3) along with the measured values for the saturate fraction of several fuels that had previously been separated into saturate and aromatic fractions. Inspection reveals that the refractive index of the saturate fractions from four jet fuels is essentially constant and very similar to the average observed for about eighty saturated hydrocarbons including cyclic alkanes.

Finally, the integrator was calibrated with Calibration Standard 2 (recombined jet fuel 82-17) and the fuels were again analyzed. The results of these analyses are reported in Tables 4 through 8 and are discussed in detail in the next section.

IV. RESULTS AND DISCUSSION

The agreement between the measured and actual values in Table 2 for the composition of several pure hydrocarbon reference mixtures shows that satisfactory analysis can be obtained for simple hydrocarbon mixtures if the relative response factors for the "fuel" components match those of the standard calibration mixture. This good agreement is accomplished by matching the refractive index of each class of the standard used for calibration to those of the corresponding class of the "fuel". For the complex mixture in each compound class of the jet fuels examined in this study, indices were matched using compound class mixtures derived from separated fractions of a typical jet fuel. Refractive index measurements (Table 1) show that these fractions are typical of the jet fuels that have been characterized to date.

For several reasons, the most critical fraction for matching is that of the saturates. First, the difference in refractive index of the saturate fraction and that of the mobile phase is the smallest (0.08 units). Since the detector measures the difference in refractive index between the mobile phase and that of the eluting solution, a fixed error in matching the refractive index will have the largest effect on the saturate fraction because of the proportionally larger error in the difference in refractive index. Second, the saturate fraction is the largest

component in the fuel and a fixed percent error in the saturate composition will cause a proportionally larger percent error in the other components.

A tacit assumption of this method is that all the fuel is eluted, detected and integrated. Based on this the values for the three fractions of interest are normalized to 100%. The analysis of several fuel derived mixtures, of known composition, after calibration with Calibration Standard 2 show excellent agreement between the measured and actual values as shown in Table 4.

The analysis of several fuels by HPLC/DRI, after calibration with Calibration Standard 1 or Calibration Standard 2, is shown in Table 5. The results are compared with other quantitative methods. The measured composition of J-22 is in excellent agreement with the LC-gravimetric data for that fuel and is believed to be accurate since essentially all of the sample was recovered (100.1% w/w) for gravimetric quantitation. Since J-22 contains very little dicyclic aromatics, the accurate determination of this fuel indicates that the integrator response factors for the saturates and monocyclic aromatics are in the correct ratio. The values for fuel 82-17 should also be quite accurate since this was the fuel used to prepare the Calibration Standard 2 and data in Table 4 could be accurately determined against Calibration Standard 2.

If one examines the table of refractive indices in Table 1 it is noted that the refractive index of the saturate fraction of 82-17 (82-17-1) is 1.436. This is exactly midway between that for 13-15 and for J-22 (J-1-1 Shale II). Since the experimental values of the composition of J-22 and 13-15 are known to be correct to within about \pm one weight percent for the saturate fraction, there is good reason to expect that the analysis of fuels whose saturate fractions have a refractive index within the range 1.431 to 1.441 will be quantitated accurately. The refractive index of the saturates for the Pax River JP-5 is also 1.441; therefore it is reasonable to expect the quantitation by HPLC/DRI for that fuel to be accurate to \pm one weight percent for the saturate fraction. (Values in Tables 6 and 8).

The LC/GC method of quantitation involves collecting the three compound class fractions, adding a known weight of internal standard to each fraction, measuring the total area of all peaks on a low resolution gas chromatogram of each fraction and calculating the weight percent with a correction for difference in average carbon percent of each fraction and the internal standard. The LC/GC method has been applied to several fuels whose compound class weight percent values were known from direct gravimetric analysis. LC/GC provides excellent results as long as 100 weight percent recoveries are maintained.

Table 4 - Direct HPLC Quantitation of Fuel Derived Mixtures;
DRI was calibrated using Calibration Mixture 2.

Fuel Mixture	Saturates	Monocyclic Aromatics	Dicyclic Aromatics
13-15 ^a			
Measured Value	82.4		17.6
Actual Value	81.9		18.1
82-17A			
Measured Value	74.8	17.5	7.7
Actual Value	74.7	17.5	7.8
82-17B			
Measured Value	78.3	17.2	4.5
Actual Value	77.9	17.5	4.5

(a) Made from fuel 13-15 (only available as two fractions: saturate and total aromatics).

Comparison between LC/GC and LC/DRI results in Table 5 show quite good agreement for the unblended fuels: J-22, 81-19, and 82-17. In general the fuel blends analyzed by the two methods do not agree as well. Two blends, 81-16 and 81-17, gave reasonably close agreement but the remaining three blends exhibited agreement somewhat outside the acceptable quantitation limits (~1 weight percent). The problems encountered in accurately determining hydrocarbon classes in experimental jet fuel blends will continue to be addressed in future work.

Table 6 compares the results of fluorescence indicator absorption (FIA) measurements [9] of total aromatics for several fuels to the value determined by direct HPLC. The FIA technique attempts to measure volume percent total aromatics. The values obtained for volume percent are multiplied by a factor of 1.08 to give approximate weight percent values for easier comparison. This factor is calculated based upon estimates of average densities of the compound class fractions.

Again, the two techniques give comparable data for JP-5 samples. The four blends 81-13 through 81-16 and one older sample of JP-5 (80-5), however, give significantly lower total aromatic values by HPLC, from 2.1 to 6.5 weight percent. In general, the LC/GC values for total aromatics of the blends (from Table 5) are in closer agreement with FIA values. These results underscore the necessity of calibrating the DRI detector with calibration mixture components which match the "fuel" components' refractive indices as closely as possible. Examination of the composition of the four fuels which are known to be accurate to \pm one weight percent for the HPLC analyses (82-17, J-22, 13-15, and Pax River), reveals that the weight percent total aromatics values by HPLC are consistently lower than FIA weight percent values by 0.1 to 1.1 weight percent.

Table 7 shows that equally acceptable results are obtained upon substitution of Freon 113 for pentane as the mobile phase. This freon has essentially the same refractive index as pentane but is less volatile and non-flammable. However, due to different chromatographic conditions the relative response factors are not the same as when pentane is the mobile phase. Perfluorohexane (Fluorinert FC-72) was also examined as a potential mobile phase because of its extremely low refractive index. This would increase the sensitivity, especially for the saturates since the RI differences between hydrocarbon class and solvent is much greater. The difference in sensitivity of the detector for the different compound classes would also be reduced thus making it less critical that the refractive index of the fraction of the standard match that for the fuel fraction being measured. Unfortunately, jet fuels are not significantly soluble in this solvent and consequently it is not a suitable mobile phase.

Table 5 - Comparative Analysis of Selected Jet Fuels (Wt%)

Sample	Saturates	Monocyclic Aromatics	Dicyclic Aromatics	Methods of Analysis
J-22 (Shale II JP-5)	75.7 75.1 76.5	23.6 23.9 23.3	0.7 0.9 0.3	HPLC-Std-1 HPLC-Std-2 LC/Gravimetric
81-13 (Sun Blend-1)	73.4 71.8 68.5	23.2 24.3 27.5	3.4 3.9 5.1	HPLC-Std-1 HPLC-Std-2 LC/GC
81-14 (Sun Blend-2)	79.1 76.2 76.5	14.6 16.2 18.6	6.2 7.6 3.5	HPLC-Std-1 HPLC-Std-2 LC/GC
81-15 (Sun Blend-3)	78.2 77.2 74.8	19.3 20.1 22.0	2.6 2.8 4.0	HPLC-Std-1 HPLC-Std-2 LC/GC
81-16 (Sun Blend-4)	81.9 79.9 77.3	15.6 17.0 18.5	2.5 3.2 2.0	HPLC-Std-1 HPLC-Std-2 LC/GC
81-17 (20/80 HCGO/JP-5)	68.9 68.7 70.0	23.6 22.8 20.9	7.4 8.5 9.7	HPLC-Std-1 HPLC-Std-2 LC/GC
81-19 (Hi-aromatic JP-5)	74.9 74.8 76.8	24.6 24.5 24.6	0.5 0.8 1.5	HPLC-Std-1 HPLC-Std-2 LC/GC
82-17 (Petro JP-5)	NA 76.4 75.2	NA 18.3 19.5	NA 5.3 5.3	HPLC-Std-1 HPLC-Std-2 LC/GC

Table 6 - Comparison of Results from FIA and Direct
HPLC Quantitation for Total Aromatics

Sample	FIA		HPLC/DRI (Wt %)
	(Vol %)	(Wt %)*	
J-22 (Shale II JP-5)	24.0	25.9	24.8
Pax River (Petro JP-5)	18.2	19.7	19.6
13-15 (Petro JP-5)	16.2	17.5	16.7
80-5 (Petro JP-5)	23.9	25.8	23.1
81-13 (Sun Blend 1)	32.1	34.7	28.2
81-14 (Sun Blend 2)	25.0	27.0	23.8
81-15 (Sun Blend 3)	23.6	25.5	22.9
81-16 (Sun Blend 4)	20.5	22.1	20.2
82-17 (Petro JP-5)	21.9	23.7	23.1

* 1.08 multiplier factor

Table 7 - Comparison of Results with Different Mobile
Phases and Columns (Wt%)

Sample	Saturates	Monocyclic Aromatics	Dicyclic Aromatics
<u>82-17A</u>			
8-82/P ^a	74.3	17.8	7.9
6-83/P	74.8	17.5	7.7
6-83/F ^b	74.8	17.5	7.7
<u>82-17B</u>			
6-83/P	78.3	17.2	4.5
6-83/F	77.4	18.0	4.6
<u>J-22</u>			
8-82/P	75.3	23.6	1.0
6-83/P	75.7	23.5	0.8
6-83/F	74.4	24.6	0.9
<u>13-15</u>			
8-82/P	82.8	14.1	3.1
6-83/P	83.7	14.2	2.5
6-83/F	83.7	13.8	2.5
<u>82-17</u>			
8-82/P	76.8	18.0	5.2
6-83/P	76.3	18.4	5.3
6-83/F	76.1	18.6	5.3

- (a) P denotes pentane mobile phase; numbers denote date of sample run.
- (b) F denotes freon (1,1,2-trichloro 1,2,2-trifluoroethane) mobile phase; numbers denote date of sample run.

Table 8 lists the average values for each compound class of thirteen fuels determined over a twelve month period using two different mobile phases on several HPLC columns. It is noteworthy that the standard deviation of the eight determinations averaged for each value in Table 8 were within the limits shown in Table 3.

V. CONCLUSIONS

The results of this study have demonstrated that the direct HPLC/DRI method is a simple, rapid technique for obtaining quantitative analysis of compound classes present in middle-distillate jet fuels. The method gives results within the limits of the precision of the electronic integrator when fuel derived, known weight percent mixtures are used as calibration standards. The refractive index of the saturate fraction is the most critical parameter to adjust, but satisfactory analyses were obtained when the refractive index of the saturates in the Calibration Standard matched the refractive index of the fuel saturates to within 0.006 RI units. It should be possible to separate small samples of the saturate fraction of fuels to determine the refractive index to enable more precise matching of refractive indices of the fuel to the Calibration Standard.

Care must be taken in setting up the instrument components to insure good chromatographic resolution while, at the same time, insuring sufficient detector response for integration of the areas of interest. Further, a refractive index detector must be chosen which will give a linear response for the sample volumes of interest.

Comparison of HPLC/DRI results with those from other measurements indicated good agreement for JP-5 samples. Agreement was somewhat poorer for fuel blends representative of broad range jet fuels.

Table 8 - Direct HPLC/DRI Determinations of Weight Percent
of Selected Jet Fuels and Hydrocarbon Mixtures^a

Sample	Saturates	Monocyclic Aromatics	Dicyclic Aromatics	Total Aromatics
J-22	75.1	23.9	0.9	24.8
Pax River	80.7	15.7	3.5	19.2
13-15	83.4	14.0	2.7	16.7
80-5	76.9	18.2	4.9	23.1
81-3	0.4	99.0	0.5	99.5
81-9	83.0	14.2	2.8	17.0
81-13	71.8	24.3	3.9	28.2
81-14	76.2	16.2	7.6	23.8
81-15	77.2	20.1	2.8	22.9
81-16	79.9	17.0	3.2	20.2
81-17	68.7	22.8	8.5	31.3
81-19	74.8	24.5	0.8	25.3
82-17	76.4	18.3	5.3	23.6

(a) This represents the average of eight determinations over a 12 month period; all standard deviations were within the limits shown in Table 3.

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