NASA
Technical
Paper
2317

May 1984

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Lewis Research Center
Cleveland, Ohio

National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

Summary

High-performance liquid chromatography (HPLC) appears to be one of the most promising methods for group-type analysis of middistillate fuels. The value of this technique is found in its precision, speed, and range of sample types. However, the accuracy of the method is affected by the suitability of the standards used for calibration. Each group type in a fuel (saturates, aromatics, and olefins) is composed of many compounds. The most accurate results would be obtained when the composition of the corresponding group in the standard and that in the fuel are identical. The multiplicity of fuel sources and refining methods suggests the need for many standards. A simple rapid method that can be used to prepare a standard for each fuel or each fuel type could fill this need.

The present paper is an extension of our initial investigation into the reaction of a fuel with sulfuric acid as a means to prepare a standard for group-type analysis of each fuel. The method involves about a 15-min reaction period, rinsing the fuel with water, and drying it to prepare the standard. This paper presents an in-depth theoretical discussion of the method and an experimental investigation using modern chromatographic instrumentation. Model fuel analyses indicated a maximum standard deviation of about ±0.4 vol% for the aromatics and saturates and an equivalent value for the accuracy. Analysis of commercial fuels revealed a slightly lower overall standard deviation.

Olefin determinations would take another 15 min for those fuels that have been shown to require this analysis. This determination uses the response of the refractive index detector for olefins and for saturates and assumes a value of 1.1 for the ratio of the olefin sensitivity to the saturates sensitivity. Theoretical analyses suggest that the error in the olefin content could be in excess of 10 percent of the olefin result if 1.1 is used for this ratio. Experimental evidence indicates that the use of this ratio led to a relative error of about 5 percent in the olefin results. Olefin concentrations as low as 0.1 percent have been determined by this method.

Experience indicated that the analysis, including standard preparation, could be carried out in about 35 to 40 min. However, this period could be reduced to about 15 min per sample by preparing several of standards simultaneously.

Introduction

Current trends in petroleum technology have led to increased attention to hydrocarbon group-type determinations of jet turbine fuels. The aromatic contents of these fuels appear to be increasing. Inasmuch as the distribution of saturates, olefins, and aromatics affects important fuel characteristics, such as combustion quality, materials compatibility, and fuel stability, the need for accurate results from this type of analysis has become more critical.

This situation has led to investigations into the use of high-performance liquid chromatography (HPLC) (refs. 1 to 6) as a replacement for the fluorescent indicator absorption method (FIA–ASTM D1319) (ref. 7). The HPLC methods have better precision, require less time, and extend over a wider range of fuel types than the FIA method (ref. 3). However, the accuracy of an HPLC method is affected by the standards. The most accurate results are obtained when the composition of the fuel group and its standard are identical. Any differences in the composition can be expected to decrease the accuracy. The composition of the groups can vary from fuel to fuel because of differences in the sources of the crudes and in the refining processes. Several attempts have been made to obtain suitable standards. They include (1) analyzing the composition of each group to prepare a standard and restricting its use to fuels with a specific boiling range (ref. 4), (2) using preparative chromatography on the fuel itself to obtain a standard to do the analyses (ref. 2), and (3) reacting the fuel with sulfuric acid (general method) to produce its standard (ref. 8). Since the last procedure can be completed in about half an hour, a standard can be readily prepared for each fuel.

The present paper describes a continuation of our investigation of the general method using chemically reacted fuels as standards for HPLC fuel analyses (ref. 8). The data reported here were obtained with a more advanced HPLC system than was used in the earlier study. This system includes a computer-controlled chromatograph, a spectrophotometer set to 200 nm, a modern refractive index detector, and two interchangeable column systems. One column system produces a chromatogram using the refractive index detector in about 5 or 6 min. It also uses the spectrophotometer to measure the absorption at 200 nm to identify those fuels that contain measurable amounts of olefins. In this system the saturate and olefin refractive index responses appear as one peak, which is separated from the aromatics peak. The other column system demonstrates sufficient resolution to separate the saturates and olefins. The two systems can be readily interchanged by means of a manual valve.

Standards can be prepared for each fuel by short treatments of portions of the fuel with sulfuric acid. The treatment removes all of the olefins, much of the aromatics, and virtually none of the saturates. This standard is unique in that none of the concentrations of the components are known. In this paper equations are derived that can be used with chromatographic responses to yield concentrations of the saturate and aromatic group-types in a middistillate fuel.

The possible errors that are due to a change in the composition of the aromatics fraction are evaluated, and the problems due to the presence of olefins are considered. The latter problems arise because the olefin response is also due to a mixture with an unknown composition. In the present work the recommendation that 1.1 be used for the ratio of the olefins to the saturates sensitivities in a fuel (Suatoni, et al., refs. 3 and 4) is investigated by some theoretical considerations and experimentally for one fuel. The fundamental equations for olefin determinations are also tested by using model fuels.

Experimental Procedure

Instrumentation

A model 324 gradient liquid chromatograph (Beckman Instruments, Inc.) equipped with a model 421 controller, model 100A pumps, a mixing chamber, an Altex modified Hitachi 100-40 variable wavelength UV/VIS spectrophotometer, and an Altex model 156 refractive index detector was used in this work. This system was modified by the addition of an on-stream solvent drying filter (Alltech Associates) between the mixing chamber and the sample valve. Sample introduction and backflushing were accomplished by air-actuated valves that were operated by the controller. The sample valve was a 1-μl, four-port internal shaft injection valve (AHCFSV-4UHPa-N60, Valco Instruments Co., Inc.) that was equipped with a syringe adapter. The backflush valve was a six-port valve (AHCV-6UHPa-N60, Valco Instruments Co., Inc.). A third valve, which was hand operated, was included in the system to facilitate conversion of the one-column configuration to a three-column configuration and vice versa. The columns were a 10-cm-long by 4.6-mm-inside-diameter 10-μm Porasil (SiO_2) precolumn (Alltech Associates); a 30-cm-long by 3.9-mm-inside-diameter 10-μm Porasil (SiO_2) column (Waters Associates); and a 25-cm-long by 4.5-mm-inside-diameter 10-μm Spherisorb (SiO_2) column (Jones Chromatography, Inc.).

A schematic drawing of the system is presented in figure 1. The solid arcs on the backflush valve indicate the forward flow configuration, and the dashed arcs show the configurations for reverse flow. The solid arcs on the manual valve indicate the flow when all columns are included in the flow path, and the dashed arcs indicate the flow when only the 10-cm column is used.

Procedure for General Group-Type Determinations

Standard preparation. – Approximately 15-ml of the fuel are combined with 75-ml of reagent-grade, concentrated sulfuric acid and stirred vigorously at, room temperature (approx 24° C) using a magnetic stirrer. The reaction period is generally between 6 and 15 min, depending on the type of fuel. About 60 to 80 percent of the aromatics fraction is removed.

The mixture is then transferred to a 125-ml separatory funnel. The acid layer is removed and discarded. The remaining fuel is washed with successive 50-ml portions of deionized water until short-range pH paper indicates that virtually no sulfuric acid is present. In those rare instances when an emulsion is formed, a small amount of reagent-grade sodium chloride can be added to the wash water. However, the final washing is always performed with deionized water. The fuel is dried by passing it through a short column consisting of the barrel of a 5-ml syringe containing about 3-ml of 8-to 12-mesh, 4A molecular sieves. A solvent-resistant syringe filter unit (Millex SR, Millipore Corp.) capable of removing 0.5-μm particles and a 7.6-cm (3-in.) hypodermic needle are attached to this column. Generally, gravity flow produces adequate filtration rates. When increased filtration rates are needed, air pressure can be used. This filter is cleaned by backflushing with hexane and is dried by using a stream of filtered air.

Chromatographic procedure. – During the fuel reaction period, the unreacted fuel can be chromatographed by using the system outlined in figure 1. The 10-cm column and both detectors are used for all fuels and their standards. The spectrophotometer is adjusted to measure absorbance at 200 nm. The eluent is n-hexane flowing at a rate of 1.00 ml/min. Initially, the system is configured as for classical HPLC (i.e., the solid lines through the backflush valve). After the elution of the saturates and olefins (if present), the column is backflushed (2.10 min). As indicated in figure 2, the chromatogram can be completed at about 5.5 min. The sample inlet is cleaned by filling the inlet joint of the syringe adapter with hexane and then allowing it to drain. This is repeated three times. The inlet is dried with a stream of air.

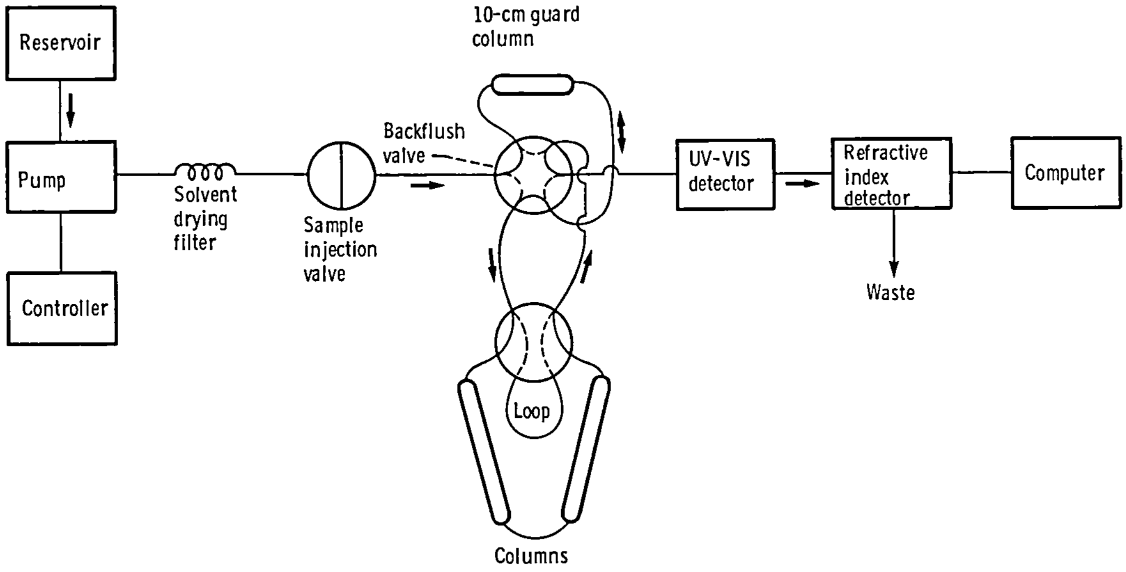

Figure 1. – Diagram of high-performance liquid chromatograph.

In the event that the absorbance at 200 nm indicates the need for olefin determinations, all three columns are used. Backflushing is started at 2.1 min after sample addition. At this time the saturates and olefins have eluted from the 10-cm column into the first of the two longer columns, where no flow reversal occurs. The aromatics remain in the 10-cm column where flow reversal occurs and therefore elute from the column and into the detectors as a single peak. The saturates and olefins continue to flow through the two longer columns and then into the precolumn. They flow through this column in the reverse direction and enter the detector after the aromatics (see fig. 3). This chromatogram requires about 15 min. In general, the resolution is sufficient to enable accurate results for olefins to be calculated by using the refractive index responses.

Saturates removal, or double backflushing (see fig. 4), can be used for some samples with such low olefin concentrations that the slight tailing of the saturates response obscures the olefin response. The saturates response of the unreacted fuel is monitored. When this response has nearly returned to baseline (about 15 to 30 sec after its maximum), the flow is reversed to forward flow in the short column for about 30 sec. This action forces a small portion of saturates and all of the olefins back into the precolumn, while most of the saturates pass to the detectors and out of the system. The spectrophotometer should be monitored at 200 nm to be sure that there is no significant loss of olefins at this point. The flow is again reversed (in the 10-cm column) to elute the remaining saturates and the olefins.

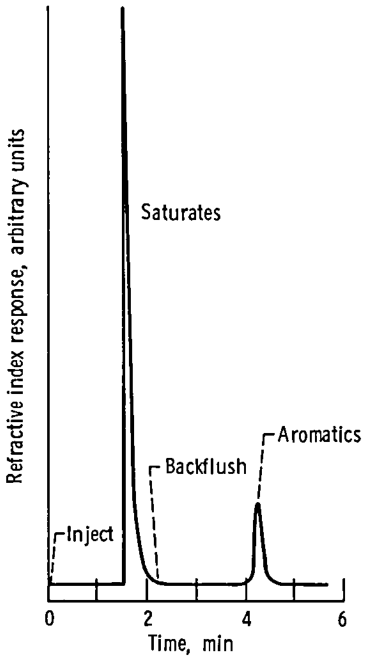

Figure 2. – Typical chromatogram of fuel.

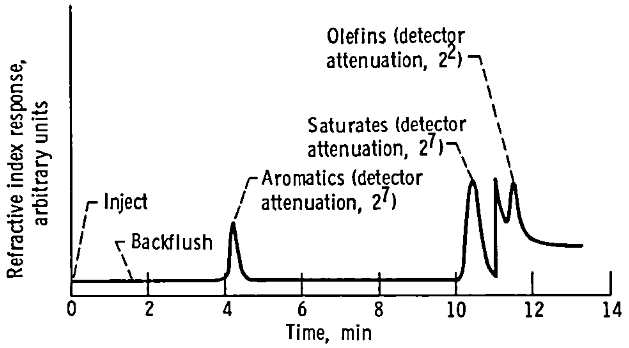

Figure 3. – Typical chromatogram for olefin determination (2 percent $C_{12}H_{24}$).

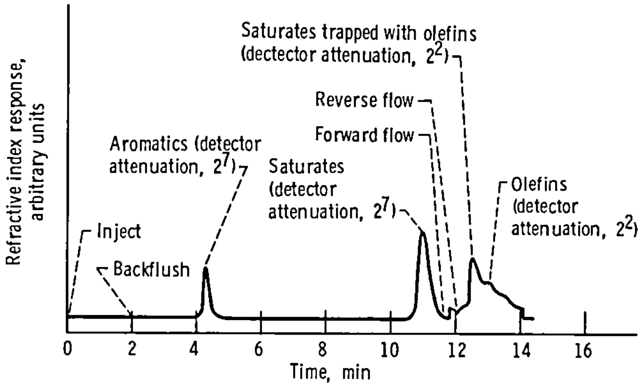

Figure 4. – Typical chromatogram for olefin determinations using double backflush (0.2 percent $C_{12}H_{24}$).

When the timing for flow reversal is optimized, measurable olefin responses can be obtained for fuels with low olefin concentrations. Our experience indicates that optimization is reached when the peak heights for the remaining saturates and the olefins are nearly equal. If the computer does not detect an olefin response, manual measurement of the peak heights yields a fairly accurate estimation of the olefin content.

Preparation of model fuels. – Table I outlines the composition of the saturates and the aromatics mixture used to prepare the three Jet A and the four ERBS model fuels. The ERBS model fuels were prepared to simulate the experimental referee broadened specification fuel, which is a blend of kerosene and gas oil that was produced to serve as a reference fuel for experimental combustor work (ref. 9). The model mixtures were prepared from representative pure compounds. Only traces of olefins were found in these fractions by spectrophotometric detection at 200 nm. One saturates fraction was used to prepare all of the model fuels studied. Iso-octane and cyclo-octane were added to the model fuels to evaluate the method for fuel light-end losses, although they are not normally found in these proportions in middistillate fuels. The aromatics fractions (table I(b)) were varied somewhat in composition to reflect some of the differences between current fuels and the experimental referee broadened specification fuels. Model fuels were prepared by using a standard 50-ml buret to add sufficient quantities of each fraction to achieve the compositions in table II. Extreme care was taken to assure complete drainage of the buret, particularly for the more viscous saturates fractions.

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

To evaluate the method used for olefins determinations, several olefin standards were prepared by using an olefin-free Jet A fuel as the diluent. The olefins used were 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and cyclo-octene. The olefin-free Jet A was prepared by using a scaled-up version of the reaction used for standard preparation. As a result, the aromatics fraction of this base fuel was substantially reduced, and the saturates fraction was proportionately increased. Therefore, it was a more severe matrix for method evaluation of olefin determinations than would be provided by using commercial jet turbine fuels.

A fuel with a relatively high olefin concentration was needed to further evaluate the method. This would permit one to obtain sufficiently accurate olefin results by an indirect method that avoided the use of the sensitivity ratio for olefins and saturates. Frontal chromatography was used to obtain a suitable fuel. Fractions were obtained in which the olefin concentration was much

TABLE I. – COMPOSITION OF FUEL FRACTIONS USED TO PREPARE MODEL FUELS

(a) Saturated hydrocarbon fraction

Compound	Concentration, wt%
Iso-octane	13
Cyclo-octane	23
Decalin	17
Dodecane	47
Olefins (contaminant)	[a]<.04

(b) Aromatic hydrocarbon fraction

Compound	Concentration, wt%			
	Jet A fuels		ERBS fuels	
	1 and 2	3	1 and 2	3 and 4
Tetralin	13.2	43.3	8.0	25.5
1,2,3,4-Tetramethylbenzene	12.0	9.5	7.2	12.4
Xylene	11.6	8.0	7.0	4.5
1,2,4-Trimethylbenzene	12.0	----	7.2	----
n-Butylbenzene	11.6	----	7.0	----
Diethylbenzene	11.8	33.0	14.1	19.2
Naphthalene	2.5	----	6.0	7.3
2-Methylnaphthalene	3.0	----	6.0	8.6
Acenaphthene	2.2	----	5.3	14.9
2,6-Dimethylnaphthalene	2.4	----	6.4	----
2,3-Dimethylnaphthalene	2.9	----	6.1	----
2-Ethylnaphthalene	2.7	----	3.2	----
1-Methylnaphthalene	2.7	6.2	6.5	7.3
Phenanthrene	.1	----	1.2	----
Anthracene	↓	----	1.1	.4
9-Methylanthracene		----	1.1	----
9,10-Dimethylanthracene		----	.4	----
1-Methylphenanthrene		----	.8	----
Olefins (contaminant)	[a]<.04	[a]<.04	[a]<.04	[a]<.04

[a] Result based on no refractive index or UV/VIS (200 nm) response for the olefins.

TABLE II. – GROUP-TYPE DETERMINATION RESULTS FOR MODEL FUEL BLENDS BY HPLC AND FIA

Model fuel	Composition, vol%								
	As prepared			HPLC (general method)			FIA method		
	Saturates	Aromatics	Olefins[a]	Saturates	Aromatics	Olefins	Saturates	Aromatics	Olefins
Jet A, 1	80.1	19.9	<0.04	80.1±0.1	19.9±0.1	0.01	----	----	---
Jet A, 2	80.0	20.0	<.04	79.9±0.2	20.1±0.2	<.01	74.8	21.2	4.1
Jet A, 3	79.7	20.3	-----	79.6±0.3	20.4±0.3	----	----	----	---
ERBS, 1	70.2	29.8	<.04	69.8±0.4	30.2±0.4	----	----	----	---
ERBS, 2	70.0	30.0	<.04	70.4±0.4	29.6±0.4	<.01	69.7	29.7	0.7
ERBS, 3	70.3	29.7	-----	70.4±0.2	29.6±0.2	----	----	----	---
ERBS, 4	70.4	29.6	-----	70.4±0.4	29.6±0.4	----	----	----	---

[a] Results based on no refractive index or UV/VIS (200 nm) response for the olefins.

greater than in the original fuel. Furthermore the compositions of the saturates fraction and the olefin fraction were the same as those in the original fuel sample.

The initial separation was carried out by using a column with a 5-cm inside diameter, packed to a depth of about 36 cm with 450 gm of activated 60- to 200-mesh silica gel. Approximately 700-ml of fuel was fractionated by using gravity flow. Fractions were collected and analyzed by HPLC. Those fractions that contained only saturates having identical integrated responses were combined to serve as a JP-5 fuel saturates standard. Similar representative fractions that contained saturates and olefins were collected and combined.

To obtain fractions with even a larger olefin concentration, fractions that contained as much as 10 percent by volume aromatics were combined and further fractionated. These fractionations were carried out in a column with a 1-cm inside diameter packed to a depth of about 35 cm under slight air pressure (approx 184 N/cm^2 (5 psi)). The aromatics were removed by using activated silica gel in the column. To increase the olefin concentration further, these fractions were then chromatographed through a 1-cm column that contained 25 cm of activated silica gel followed by 10 cm of silica gel, which was impregnated with 20 wt% silver nitrate using the method described in reference 10. Final elution of a large protion of the olefins was accomplished by using 40 ml of pentane under slight pressure. The final fraction of olefins and saturates was obtained by evaporating the pentane in a rotary evaporator in a manner developed through earlier experimentation. These tests had demonstrated that pentane could be removed from the saturates fraction to the extent that there was no significant change in its refractive index detector response. Evaporation was carried out with the rotating bulb placed in an ice bath. The system was kept under a vacuum of 333 N/m^2 (2.5 torr) for about 8 min after reaching this pressure. Measurable changes in sensitivity did occur if this vacuum was maintained for times over 13 min.

Results and Discussion

Preliminary Comments

The standards prepared by the general method are unique in that the concentrations of none of the group types are known. This leads to two types of problem. The units of the concentration results are not immediately apparent, nor is it obvious how the results can be obtained with this type of standard.

To resolve the problem of concentration units, the relationship between the group-type concentrations and the refractive index detector integrated response (hereinafter referred to as the response) was established. For an ideal solution the refractive index is a linear function of the volume fractions of its components (ref. 11). With the detector used in this study, a linear relationship was found to exist between the response and the volume fraction of any component; the use of weight fractions produced a nonlinear relationship. Therefore, all results are reported as volume fractions.

Algebraic manipulation of several equations can produce the final equations needed to obtain results when the specimen is compared with a standard in which none of the concentrations are known. Some of these equations describe the composition of the fuel end; others, the relationship between the response and the concentration of a fuel fraction. Detailed derivations of the equations to do this are presented in the appendix. In this section only the equations used to obtain the results from the raw data and an assumption required to derive two of these equations will be presented. The following equation can be written for a fuel that contains only saturated hydrocarbons, olefins, and aromatics:

$$1 = F_s + F_o + F_a \qquad (1)$$

where F_s, F_o, and F_a are the volume fractions of saturates, olefins, and aromatics, respectively. After sulfuric acid treatment of the fuel, all of the olefins, most of the aromatics, and none of the saturates have been removed; hence

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

where these subscripts refer to the saturates and the aromatics in the fuel after reaction with sulfuric acid. It is convenient to define F_m by the following equation for the chromatograms in which olefins and saturates elute as one peak:

$$F_m = F_s + F_o \tag{3}$$

The relationship between the responses R of the refractive index detector for any component x and the concentration of that component is

$$R_x = k_x F_x \tag{4}$$

where x indicates any one of the groups denoted by the subscripts used in equations (1) to (3) and where k_x is the sensitivity of that group. Using this relationship, the following equations can be written

$$\frac{R_s}{R_{sr}} = \frac{k_s}{k_{sr}} \frac{F_s}{F_{sr}} \tag{5}$$

and

$$\frac{R_a}{R_{ar}} = \frac{k_a}{k_{ar}} \frac{F_a}{F_{ar}} \tag{6}$$

Inasmuch as no change in the saturates composition occurs, $k_s = k_{sr}$, and equation (5) becomes

$$\frac{R_s}{R_{sr}} = \frac{F_s}{F_{sr}} \tag{7}$$

If we assume that $k_a = k_{ar}$, equation (6) becomes

$$\frac{R_a}{R_{ar}} = \frac{F_a}{F_{ar}} \tag{8}$$

An equation that can be derived for an olefin-free fuel using equations (1), (2), (7), and (8) is

$$F_s = \frac{1 - \dfrac{R_{ar}}{R_a}}{\dfrac{R_{sr}}{R_s} - \dfrac{R_{ar}}{R_a}} \tag{9}$$

If the fuel contains olefins that elute with the saturates, the equation is

$$F_m = F_s + F_o = \frac{1 - \dfrac{R_{ar}}{R_a}}{\dfrac{k_m}{k_s} \dfrac{R_{sr}}{R_m} - \dfrac{R_{ar}}{R_a}} \tag{10}$$

If the olefin peak is then separated from the saturates peak, one finds

$$\frac{k_m}{k_s} = 1 + \frac{0.1\, R_o}{1.1\, R_s + R_o} \tag{11}$$

and

$$F_o = \frac{R_o}{1.1\, R_s + R_o} F_m \tag{12}$$

It should be noted that all the responses in equations (9) and (10) are obtained by using the shortest column system and those in (11) and (12) are obtained by using the longest column system. The coefficient 1.1, which appears in the last two equations, is the value for k_o/k_s that Suatoni, et al., (refs. 3 and 4) has used for the determination of olefins in fuels.

Evaluation of k_o/k_s

The accuracy of olefin determinations obtained using the equations (10) to (12) is directly proportional to the accuracy of the value used for k_o/k_s. Suatoni, et al., recommended that the value 1.1 be used for this ratio when determining olefins in gasoline range fuels (ref. 3) and for petroleum fractions in the 190° to 360° C boiling range (ref. 4). This recommendation is based on their observations that the ratio of refractive index differences (i.e., differences between refractive indices of the olefins and the solvent divided by the differences between the refractive indices of saturates corresponding structure and the solvent) was determined to be 1.1 for these fuels. They also confirmed this value for a furnace oil using standards obtained by preparative chromatography. We felt that additional information was required to fully determine the reliability of the value 1.1 for routine use.

Similar work was carried out in this laboratory to provide the needed information. The experimental work will be considered in a later section. The theoretical treatment is based on several considerations. One is the fact that the sensitivity of a substance k_x with a refractive index detector is equal to a proportionality constant times the differential refractive index (the difference between the refractive indices of the substance and eluent). The second is the assumption that the proportionality constant for this relationship is the same for both the olefins and the saturates. The third is the assumption that the compositions of the saturates fraction and the olefin fraction are the same with respect to the carbon structure. These fractions differ only in that double bonds are present in the olefin molecules and in the concentration of each fraction in the fuel. These considerations enable the theoretical evaluation of k_o/k_s based on literature values of the refractive indices of the hydrocarbons.

Forty-one pairs of olefins and saturates with the same carbon structure that have values for their refractive indices were found for molecules with 10 to 18 carbon atoms (ref. 12, Vol. V). Values of k_o/k_s for each such pair were calculated by using these refractive indices and that of the eluent (hexane). The values ranged from 1.05 to 2.04. Most were in the 1.1 range. Thus an average of the ratios is required to obtain a meaningful theoretical value of k_o/k_s for fuel. Simple averaging of the ratios resulted in a value of 1.12. Weighting the individual k_o/k_s values to better reflect the composition of the particular middistillate fuels studied yielded results that varied between 1.20 and 1.26, depending on the weighting factors selected. These differences indicate that errors in the olefin results due to the use of average k_o/k_s values could be relatively high. It should also be noted that the 41 olefin/saturate pairs employed in this study are only a small portion of the number of these types of compound that could be present in fuels. Hence, experimental studies should be made for those fuels where accuracy better than ±10 percent of the olefin concentration is desired.

Error due to Assuming $k_a = k_{ar}$

Although the assumption that $k_a = k_{ar}$ is probably not strictly true, several factors keep within acceptable limits the error in the final result caused by its use. The first is due to the nature of equations (9) and (10), where R_{ar}/R_a is the second term of both the numerator and the denominator and R_{sr}/R_s is the first term of the denominator only. This means that any deviation in the function of R_{ar}/R_a, such as including $k_a/k_{ar} \neq 1$ would cause a smaller difference in the value of F_s (or F_m) than would an equivalent change in the function of R_{sr}/R_r (or R_{sr}/R_m). Hence, the error introduced by erroneously assuming that $k_m/k_s = 1$ can be greater than that due to the same assumption for k_a/k_{ar}, even if both ratios have the same value. Mathematical analysis indicates that the error in F_s is less than one-tenth of the amount that the ratio k_a/k_{ar} differs from unity for a fuel that is 30 percent aromatics (when the procedure has removed 70 percent of this group). The error would be less for fuels that contain less aromatics or if a greater portion of aromatics were to be removed by the treatment.

There are other factors that help to minimize the error in the final result and influence the value of k_a/k_{ar}. One is the limit in the maximum difference in the refractive indices observed for compounds in an aromatic class. For instance, an examination of the refractive indices listed for a large number of alkyl substituted benzenes (ref. 10, Vol. III) revealed the greatest difference to be about 2 percent. However, it should be stressed that the refractive index detector responds proportionally to the difference in refractive indices of the substance detected and the eluent. This means that for the aromatics fraction of the fuel before and after reaction, the difference in response would be larger than the difference in their refractive indices. The presence of more than one aromatics class could cause even larger differences. The change in sensitivity of the aromatics fraction due to reaction with sulfuric acid also depends on the relative rates of reaction of the various compounds in the aromatics fraction. However, sulfonation mechanism information combined with the few rate measurements available suggests that the rate differences are not large for the components of the aromatics fraction. More rate measurements would be of value. However, experimental confirmation has been obtained that the deviation of k_{ar}/k_a causes only small, acceptable errors for the types of fuel that were analyzed. Data that are used to evaluate the error due to changes in aromatic sensitivity will be considered later.

Validity of the Assertion that $k_s = k_{sr}$

The assertion that $k_s = k_{sr}$ requires some discussion because of evidence that saturated hydrocarbons can react with concentrated sulfuric acid at room temperature (ref. 13). Our chromatograms revealed no measurable change in the response of the alkane fraction of a JP-5 fuel even after room temperature sulfuric acid reaction for more than an hour. Inasmuch as no treatment lasted as long as 30 min, the assertion that $k_s = k_{sr}$ should be valid for the analyses reported herein.

Results Obtained by General Method

Table II presents results obtained by the general method (eq. (9)) for three model Jet A type fuels and for four model ERBS type fuels. The values presented for the general method are the average of at least five determinations. The standard deviations are also included. The FIA results are presented for comparison. Although the small quantities of olefins listed were observed in the model fuels by using the UV detector at 200 nm, none were found to exceed 0.04 vol%.

Generally, the results appear to lend support to the original assumption that k_a and k_{ar} are approximately equivalent, as well as to support the overall technique. An evaluation of the accuracy indicates that the largest absolute error in the model fuel results occurred in ERBS fuel 2 at a level of 0.4 percent, for a relative error in the aromatics fraction of 1.3 percent and in the saturates fraction of 0.6 percent.

In general, the results agreed quite well with the as-prepared values. However, standard deviation values indicate that such good agreement could be fortuitous. The FIA results show high values for olefins. If these are combined with the saturates results, the FIA results agree with the as-prepared values within the acceptable repeatability of 1.0 to 1.1 for the ASTM D1319 FIA method (ref. 7).

Table III presents group type results obtained by three methods: the general method, the FIA method (ref. 7), and other methods (infrared (ref. 14) and general methods). Also included are data obtained in an earlier investigation of the general method (ref. 8). The types of fuel include Jet A, diesel, ERBS, ERBS blends, ERBS blending stock, two shale-derived fuels, and a coal-derived fuel. The results of the FIA agree within 3 percent with those obtained by the general method in all cases. The infrared spectroscopy results were within 1 percent of the HPLC results except for two of the ERBS type fuels. All were within the reproducibility of the ASTM FIA method for these fuels (ref. 7). The average standard deviation of all the commercial fuels is ±0.2 vol%. The anomalous value obtained for the shale-derived JP-5 (±0.7 vol%) cannot be explained. The standard deviation results (ref. 8) for this fuel (±0.5 vol%) did not differ from those found for the model fuels used in this earlier work. Excluding the JP-5 result yielded a maximum standard deviation of ±0.3 percent.

Some fuels were analyzed earlier by the general method (ref. 8). These values agreed with those obtained in the present work within 1 percent except for one fuel (Jet A-2). The difference was 1.3 percent. The reason for this slightly greater difference is not known. The lower olefin value of the JP-5 shale-derived fuel could be due to a decrease in olefin content that occurred when the fuel was aged a year.

Two types of repeatability studies of the method used for a Jet A fuel are given in tables IV and V. Table IV reveals the effect of minor variations in the sulfuric acid reaction that occur when the amounts of reactants and reaction periods are merely approximated and when the control of the stirring rates and the temperature is minimal. The extent of the reaction is approximated by the ratio R_{ar}/R_a. This ratio is given because it appears to be a function of temperature, stirring rates, and reaction time. The aromatics concentrations presented in this table are the averages of all the results obtained for the indicated treatment. It should be noted that the maximum difference in these values is less than 0.4 percent.

Table V shows that the results obtained over a 21-day period did not differ significantly. This is demonstrated by each of the three ways of handling the data. The first

TABLE III. - GROUP-TYPE RESULTS FOR COMMERCIAL FUELS

Fuel	Composition, vol%									
	General method (HPLC)			FIA method			Other methods			
	Saturates	Aromatics	Olefins	Saturates	Aromatics	Olefins	Saturates	Aromatics	Olefins	Footnote
Jet A, 1	84.6±0.3	15.4±0.3	0.1	84.1	15.4	0.5	84.5	15.5±0.2	<0.3	(b)
Jet A, 2	82.9±0.2	16.9±0.2	.1	82.3	17.2	.5	82.6	17.4±0.3	<.3	(b)
Diesel cracked	60.7±0.2	39.3±0.2	.14	58.0	41.0	.9	60.2	39.0	.8	(a)
Diesel premier	82.0±0.1	18.0±0.1	.1	82.1	16.9	.6	----	--------	----	---
ERBS-1	71.6±0.2	28.4±0.2	----	70.7	28.8	.5	72.5	27.1	.4	(a)
							71.3	28.7±0.3	<.3	(b)
ERBS-2	73.4±0.2	26.5±0.2	.1	71.9	27.6	.5	72.7	27.3±0.1	<.3	(a)
ERBS-3B	73.7±0.2	26.3±0.2	<.1	70.3	28.9	.8	73.2	26.3	.4	(a)
							73.7	26.3	<.3	(b)
ERBS-3B-11.8	52.2±0.1	47.8±0.1	.1	49.5	49.9	.6	59.6	39.9	.5	(a)
							52.6	47.4	<.3	(b)
ERBS-3B-12.3	62.2±0.2	37.8±0.2	.1	59.4	39.9	.7	67.0	35.5	.5	(a)
							62.3	37.7	<.3	(b)
ERBS-blend stock	20.8±0.1	79.2±0.1	.1	15.9	83.3	.8				
ERBS-cut, shale (250° - 650°)	85.3±0.3	14.7±0.3	<.1	85.1	14.6	.6	84.6	14.2	1.2	(a)
JP-5, shale	77.8±0.7	21.5±0.7	.7	76.5	22.2	1.3	77.9	20.2	1.9	(b)
				79.6	19.2	1.2				
Coal derived distillate (250° - 550°F)	70.8±0.3	29.2±0.3	.1	71.2	28.2	.5	65.8	29.6	4.6	(a)

[a] Infrared spectroscopy from ref. 14.

[b] Data obtained from ref. 8

TABLE IV. - EFFECT OF SMALL VARIATIONS IN REACTION CONDITIONS ON AROMATICS RESULT

Treatment	R_{ar}/R_a	Aromatics concentration, vol%
A	0.484	17.07 ±0.34
B	.478	16.98 ±0.39
C	.313	16.99 ±0.35
D	.316	16.92 ±0.16
E	.590	16.90 ±0.30
F	.320	16.70 ±0.31

TABLE V. - REPEATABILITY OF THE GENERAL METHOD

Day	Treatment	Calculated concentration of aromatics, vol%			
		Using 1st and 3rd chromatogram	Using 2nd and 4th chromatogram	Average of all data	Number of results averaged
1	D	17.2	16.9	17.1 ±0.2	5
2	D	16.9	17.2	17.1 ±0.1	5
3	D	17.2	16.9	17.0	2
6	D	17.1	16.7	16.9	↓
8	D	17.0	17.1	17.1	
8	E	17.0	16.6	17.1	
8	F	16.9	16.7	16.8	
9	E	16.4	17.0	17.0	
9	D	17.0	17.0	17.0	
10	A	16.8	17.1	16.8	
10	D	16.7	17.0	16.8	
10	D	17.1	16.7	16.9	
13	D	16.8	17.0	16.9	
14	D	16.6	17.0	16.8	
16	E	16.8	16.3	16.6	
21	C	16.6	17.1	16.8	
21	C	16.9	17.4	17.1	
22	B	17.1	16.9	17.0 ±0.3	5
Average		16.9 ±0.2	16.9 ±0.3	16.9 ±0.15	

result column represents data obtained from samples chromatographed immediately after the inlet was cleaned and dried. The second represents only those samples that were chromatographed after a similar sample had been chromatographed. The general agreement here demonstrates that the cleaning and drying technique described earlier was quite adequate for this work. In the next column the average value of all the data obtained on the indicated day is presented. The agreement in the data (maximum difference, 1.1 percent) and the standard deviations (maximum, 0.3 percent) indicate the suitability of this method for routine analysis.

Olefin Analysis

Tables VI to IX provide information for evaluating the olefin results. The data in table VI can be used to evaluate the usefulness of the relationship based on equation (4)

$$\frac{R_o}{R_s} = \frac{k_o}{k_s}\frac{F_o}{F_s} \tag{13}$$

The values of R_o+R_s can be obtained from the chromatogram; F_s can be obtained by determining F_s in the olefin-free fuel by the general method and correcting for the dilution due to the addition of the olefin. The value of k_o/k_s is different for each olefin. Those presented in this table can be obtained by using the equation

$$\frac{k_o}{k_s} = \frac{n_o-n_e}{n_s-n_e} \tag{14}$$

where n_o, n_e, and n_s are the refractive indices of the olefin, the eluent (hexane), and the saturates fraction, respectively. Only n_s cannot be obtained from the literature; it was estimated by using the following relationships for both the sulfuric-acid-treated and untreated Jet A fuel and measuring the refractive indices of these portions of the fuel:

$$n_f = n_s f_s + n_a f_a \tag{15}$$

Equation (15) can be derived from one given by Partington (ref. 11) if the fuel is assumed to be an ideal solution. Two equations with two unknowns can be obtained if the assumption is made that the treatment did not alter the refractive index of either the saturates or the aromatics fraction to any great extent. It should be noted that relatively large changes in the aromatics fraction can be tolerated without significantly affecting the results.

The data presented in table VI were calculated by using equation (13), and the value of k_o/k_s was obtained for each olefin by the method described above. The olefin values are the average of at least five results except where noted. In these cases the number in parentheses following an olefin concentration indicates the number of results

TABLE VI. – OLEFIN RESULTS OBTAINED WITH MODEL FUELS

Olefin	Time between appearance of saturates and of olefin, Δt, min	Sensitivity ratio, k_o/k_s	Olefin added, vol%	Olefin found, vol% (a), (b), (c)			
				After single backflush		After double backflush (saturates removal)	
				Area response	Peak height measurement	Area response	Peak height measurement
1-Dodecene	1.13	1.005	1.98	1.81 ±0.15	1.84 ±0.2	------------------	----------
			.99	1.00 ±0.10	1.90 ±0.1	------------------	----------
			.40	.37 ±0.02	.41 ±0.1	------------------	----------
			.20	.14(2), SNC(3)	.18 ±0.03	0.18 ±0.05	0.16 ±0.03
			.10	(3)	----------	SNC	.08 ±0.02
1-Tetradecene	1.05	1.089	1.97	2.18 ±0.04	2.13 ±0.11	------------------	----------
			.98	1.01 ±0.01	1.02 ±0.02	------------------	----------
			.39	.31 ±0.03	.36 ±0.02	0.34 ±0.01	0.37 ±0.01
			.20	.05(1), SNC(4)	.13 ±0.03	.22(1), PNC(4)	.19 ±0.03
			.10	------------	SNC	SNC(5)	.10 ±0.01
1-Hexadecene	1.00	1.170	1.97	2.13 ±0.03	2.17 ±0.05(3)	------------------	----------
			.99	.93 ±0.02	.96 ±0.02	------------------	----------
			.39	.27 ±0.02	.32 ±0.03	0.31 ±0.04	0.38 ±0.02
			.20	SNC	.13 ±0.03	PNC	.15 ±0.05
			.10	------------	----------	SNC	.07 ±0.02
1-Octadecene	0.95	1.241	1.96	2.00 ±0.05	2.06 ±0.03(4)	------------------	----------
			.98	.89 ±0.07	.91 ±0.03	------------------	----------
			.39	PNC	.25 ±0.05	0.25 ±0.01(4), SNC(1)	0.34 ±0.01
			.20	SNC	SNC	SNC	.14 ±0.02
			.10	------------	----------	SNC	SNC
Cyclo-octene	1.80	1.721	2.0	2.31 ±0.02	2.36 ±0.03	------------------	----------
			1.0	1.18 ±0.07	1.20 ±0.01	------------------	----------
			.4	.44 ±0.02	.46 ±0.01	------------------	----------
			.2	.21 ±0.01	.21 ±0.01	------------------	----------
			.1	.10 ±0.01	.10 ±0.01	------------------	----------
			.05	.04 ±0.01	0.5 ±0.01	------------------	----------

[a] Number of values (if less than 5) used to produce the reported result are in parentheses following the result.
[b] SNC shoulder not counted or measured.
[c] PNC peak not counted or measured.

used to obtain the average. Two types of chromatographic methods were used: the single backflush and the double backflush (saturates removal) methods. Two types of raw data were obtained: the computer-integrated area measurement and the manual peak height measurement. A typical value for the time Δt between the maximum for the saturates peak and that for the olefin peak is given for each olefin.

As expected these data clearly show that the resolution of these two peaks affects the limit of detection for olefins. As the resolution increases, the concentration of olefin that can be detected decreases. Furthermore, double backflushing (saturates removal), which decreases the amount of saturates eluting just before the olefins, also improves the accuracy of the results obtained for low olefin concentrations. Manually measured peak height responses were used to calculate olefin concentrations for fuels with low olefin contents. In this way results were obtained for olefins where their response was apparent on the chromatogram but was not counted (integrated) by the computer. Cyclo-octene concentrations as low as 0.05 ±0.01 percent were measured without backflushing. On the other hand, results were obtained for octadecene at 0.2 percent only with double backflushing and manual measurement of the peak heights. The detection limits for the other olefins were between these extremes. The errors obtained by using equations (13) and (14) were much less than the 0.3 percent spread in results and allowed for the repeatability of olefins in this range by the FIA (ASTM D1319) method (ref. 7).

Table VII presents the olefin responses for spectrophotometric detection at 200 nm after passing through the 10-cm column. The saturates did not absorb at this wavelength. The last column is a list of the estimated

TABLE VII. – OLEFIN RESPONSE AT 200 nm USING THE 10-cm COLUMN

Olefin	Olefin content, vol%	Response at maximum absorbance	Estimated response at 0.1 vol%
1-Dodecene	0.25	0.040	0.016
1-Tetradecene	.25	.037	.015
1-Hexadecene	.50	.059	.012
1-Octadecene	.20	.033	.017
Cyclo-octene	.10	.14	.140

TABLE VIII. – OLEFIN RESULTS OBTAINED BY SEVERAL INDEPENDENT METHODS FOR SHALE-DERIVED JP-5 FUEL AND ITS FRACTIONS

Fuel	Olefin concentration, Co, vol%		
	Recommended method, $\frac{R_o}{1.1\,R_s+R_o}F_m\,100$	Indirect method, $100-\left[\frac{R_s}{(R_s)_{100}}\right]100$	Direct method, $\frac{R_o}{(R_o)_{16.7}}16.7$
JP-5	0.66 ± 0.03	[a]0.66 ± 0.01	0.63 ± 0.03
Fraction 1	[b]6.57 ± 0.04	6.32 ± 0.3	6.45 ± 0.2
Fraction 2	[b]8.52 ± 0.06	8.45 ± 0.6	8.15 ± 0.05
Fraction 3	[b]17.36 ± 0.17	16.7 ± 0.6	---------

[a] This sample also contained aromatics. Both the aromatics concentration and the saturates concentration were subtracted to yield this value.

[b] The aromatic content was extremely low in these samples; so $F_m = 1$ was used for the calculation of these concentrations.

TABLE IX. – OLEFIN CONCENTRATIONS IN DILUTED PORTIONS OF A SHALE-DERIVED JP-5 FUEL

Dilution ratio of JP-5 fuel[a]	Concentration from dilution, percent	Calculated olefin concentration, vol%			
		After single backflush		After double backflush	
		Using computer response	Using manual measurement	Using computer response	Using manual measurement
1/4	0.16	0.17, 0.14	---------	0.14, 0.15	---------
1/8	.08	.07, 0.04	0.11, 0.11	.08, 0.04	0.11, 0.11
1/16	.04	.003, SNC[b]	.07, 0.03	SNC, SNC	.07, 0.07

[a] Original olefin concentration is 0.66 percent. See table VIII.

[b] Shoulder not counted.

responses for fuels containing 0.1 percent of the indicated olefins. The variation in these values indicates that spectrophotometric detection at 200 nm would not be suitable for the determination of olefins in fuels. However, this information is useful in selecting those fuels that should have more accurate and time-consuming olefin determinations.

Table VIII presents results for the olefin concentration of a shale-derived JP-5 fuel and several fractions of it. The results were obtained by three methods of quantitation. The olefin content of the selected fractions had been increased by frontal chromatography. The results obtained by the recommended method using equation (12) are shown in the first column. They are virtually equivalent to those calculated by using the equation

$$F_o = \frac{R_o}{1.1\,R_s} F_s \tag{16}$$

This equation was not used because iteration was often required to obtain results for $F_o + F_s$ without error due to the mode of calculation.

The indirect method involved the use of equation (1) and the determination of F_s and F_a by other means. The method relied on the use of fractions of the fuel containing only saturates, as well as fractions with saturates and olefins, which were produced through frontal chromatography. The value of F_a was zero for these fractions, and F_s was determined by using the pure saturates as a standard. The value of F_a for the untreated JP-5 fuel was obtained from table III. Thus, the values for the olefin concentrations could be obtained by the indirect method using no olefin sensitivity value.

The olefin results for the direct method were obtained by using the following relationship:

$$C_o = 100\,F_o = \frac{R_o}{(R_o)_{16.7}} 16.7 \tag{17}$$

The value, 16.7, was obtained by the indirect method for the fraction with the largest olefin content. The 1.1 response factor was not used to obtain the fraction 3 result. Hence, the data of the direct method results can be used to test the olefin to a saturate sensitivity ratio of 1.1, which was assumed for this fuel.

The relative difference in the average values obtained for each fuel by each of the methods was less than 5 percent of the olefin content. Hence, the use of the response factor value of 1.1 appeared to cause less than a 5 percent relative error in the olefin results for this fuel.

Table IX presents results for the olefin concentrations in diluted portions of a shale-derived JP-5 fuel that originally contained 0.66 percent olefins. This fuel was diluted with its saturates fraction. The techniques used are single backflush and double backflush (saturates removal) with the responses measured both by area and by peak height. At 0.16 and 0.08 percent olefins, the results were reasonably accurate for both single and double backflush. At 0.04 percent olefins, only one response in four could be measured by the computer. Peak height measurements generally yielded results that were erroneously high.

Concluding Remarks

This study revealed the increased versatility of HPLC group-type analyses by providing a simple, rapid method for obtaining good petroleum and nonpetroleum middistillate standards. A standard for each fuel is made from the fuel itself. Hence, no decrease in accuracy due to the variations in composition of the groups would occur when different fuels are analyzed. The standards are unique in that the concentration of none of the groups types is known. Equations were developed that yield group-type results when these standards are used. Sources of error were evaluated both theoretically and experimentally.

This study also showed that automation of valves, a modern refractive index detector, accurate flow controllers, and a 10-cm column packed with 10-mm Porasil can yield results with a 0.4 vol% accuracy for group-type analyses of middistillates. The maximum standard deviation in the results of the saturates or aromatics was about ±0.4 vol% for both model and commercial fuels. For one fuel analyzed over a 21-day period, the range of results was 1.1 vol%. These data compare favorably with the deviation permitted in ASTM D1319 (ref. 7) and with the results reported in our previous investigation (ref. 8). Furthermore, a chromatogram can be obtained in about 5.5 min with the 10-cm column. The column system is such that two columns (25 and 30 cm) can be added by merely turning a valve. In this configuration, determinations can be made for olefin contents as low as 0.1 percent.

Analyses for saturates and aromatics involving preparation of the standards would require about 30 to 40 min, which is considerably less time than is required for the overall FIA method. Inasmuch as most of the analysis time is due to standard preparation, the time could be reduced by treating a number of fuels concurrently. Thus, the time required for an analysis could approach the time needed to obtain two chromatograms, one for the unreacted and one for the reacted fuel (about 10 to 12 min), since little preparation and cleanup time is needed.

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio, September 23, 1983

Appendix – Derivation of the Relationships Between Concentrations and Chromatographic Responses

For a fuel that contains saturated hydrocarbons, olefins, and aromatics, the following equation is valid:

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

where F_s, F_o, and F_a are the volume fractions of saturates, olefins, and aromatics, respectively. If the fuel has been treated with sulfuric acid to remove all of the olefins and most of the aromatics, the following equation is valid:

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

where F_{sr} and F_{ar} are the volume fractions of saturates and aromatics in the fuel after reaction with sulfuric acid.

The response of the refractive index detector for each of the fuel components R_x is given by the general equation

$$R_x = k_x F_x \tag{4}$$

where the subscript x can be any of the five subscripts in equations (1) and (2) and k is the response factor (or sensitivity). The following useful relationships can be obtained by division of selected forms of equation (4):

$$\frac{F_{sr}}{F_s} = \frac{k_s}{k_{sr}} \frac{R_{sr}}{R_s} \tag{5a}$$

$$\frac{F_{ar}}{F_a} = \frac{k_a}{k_{ar}} \frac{R_{ar}}{R_a} \tag{6a}$$

$$\frac{F_o}{F_s} = \frac{k_s}{k_o} \frac{R_o}{R_s} \tag{9a}$$

If equations (5a) and (6a) are substituted in equation (2), one finds

$$1 = \frac{k_s}{k_{sr}} \frac{R_{sr}}{R_s} F_s + \frac{k_a}{k_{ar}} \frac{R_{ar}}{R_a} F_a \tag{A1}$$

Upon substituting equation (1) into equation (A1), one finds

$$1 = \frac{k_s}{k_{sr}} \frac{R_{sr}}{R_s} F_s + \frac{k_a}{k_{ar}} \frac{R_{ar}}{R_a} (1 - F_s - F_o) \tag{A2}$$

$$1 - (1 - F_o) \frac{k_a}{k_{ar}} \frac{R_{ar}}{R_a} = \left[\left(\frac{k_s}{k_{sr}} \frac{R_{sr}}{R_s} \right) - \left(\frac{k_a}{k_{ar}} \frac{R_{ar}}{R_a} \right) \right] F_s \tag{A3}$$

$$F_s = \frac{1 - (1 - F_o) \dfrac{k_a}{k_{ar}} \dfrac{R_{ar}}{R_a}}{\left(\dfrac{k_s}{k_{sr}} \dfrac{R_{sr}}{R_s} \right) - \left(\dfrac{k_a}{k_{ar}} \dfrac{R_{ar}}{R_a} \right)} \tag{A4}$$

This equation is readily simplified. No saturates are removed by the treatment; hence, $k_s = k_{sr}$. Moreover, the assumption that $k_{ar} = k_a$ is made because, for many fuels, it causes only little or no error in F_s. This assumption is discussed in the body of the paper. Hence,

$$F_s = \frac{1 - (1 - F_o) \dfrac{R_{ar}}{R_a}}{\dfrac{R_{sr}}{R_s} - \dfrac{R_{ar}}{R_a}} \tag{A5}$$

For those fuels that contain virtually no olefins, the relationship becomes

$$F_s = \frac{1 - \dfrac{R_{ar}}{R_a}}{\dfrac{R_{sr}}{R_s} - \dfrac{R_{ar}}{R_a}} \tag{5}$$

In the event the fuel does contain olefins and the olefins and saturates responses are combined in the same response, the relationship is found by similar reasoning to be

$$F_m = \frac{1 - \dfrac{R_{ar}}{R_a}}{\dfrac{k_m}{k_s} \dfrac{R_{sr}}{R_m} - \dfrac{R_{ar}}{R_a}} \tag{10a}$$

where F_m, R_m, and k_m refer to the volume fraction, the response, and the sensitivity of the olefin/saturates mixture. To use this equation, the responses can be obtained from chromatograms obtained for the fuel before and after sulfuric acid treatment, but k_m/k_s must be evaluated by using a chromatogram in which responses for saturates and olefins are obtained.

The following identities are used in the derivation of the required equality:

$$F_m = F_s + F_o \tag{3}$$

$$R_m = R_s + R_o \tag{A6}$$

From equations (4) and (3) it is evident that

$$R_m = k_m F_m = k_m (F_s + F_o) \tag{A7}$$

From equation (A6)

$$R_m = R_s + R_o = k_s F_s + k_o F_o \tag{A8}$$

Equating (A7) and (A8) yields

$$F_s + F_o = \frac{k_s}{k_m} F_s + \frac{k_o}{k_m} F_o = \frac{k_s}{k_m} F_s + \frac{k_s}{k_m} \frac{k_o}{k_s} F_o \tag{A9}$$

Substituting the observation that $k_o/k_s = 1.1$ (Suatoni, et al., refs. 3 and 4) in this equation and rearranging yield

$$F_m = \frac{k_s}{k_m} (F_s + 1.1\,F_o) \tag{A10}$$

and

$$\frac{k_m}{k_s} = \frac{F_s + F_o + 0.1\,F_o}{F_m} = 1 + 0.1\,\frac{F_o}{F_m} \tag{A11}$$

From equation (4), it is evident that

$$\begin{aligned} F_o &= \frac{k_m}{k_o} \frac{R_o}{R_m} F_m = \frac{k_m}{k_s} \frac{k_s}{k_o} \frac{R_o}{R_m} F_m \\ &= \left(1 + 0.1\,\frac{F_o}{F_m}\right) \left(\frac{R_o}{1.1\,R_m} F_m\right) \\ &= \frac{R_o}{1.1\,R_m} F_m + \frac{0.1\,F_o R_o}{1.1\,R_m} \end{aligned} \tag{A12}$$

Rearranging results in

$$\begin{aligned} \frac{R_o}{1.1\,R_m} F_m &= \left(1 - \frac{0.1\,R_o}{1.1\,R_m}\right) F_o \\ &= \left(\frac{1.1\,R_s + 1.1\,R_o - 0.1\,R}{1.1\,R_m}\right) F_o \\ &= \left(\frac{1.1\,R_s + R_o}{1.1\,R_m}\right) F_o \end{aligned} \tag{A13}$$

$$F_o = \left(\frac{1.1\,R_m}{1.1\,R_s + R_o}\right) \left(\frac{R_o}{1.1\,R_m}\right) F_m = \left(\frac{R_o}{1.1\,R_s + R_o}\right) F_m \tag{A14}$$

Substituting equation (A14) into (A11) yields

$$\frac{k_m}{k_s} = 1 + 0.1 \left(\frac{R_o}{1.1\,R_s + R_o}\right) \tag{11}$$

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1. Report No.
NASA TP-2317

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Group-Type Hydrocarbon Standards for High-Performance Liquid Chromatographic Analysis of Middistillate Fuels

5. Report Date
May 1984

6. Performing Organization Code

7. Author(s)
Dumas A. Otterson and Gary T. Seng

8. Performing Organization Report No.
E-1931

10. Work Unit No.

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered
Technical Paper

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract
A new high-performance liquid chromatographic (HPLC) method for group-type analysis of middistillate fuels is described. It uses a refractive index detector and standards that are prepared by reacting a portion of the fuel sample with sulfuric acid. A complete analysis of a middistillate fuel for saturates and aromatics (including the preparation of the standard) requires about 15 min if standards for several fuels are prepared simultaneously. From model fuel studies, the method was found to be accurate to within 0.4 vol% saturates or aromatics and provides a precision of ±0.4 vol%. Olefin determinations require an additional 15 min of analysis time. However, this determination is needed only for those fuels displaying a significant olefin response at 200 nm (obtained routinely during the saturates/aromatics analysis procedure). The olefin determination uses the responses of the olefins and the corresponding saturates, as well as the average value of their refractive index sensitivity ratios (1.1). Studies indicated that, although the relative error in the olefins result could reach 10 percent by using this average sensitivity ratio, it was 5 percent for the fuels used in this study. Olefin concentrations as low as 0.1 vol% have been determined using this method.

17 Key Words (Suggested by Author(s))
Fuel analysis; High-performance liquid chromatography; Fuels characterization; Fuel group-type analysis

18. Distribution Statement
Unclassified - unlimited
STAR Category 28

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price
Unclassified	Unclassified	17	A02

For sale by the National Technical Information Service, Springfield, Virginia 22161

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