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High Performance Liquid Chromatographic Hydrocarbon Group-Type Analyses of Mid-Distillates Employing Fuel-Derived Fractions as Standards

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SUMMARY

Currently, a number of analytical methods are available for group-type determinations in mid-distillate fuels; however, high performance liquid chromatography (HPLC) appears to be among the most promising techniques in terms of accuracy, precision, speed, and range of sample types. One problem in the application of HPLC is the requirement for group-type standards and a second is in determining the low concentrations of olefins present in the fuels.

This report presents two HPLC methods which partially solve these problems. In one method, the fuel to be analyzed is reacted with sulfuric acid to remove a substantial portion of the aromatics, and HPLC data from this reacted fuel fraction is combined with that from the original sample to determine the quantities of saturates, olefins (if present) and aromatics in the mid-distillate. Model fuel analyses indicated that the method is accurate to within 0.7 volume percent of aromatics or saturates with a standard deviation of 0.5 volume percent. Real fuel sample trials yielded the same precision.

The second method involves the removal of a substantial portion of the saturates fraction from the HPLC system by precise backflushing to permit the determination of the olefins in concentrations as low as 0.3 volume percent and to improve the accuracy and precision of olefins determinations. This procedure was evaluated using known olefin additions to an olefin-free Jet A fuel, as well as through the analysis of a shale-derived JP-5 fuel.

INTRODUCTION

With the present trend of increasing aromatic contents of jet turbine fuels, the potential introduction of synfuels, and possible changes in refinery processing technology, hydrocarbon group-type determinations are receiving increased attention. The distribution of saturates, aromatics, and olefins affects a number of critical fuel characteristics including combustion quality, materials compatibility, and stability, among others. One of the most common techniques for group-type determinations in mid-distillate fuels is the fluorescent indicator adsorption method (FIA-ASTM D-1319) (ref. 1). This method is time-consuming, limited to fuels distilling below 316° C (600° F), and subject to a number of fundamental errors. Other methods providing similar information for the same or higher boiling ranges, are subject to many of the same problems (refs. 2 and 3). High performance liquid chromatography (HPLC) has been employed as an alternative approach which improves all aspects of group-type determinations (refs. 4-7). By varying procedures, this technique is applicable to all petroleum fuels and synfuels boiling above 60° C (140° F) (refs. 4-8). One major difficulty, however, is obtaining suitable calibration standards for each fuel type. Standards are generally prepared using representative blends of pure compounds or are

derived from fuels in the correct boiling range by column chromatography. However the work is time-consuming, and good representative mixtures for each fuel type are difficult to obtain (ref. 9). One approach which has been reported involves the use of HPLC preparative-scale separations to provide the necessary fractions (refs. 9 and 10). However, for mid-distillate fuels, the loss of light ends during the solvent removal process remains a major problem.

This paper describes an alternative technique to those previously discussed, which increases the versatility of HPLC group-type determinations by providing a simple, rapid method for obtaining mid-distillate fuel fractions for use as standards in quantitative determinations. The technique, termed the General Method, involves the preparation of these standards by reacting fuels with sulfuric acid, which substantially reduces their aromatics concentrations.

In the present work, General Method HPLC group-type analyses were performed on a variety of fuels including model compound mixtures, Jet A, diesel fuels, a shale-derived JP-5 and a broadened-properties research fuel. The broadened-properties research fuel, known as the experimental referee broadened-specification (ERBS) fuel, is a blend of kerosine and gas oil procured and characterized to serve as a referee fuel for experimental combustor work (ref. 11).

Generally, the olefin content of straight run fuels boiling above 204° C (400° F) is low (ref. 12). Even in those cases where the olefin content might be expected to be somewhat elevated, such as for mid-distillates derived from shale oil, or those containing cracked stock, the olefin levels are generally not high in the finished product. For HPLC analysis employing the classical refractive index detector, the olefins peak is found to lie in close proximity to the saturates peak, and the olefins are often totally obscured, or at best, the results are inaccurate and imprecise. Increased resolution can be achieved by increasing the total column plate number at the cost of time and band broadening which in itself may ultimately bury the olefin peak in detector noise. The use of fluorocarbon mixtures as the mobile phase can improve the olefin results, however, these solvents are expensive and of limited availability. The ultraviolet (UV) absorption detectors, operated at the proper wavelength, are more sensitive than the refractive index detectors, but large variations in compound absorptivities preclude their use in obtaining good quantitative results for olefin fuel fractions. One possible alternative is the infrared detector; however, mobile phase selection is strictly limited to nonhydrocarbon solvents, and detector sensitivity variations within a group-type are not significantly better than is found for the standard refractive index detector (ref. 13). Other techniques for olefin determinations in fuels include the Bromine Number method (ASTM D-1159), preparative HPLC, and conversion to alcohols by hydroboration (refs. 12, 14-17). A number of problems are associated with each of these methods.

The approach examined in this study involves the physical removal of a substantial portion of the interfering saturate fraction by diverting this portion out of the system while preserving the olefin fraction intact. This technique, referred to as the Saturates Removal Method, is a simple and rapid, but effective extension of HPLC group-type methods to more accurately and precisely determine olefin contents in fuels. The method was evaluated using olefin standards in an olefin-free Jet A fuel matrix, as well as by using appropriate fractions of a chromatographed shale-derived JP-5.

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EXPERIMENTAL

Instrumentation

A model 830 high performance liquid chromatograph (E. I. du Pont de Nemours & Co., Inc.), equipped with a model 833 flow controller, a model 837 variable wavelength ultraviolet-visible spectrophotometer and a model 845 differential refractometer, was employed in this study. Sample injection and backflush were performed using a 5 μl, four port internal shaft injection valve and four ports of a ten port backflush valve, respectively. Separation was accomplished using two 30 cm by 4 mm i.d. columns packed with ten micron πPorasil (Waters Associates, Inc.). A 5 cm by 3.2 mm i.d. guard column with identical packing was also employed to protect the analytical columns. The mobile phase, pentane (hexane was found to be a viable alternative), was dried on-stream using a solvent drying filter (Alltech Associates, Inc.). Data acquisition and reduction was provided by a model 3353 Laboratory Automation System (Hewlett-Packard Co.). Figure 1 is a diagram of the complete HPLC system.

Procedure for General Group-Type Determinations

Approximately 15 ml of the fuel was combined with 75 ml of reagent grade concentrated sulfuric acid in a 125 ml erlenmeyer flask and stirred vigorously at room temperature (approximately 24° C) using a magnetic stirrer. Attempts were made to maintain a relatively constant stirring rate during the study to achieve consistency in the reaction period. The reaction period was varied between 6 and 15 minutes depending on the general fuel type, such that 60 to 80 percent of the aromatics fraction was sulfonated. The ERBS and diesel fuels required less time to reach the required aromatics range than did the Jet A or JP-5 fuels.

Following the reaction period, the mixture was transferred to a 125 ml separatory funnel to remove the acid. A small portion of the reacted fuel standard was drained to reduce the number of subsequent washings required to remove the sulfuric and sulfonic acids which remained in the separatory funnel. Washing was performed using 50 ml portions of deionized water and was repeated until the wash water tested neutral to short range pH indicating paper. In those rare instances where an emulsion formed, a small amount of reagent grade sodium chloride was added to following portions of the wash water, however, the final wash always remained pure deionized water. Drying was accomplished using a short column of 4 Åmolecular sieves (8-12 mesh) prepared by packing a gas dispersion tube (glass tubing 25 cm by 8 mm i.d., cylindrical frit) to a height of 15 cm. To remove particulates, a syringe attachment containing a 0.3 micron glass fiber filter (Schleicher & Schull GmbH) was employed prior to HPLC analysis of the reacted fuel standard.

During the fuel reaction period, the unreacted fuel was chromatographed, employing the system outlined in figure 1. The system and procedure were similar to those employed by Suatoni et. al (refs. 4-6). The flow rate employed was 2.0 ml/min. During sample injection, the system was configured as a classical HPLC (i.e., solid line through the backflush valve). Following the elution of the saturates and olefins (if present), which was completed at 4.5 minutes, the columns were backflushed (i.e., dashed lines through the backflush valve) to elute the aromatics as a single, sharp peak. As is shown in figure 2, a complete chromatogram requires 10.5 minutes. The reacted fuel

standard was analyzed in an identical manner. A complete fuel analysis re-
quires approximately 30 minutes.

Preparation of Model Fuels for Evaluation of the General Method

Table I outlines the composition of the two Jet A and three ERBS model
fuels prepared from representative pure compounds to evaluate the General
Method previously described. One saturates fraction was employed to prepare
all model fuels studied. Although it is acknowledged that isooctane and
cyclooctane are not found in the mid-distillates studied in the proportions
which were included in the model fuels, these compounds were added to evaluate
the method for fuel light-end losses. Aromatics fractions, presented in part
b of table I were varied somewhat in composition to provide a limited matrix.
Model fuels were prepared using a standard 50 ml buret to determine the quan-
tities of each fraction indicated in part c of table I. Extreme care was
taken to assure complete drainage of the buret, particularly for the viscous
saturates fraction.

Procedure for Improved Olefins Determinations
by Saturates Removal

The technique developed to improve the determination of olefins in mid-
distillate fuels employed the same chromatographic system as was presented
previously. However, pentane was employed exclusively as the mobile phase for
this portion of the studies. Following injection of the unreacted fuel sam-
ple, the differential refractometer recorder trace was monitored. Five sec-
onds following the saturates trace maximum (approximately 3.3 minutes), the
system was backflushed. This action forces the olefins and a relatively small
portion of the saturates back onto the column, while the saturates on the
detector side of the backflush value were routed out of the system. The UV
detector was monitored at 210 nm to assure that no significant loss of olefins
occurred. After one minute of backflushing, the system was returned to for-
ward flow. The resulting peak was primarily composed of olefins which could
then be more accurately quantified. To complete the method, and remove the
aromatics fraction, the backflush was repeated. Figure 3 shows a typical
chromatogram, which requires 12 minutes to complete.

Preparation of Olefin Standards and Fractionation
of Shale-Derived JP-5

To evaluate the Saturates Removal Method for olefins determinations,
a number of olefin standards were prepared using 1-decene, 1-dodecene,
1-tetradecene, 1-hexadecene, 1-octadecene, and cyclooctene with an olefin-free
Jet A as the diluent. The olefin-free Jet A was prepared using a scaled-up
version of the fuel reaction portion of the General Method procedure previous-
ly presented. As a result, of course, the aromatics fraction of this base
fuel was substantially reduced and the saturates fraction proportionately
increased. It therefore served as a more severe matrix for method evaluation
than would be provided by employing real jet turbine fuels.
To further characterize the method, a shale-derived JP-5 was selected for
olefin fraction concentration. One method for obtaining the quantities of a
concentrated olefin fraction in a matrix which permits accurate quantitation
by HPLC, is frontal open-bed chromatography. In preparation for the initial
separation, 450 grams of 60-200 mesh silica gel (grade 950, Fisher Scientific

Co.) was dried at 150° C for eight hours and packed into a column 36 cm by 5 cm i.d. Approximately 700 ml of the fuel was separated using gravity flow. Fractions of the saturates were collected and analyzed by HPLC. Those saturate fractions having identical integrated responses were combined to serve as a JP-5 fuel saturates standard. Similar representative fractions of that portion containing saturates and olefins were collected and combined. Obtaining a representative olefin sample of sufficient concentration also required including several samples with aromatics concentrations ranging from 1 to 10 volume percent in the combined fraction. Removal of the aromatics from the combined olefin/saturates fraction was achieved using a second activated silica gel column, 35 cm by 1 cm i.d., under slight pressure (approximately 184 N/m² (5 psi)). To complete the separation procedure, and further concentrate the olefins, fractions from the second separation containing only saturates and olefins were introduced onto a third column with dimensions identical to the second. However, in this case, the column packing consisted of 25 cm of activated silica gel followed by 10 cm of 20 weight percent silver nitrate-impregnated silica gel prepared as described in reference 18. Final elution of a large portion of the olefins was accomplished using 40 ml of pentane under slight pressure. The final fraction of olefins and saturates was obtained by slow evaporation of the pentane using a directed stream of nitrogen at room temperature.

RESULTS AND DISCUSSION

General Method Introduction

Prior to any quantitative measurements, it was necessary to establish the relationship between the group-type concentrations, and the differential refractometer integrated response (hereafter, referred to as response). For ideal solutions, the refractive index of the solution is a linear function of the volume fractions of its components (ref. 19). For the detector employed in this study, a linear relationship was found to exist between the response and the volume fraction of any component, whereas the use of weight fractions produced a nonlinear relationship. Therefore, all report results are presented as volume fractions.

Several self-evident equalities, and several assumptions were employed to derive the final equations which yield group-type concentrations from the raw data. Obviously, for fuels containing negligible quantities of olefins and polar compounds, the quantities of saturates and aromatics injected into the HPLC for both the unreacted fuel and the reacted fuel must be equivalent to the volume of the sampling valve, or the total of the volume fractions must equal unity, as:

$$F_s + F_a = 1 \tag{1}$$

$$F_{sr} + F_{ar} = 1 \tag{2}$$

where F_s and F_a are the volume fractions of saturates and aromatics, respectively, and the subscript, r, denotes the reacted fuel standard. Since the differential refractometer response was found to be linear as a function of volume fraction, a series of four similar equations are apparent, two for the fuel and two for the reacted fuel, of the general form:

$$R_x = k_x F_x \quad (i.e. \; R_s = k_s F_s) \tag{3}$$

where R_x is the detector response, and k_x is a proportionality constant which varies with each fraction. One requirement of this method is that the saturates fraction not be involved in the sulfonation reaction, and thus, k_s is equivalent to k_{sr}. This leads to the relationship:

$$\frac{R_s}{R_{sr}} = \frac{F_s}{F_{sr}} \tag{4}$$

A report published in 1979 by Zrelov et al. indicated that at room temperature, sulfuric acid concentrations above 96 percent by weight (note that reagent grade sulfuric acid ranges from 95 to 98.5 percent by weight) did produce some loss of the saturates fraction (ref. 20). However, in the present study, complete removal of the aromatics fraction is never realized, and no evidence of saturates losses was found during the study.

The final method requirement is that the sulfonation process does not significantly affect the value of the proportionality constant k_a and therefore, k_a is approximately equivalent to k_{ar}. Assuming this is true, equation (4) can be repeated for the aromatics fraction as:

$$\frac{R_a}{R_{ar}} = \frac{F_a}{F_{ar}} \tag{5}$$

Substituting equations (1), (4) and (5) into equation (2), yields:

$$1 = (R_{sr}/R_s)F_s + R_{ar}/R_a(1 - F_s) \tag{6}$$

which can be rearranged to the following final relationship:

$$F_s = \frac{1 - R_{ar}/R_a}{\dfrac{R_{sr}}{R_s} - \dfrac{R_{ar}}{R_a}} \tag{7}$$

for those mid-distillate fuels which contain negligible quantities of olefins and polar compounds.

Although the assumption leading to equation (5) may, on initial inspection seem questionable, further analysis indicates that there are several factors which favor its use. One factor involves the similarity of the refractive indices of compounds within one class of aromatics, i.e., alkylbenzenes, cycloalkylbenzenes, alkylnaphthalenes, cycloalkylnaphthalenes, and alkylanthracenes/phenanthrenes (refs. 7 and 21). Therefore, any significant variation occurring in the k_{ar} value will be predominately produced by one aromatics class reacting at a much greater rate than another. Although the alkylnaphthalenes and alkylanthracenes/phenanthrenes do generally display larger values for the reaction rate constants than does the monoaromatics class, rate constants vary sufficiently through any given class that rate constant overlap does occur between classes. Furthermore, the higher concentra-

tion of monoaromatics partially compensates for this rate constant difference, and the extent of the sulfonation reaction is limited to a maximum value of 80 percent in the method procedure. Finally, the method intrinsically reduces errors in the results due to any variation in k_{ar}. For example, a 1 percent difference between this parameter and k_a yields a maximum relative error of 0.34 percent in the aromatics fraction result. Final verification of the k_a and k_{ar} equivalency assumption, and the validity of the method, in general, was accomplished through the analysis of model fuels.

Group-type determinations performed on fuels containing significant fractions of olefins are also possible using a variation of equation (7). Obviously, for this case, equation (1) must be modified to include the olefin fraction, F_o. However, due to the fact that the reaction with sulfuric acid removes the olefins, equation (2) remains valid as is.

One additional equation necessary for a final solution is provided by employing a method suggested by Suatoni et al. (ref. 5). They observed that the response of a given olefin ratioed to the response of the saturate corresponding in structure, was generally a constant value of 1.1. This relationship can be expressed as:

$$\frac{R_o}{1.1R_s} = \frac{F_o}{F_s} \tag{8}$$

Combining equation (1) (modified, $F_s + F_a + F_o = 1$), 2, 4, 5 and 8, and solving for F_s , one obtains the following equation:

$$F_s = \frac{1 - R_{ar}/R_a}{\dfrac{R_{sr}}{R_s} - \left(\dfrac{R_o}{1.1R_s} + 1\right)\dfrac{R_{ar}}{R_a}} \tag{9}$$

which is very similar to equation (7). Following the determination of F_s, F_o and F_a can be calculated using equation (8) and the modified version of 1, respectively.

Evaluation of Results for the General Method

Table II presents the General Method (eq. (7)) results, which are averages of a minimum of 5 analyses, for the model fuels listed in table I. FIA results are also included for comparison purposes. Although small quantities of olefins were observed in the model fuels using the UV detector at 210 nm, none were found to exceed 0.3 volume percent, and in a majority of cases appeared to be present at a substantially lower level. Generally, the results appear to lend support to the original assumption that k_a and k_{ar} are approximately equivalent, as well as support the overall technique. An evaluation of the accuracy indicates that the largest absolute error in the model fuel results occurred in Jet A – fuel 2 at a level of 0.7 for a relative error in the aromatics fraction of −3.4 percent and in the saturates fraction of +0.9 percent. The smallest, obtained for ERBS – fuel 2, is 0.1 for a relative aromatics fraction error of +0.3 percent, and a relative saturates fraction error of −0.1 percent. Furthermore, there is no apparent bias of results with regards to consistently high or low values. Standard deviations range from 0.1 to 0.5 for a relative standard deviation range for the aromatics fractions of 0.5 percent to 1.7 percent, and in the saturates fraction from 0.1 to

0.7 percent, respectively. The FIA results obtained through a single analysis of each of the model fuels demonstrate accuracies similar to those found by HPLC for the aromatics fractions, but overestimate the olefin concentrations, and are therefore less accurate for the saturates fractions.

Table III presents the group-type results obtained for several true mid-distillate fuel samples which vary in composition. The three Jet A fuels and two ERBS fuels reported were obtained from separate fuel shipments. As is evident from the data, the FIA results generally agree fairly well with those determined using the HPLC General Method. By far, the largest difference occurs for the shale-derived JP-5, and a portion of this difference is elimi-nated with more accurate HPLC olefin results (see the following section for the HPLC olefin determination employing equation (9) and using the Saturates Removal Method). As was previously found for the model fuels, the maximum standard deviation was 0.5 percent, yielding a maximum relative standard deviation of 2.5 percent for the aromatics fraction.

To evaluate the reproducibility of the method, two fuels were selected to be studied, a Jet A and the shale-derived JP-5. The Jet A was reacted at five different times under ambient conditions and analyzed over a thirteen day period, while the JP-5 fuel was reacted at three different times under ambient conditions and analyzed over a nine day period. Two operators performed the analyses. The results of the studies are presented in table IV. As is shown in the table, the maximum standard deviation remains unchanged from the re-sults presented earlier at 0.5 percent. The overall range of the results varied between 1.0 percent for the JP-5 fuel and 1.3 percent for the Jet A fuel.

Olefin Determinations by HPLC Saturates Removal

As was stated in a previous section, the Saturates Removal Method proce-dure produced chromatograms shown in figure 3. Peaks A and B are saturates peaks. Peak B results from the system configuration associated with the ten port backflush valve and can be eliminated using a four or six port valve. Peak C is due to the olefins in the sample. Studies correlating various methods of area integration (response) and peak height with known concentra-tions of a number of olefins in the olefin-free Jet A, indicated that the most accurate results were produced using the method outlined in the figure (shaded area). Olefin peak area is determined by employing a lower boundary defined by the valley between peaks A and B, and a tangent to the tailing edge of peak C. The vertical boundary is defined by a "drop-line" between the valley formed by peaks B and C, and the lower boundary. The peak heights found to yield the best results also employ the lower area boundary as the lower limit.

Table V presents the results for the method using the standard olefin solutions (in the olefin-free Jet A matrix). As is expected from the reten-tion times of olefins on silica gel, the detection limits and standard devia-tions of the results reported generally increase as a function of increasing alkyl chain length. Accuracy, however, does not appear to vary in any uniform fashion. Cyclooctene, which displays a relatively late retention time is more easily quantified and can be detected to lower concentrations than is possible for the other compounds. Furthermore, the Saturates Removal Method does not appear to significantly improve the results for this olefin.

Table VI outlines the results obtained by employing the Saturates Removal Method for the shale-derived JP-5 (sample 1 in table VI, initially reported in the table III footnote) a sample from the second silica gel fractionation of the JP-5 (sample 2, saturates and olefins only) and the sample obtained from

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the final separation of the JP-5 (sample 3, saturates and olefins only). Area (response) data obtained for the olefins were employed in all cases. In the first data column, the JP-5 result (sample 1) was obtained using the Saturates Removal Method and equation (9), followed by equation (8), while samples 2 and 3 employed only equation (8).

To confirm the observation which resulted in equation (8), an indirect method was employed which required data from the JP-5 fuel saturates standard, obtained from the initial silica gel separation, as well as data from samples 2 and 3. The relationship employed was:

$$F_s = \frac{R_s}{R_{st}} F_{st} \tag{10}$$

where F_s is the saturates fraction in samples 2 or 3, R_s is the saturates response for samples 2 or 3, R_{st} is the total saturates response for the JP-5 fuel saturates standard, and F_{st} is unity, since this sample is totally composed of saturates. Since samples 2 and 3 contain only saturates and olefins, the olefin content of each of the two samples is easily determined. Despite the inherent inaccuracies in a method of this type, the agreement with the equation (8) data is fairly good.

One final method, which evaluates the consistency of the results, assumes that the equation (8) olefin result for sample 3 is correct, and employs the following simple relationship to calculate sample 1 and 2 results:

$$F_o = \frac{R_o}{R_{o_3}} \times 0.105 \tag{11}$$

where F_o is the fraction of olefins in samples 1 or 2, R_o is the response of the olefins in samples 1 or 2, and R_{o_3} is the olefin response of sample 3. Again the results display reasonable agreement with others in the table.

For comparison purposes, FIA olefin results are also presented for samples 1 and 2 in table VI. From the results presented in tables III, V and VI, the Saturates Removal Method appears to be superior to both the General Method, described earlier, and the FIA method for olefin determinations, particularly for the low concentrations normally associated with mid-distillate fuels.

CONCLUDING REMARKS

This study increases the versatility of HPLC group-type determinations by providing a simple, rapid method for obtaining good petroleum and shale-derived mid-distillate fractions for use as standards, directly from the fuels, and for improving the detection limit, precision, and accuracy of the olefin determinations. The overall findings support the conclusions drawn by others, that the HPLC group-type determination methods are superior in accuracy, precision, speed, and latitude to several widely-employed methods, such as the FIA technique (refs. 4-11).

Although polar compounds are generally present in small quantities in mid-distillates, samples containing polar fractions analyzed by the method presented, will realize a small positive error in each hydrocarbon fraction result. Recently, C. Bollet et al., reported an HPLC method which permits the determination of saturates, aromatics, and polars in heavier petroleum products such as vacuum distillates and residuals (ref. 22). However, polar

determinations employing this method require preparative-scale separations to obtain the necessary fraction standards or rely on the use of previously determined detector calibration curves which vary between each fuel type. A logical extension of the present technique to include the determination of the polar fractions in heavier petroleum products or synfuels might consist of exchanging the silica packing for an alkylamine bonded-phase packing, one additional reaction step to remove the polar fraction using dilute acid and dilute base or a very small silica gel column, and an HPLC analysis of the polar-free fuel. The HPLC silica gel column could be retained as a part of the system for olefin determinations, as well.

Increased accuracy and precision of all HPLC methods presented could be achieved by automating the sample and backflush valves, employing a more advanced refractive index detector, improving the detector temperature control and improving the mobile phase flow control. Analysis times for the general method could be substantially reduced by employing a 10 cm silica gel column which would still provide sufficient efficiency to resolve the saturates and aromatics. One or more of the 25 cm columns employed in this study could be easily added to the system under automated control as is required for performing olefins determinations.

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TABLE I. – COMPOSITION OF MODEL FUELS

(a) Saturated hydrocarbon
fraction, in vol. %

Compound	Concentration
Isooctane	13
Cyclooctane	23
Decalin	17
Dodecane	47

(b) Aromatic hydrocarbon fraction, in vol. %

Compound	"Jet A" model fuels		"ERBS" model fuels	
	1	2	1 and 2	3
Xylenes (Isomer mix)	1.5	6.9	9.8	5.0
Diethylbenzenes (Isomer mix)	15.2	27.7	9.8	21.1
n-Butylbenzene	15.2	6.9	----	----
Tetralin	35.3	33.2	23.0	25.3
Durene	22.7	20.7	9.8	11.8
Naphthalene	10.1	----	11.5	7.0
1-Methylnaphthalene	----	----	9.8	7.0
2-Methylnaphthalene	----	4.6	16.4	8.2
Acenaphthene	----	----	9.2	14.2
Anthracene	----	----	.7	.4

(c) Model fuel blends, in vol. %

Fraction	"Jet A" model fuels		"ERBS" model fuels		
	1	2	1	2	3
Saturates	78.94	80.10	70.17	70.16	66.90
Aromatics	21.06	19.90	29.83	29.84	33.10

TABLE II. - GROUP-TYPE DETERMINATION RESULTS FOR MODEL FUEL BLENDS BY HPLC AND FIA, IN VOL. %

Model fuel	Composition, Table I(c)			HPLC (General Method)			FIA		
	Saturates	Aromatics	Olefins[a]	Saturates	Aromatics	Std. Dev.	Saturates	Aromatics	Olefins
Jet A, 1	78.9	21.1	<0.3	79.2	20.8	0.3	77.8	21.2	1.0
Jet A, 2	80.1	19.9	↓	79.4	20.6	.1	79.0	20.2	.8
ERBS, 1	70.2	29.8		70.1	29.9	.2	69.7	29.7	.6
ERBS, 2	70.2	29.8		70.0	30.0	.5	69.7	29.6	.7
ERBS, 3	66.9	33.1		67.3	32.7	.5	65.0	33.9	1.0

[a]Olefins were present as low concentration impurities in the saturates and aromatics fractions (results determined using the Saturates Removal Method).

TABLE III. – GROUP-TYPE DETERMINATION RESULTS FOR
COMMERCIAL FUELS BY HPLC AND FIA, IN VOL. %

Fuel sample	HPLC (General Method)				FIA		
	Saturates	Aromatics	Std. Dev.	Olefins	Saturates	Aromatics	Olefins
Jet A, A	84.5	15.5	0.2	b___	84.1	15.4	0.5
Jet A, B	82.4	17.6	.4		81.6	17.9	.5
Jet A, C	82.6	17.4	.3		82.3	17.2	.5
ERBS, A	71.3	28.7	.3		70.7	28.8	.5
ERBS, B	72.7	27.3	.1		71.9	27.6	.5
Diesel	83.1	16.9	.3		82.4	16.7	.8
Shale JP-5	a78.9	20.2	.5	a0.9	76.5	22.2	1.3

aThe results as determined by the HPLC Saturates Removal Method are:
   Saturates – 77.9, Aromatics – 20.2, Olefins – 1.9 (see table VI).
bNo olefins observed using the General Method. The Saturates Removal Method
   confirmed olefin concentrations were <0.3 vol. %.

TABLE IV. – HPLC GENERAL METHOD REPRODUCIBILITY STUDY

Fuel sample		Aromatics, vol. %						Average	Std. Dev.	HPLC range	FIA[a] reprod.
Jet A, Sample B	Day	1	4	5	6	12	13	----	---	---	---
	Result	17.0	17.8	18.3	17.5	17.6	17.8	17.7	0.4	1.3	3.2
Shale-Derived JP-5	Day	1	2	4	7	8	9	----	---	---	---
	Result	21.9	22.6	22.4	22.6	21.6	21.7	22.1	0.5	1.0	3.4

aObtained from the ASTM D-1319 method description.

TABLE V. – OLEFIN DETERMINATIONS OF STANDARDS IN OLEFIN-FREE
JET A FUEL BY HPLC SATURATES REMOVAL

Olefin	Vol. % in standard	Vol. % determined by area	Std. Dev.	Vol. % determined by peak ht.
1-Decene	1.0 .5 .25	1.36 .54 .40	0.13 .12 .12	1.4 .6 .5
1-Dodecene	1.0 .5 .25	1.13 .72 ND[a]	0.15 .05 ----	1.3 .8 .5
1-Tetradecene	1.0 .5 .25	0.99 .61 ND[a]	0.28 .19 ----	1.3 .6 .5
1-Hexadecene	1.0 .5 .25	1.24 .57 ND[a]	0.34 .02 ----	1.4 .7 Shoulder
1-Octadecene	1.0 .5 .25	1.06 .86 ND[a]	0.11 .36 ----	1.3 .6 Shoulder
Cyclooctene	1.0 .5 .05	0.93 .39 ND[a]	0.18 .08 ----	1.1 .4 .1

[a]ND indicates not detected by data acquisition system.

TABLE VI. – OLEFIN DETERMINATIONS FOR A SHALE-DERIVED JP-5 EMPLOYING
THE HPLC SATURATES REMOVAL METHOD, IN VOL. %

Fuel sample	HPLC (Saturates Removal)						FIA		
	Equations (8), (9)		Equation (10)		Equation (11)		Result	Std. Dev.	Repeat-ability
	Result	Std. Dev.	Result	Std. Dev.	Result	Std. Dev.			
(1) Shale-Derived JP-5	1.9	0.14	----	----	1.9	0.14	1.4	0.7	0.4
(2) JP-5, Separation 2	1.5	.15	1.5	0.28	1.4	.16	2.6	---	.8
(3) JP-5, Final Separation	10.5	.2	10.1	.5	---	----	---	---	[a]1.1

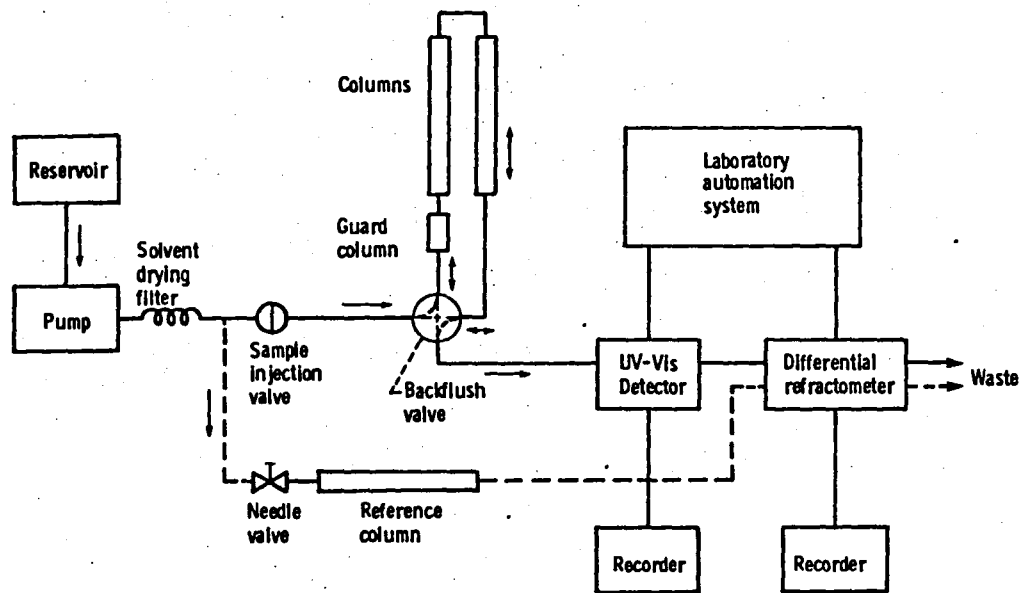[a]Based on HPLC results (10.5%) for the olefin concentration.

Figure 1. - Diagram of High Performance Liquid Chromatographic System.
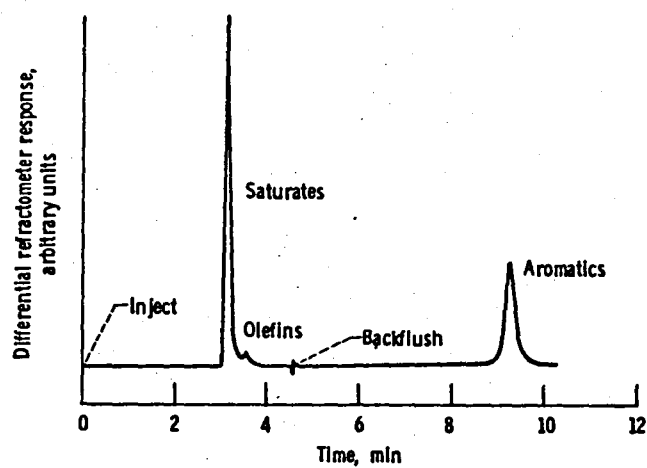

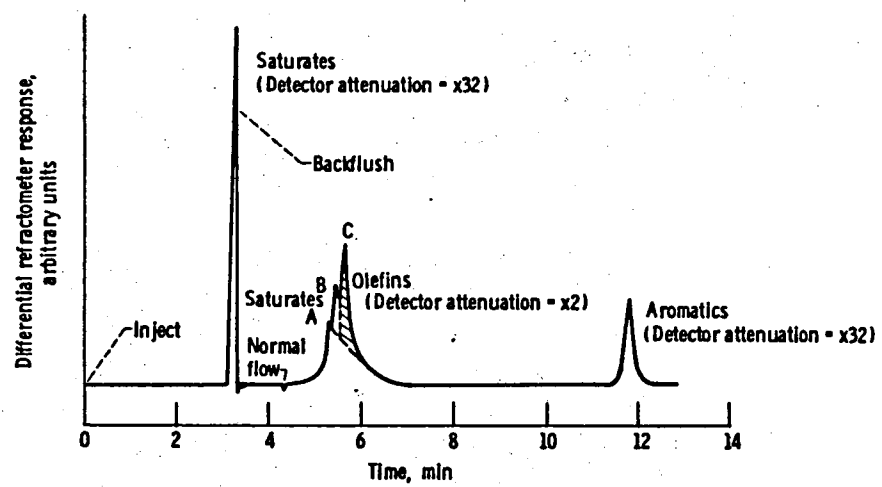Figure 2. - HPLC chromatogram of shale-derived JP-5.

Figure 3. - HPLC chromatogram illustrating olefin determination by Saturates Removal Method.

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15. Supplementary Notes

16. Abstract

Two high performance liquid chromatographic (HPLC) methods have been developed for the determination of saturates, olefins and aromatics in petroleum and shale-derived mid-distillate fuels. In one method the fuel to be analyzed is reacted with sulfuric acid, to remove a substantial portion of the aromatics, which provides a reacted fuel fraction for use in group-type quantitation. The second involves the removal of a substantial portion of the saturates fraction from the HPLC system to permit the determination of olefin concentrations as low as 0.3 volume percent, and to improve the accuracy and precision of olefins determinations. Each method was evaluated using model compound mixtures and real fuel samples.

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