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Summary

High-performance liquid chromatography (HPLC) is one of the most promising methods for the general characterization of middistillate fuels. The value of this technique is 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 aromatic class in a fuel is composed of many compounds. The most accurate results would be obtained if the composition of the corresponding group in the standard and that in the fuel were identical. The multiplicity of fuel sources and refining methods suggests the need for many standards or other ways to quantitate the HPLC data.

This report presents the results of an investigation into quantitative HPLC methods. The data were obtained by using modern chromatographic instrumentation equipped with a 25-cm aminosilane column and a refractive index detector. The eluent was hexane. Accurate values for the concentrations of the classes were obtained by using standards that were derived from each fuel by preparative HPLC. Inasmuch as standard preparation by this means may require several days, other quantitative methods were investigated. The method that was developed requires only one chromatogram (~20 min) for the estimation of aromatic class concentrations if the total aromatic concentration is known. The estimations also use one average value of the refractive index for each aromatic class for all fuels.

The seven fuels used in this study covered a wide range of composition. The amounts of the monocyclic aromatics ranged from 13 to 55 vol %; those of the fused dicyclic aromatics from 1 to 20 vol %; and those of the fused tricyclic aromatics from 0 to 1.5 vol %. The relative errors obtained for each class by using the method developed varied among the fuels. For the monocyclic aromatic class, the relative errors ranged from 0.3 to 8.8 percent. More than half of them were less than 1 percent. The relative errors for the fused dicyclic aromatics ranged from 0.6 to 10.1 percent with more than half being greater than 6.5 percent. The absolute errors in the concentrations of both the miscellaneous polycyclic aromatics and the fused tricyclic aromatics were less than 0.3 vol % with most being less than 0.1 vol %.

There was also evidence that the presence of polycyclic aromatics may introduce errors in the determination of the aromatic group in which the standards are prepared by the reaction of the fuel with sulfuric acid. Corrections based on the change in the refractive index that accompanies a change in composition of the aromatic fraction improved both the precision and accuracy of the values obtained for the aromatic group concentration.

Introduction

Current trends in petroleum technology have led to increased attention to hydrocarbon group-type determinations (saturates, olefins, and aromatics) for jet turbine fuels. In addition to increasing aromatic contents, future jet fuels may exhibit a change in the distribution of monocyclic and polynuclear aromatics. Such changes may occur as a result of an increase in the final boiling points of the fuels, an increase in the amount of cracked stock streams employed to produce the fuels, or the eventual introduction of syncrudes into the refineries. Consequently, several important fuel properties, including combustion quality, materials compatibility, and fuel stability, may be affected. Thus, the need for class determinations of aromatics (i.e., the quantities of monocyclic, dicyclic, tricyclic, etc. aromatics) is becoming increasingly critical for a complete characterization of fuels.

Aromatic class analyses can be performed with various degrees of accuracy and precision through the use of several modern instrumental techniques. These techniques are generally quite time consuming. Mass spectrometry (MS) can be employed following a separation of the fuel into fractions of saturates and aromatics (ref. 1). Nuclear magnetic resonance (NMR) spectrometric methods for both fractionated and whole fuels have been reported to provide relatively good results. However, these methods require C-13 NMR results and/or other characterization data in addition to proton results (refs. 2 and 3). Ultraviolet (UV) spectrophotometric methods have also been attempted with varying degrees of success (refs. 4 and 5). Gas chromatographic (GC) determinations are also possible, although most current studies are aimed at more detailed separations to identify individual components (ref. 6). One method which has demonstrated much promise for determinations of this type is high-performance liquid chromatography (HPLC) employing a bonded aminosilane column (refs. 7 to 10). This technique is relatively fast, simple, accurate, and precise. However, as is the case for the MS, UV, and GC methods, quantitative HPLC work requires the use of accurately prepared standards or a fuel fractionation step. Preparation of accurate standards from pure compounds requires a detailed analysis of each fuel class for each fuel to be analyzed. The excessive time required for these analyses can be avoided by fractionation of the fuel by using high-performance preparative liquid chromatography. Even this technique can require several days of operator time to produce sufficient amounts to be used as aromatic class standards.

Rapid fuel characterization would greatly facilitate the study of the effect of aromatic classes on a number of important fuel properties. Sink, Hardy, and Hazlett recently published a paper about compound class quantitation in JP-5 jet fuels (ref. 11). The quantitation procedure utilized standards which had the same refractive index as the average values that were obtained for the classes of a number of JP-5 fuels. Semipreparative chromatography was used to prepare sufficient amounts of the saturates, and monocyclic and dicyclic aromatic classes for the measurement of their refractive indices.

In this investigation, a variety of middistillate fuels are employed to develop quantitative HPLC methods for four aromatic classes which individually require less than 1 hr to complete. In addition to JP-5 fuels, this study also includes diesel fuels and experimental referee-broadened specification (ERBS) fuels. Quantitation is accomplished by using various types of standards as well as a method based on refractive indices. The results so obtained are compared with those obtained by using standards produced by preparative HPLC and in specific cases with those obtained by mass spectroscopy.

Experimental Procedure

Instrumentation

Analytical chromatograph.—A model 324 gradient liquid chromatograph (Beckman Instruments, Inc.) was employed in this work. It was equipped with several columns, a model 421 controller, model 100A pumps, a mixing chamber, a diode array detection system (Hewlett-Packard 1040A HPLC UV-VIS), and a refractive index detector (Altex model 156). This system was modified by the addition of an onstream 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 sampling 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 25-cm-long by 4.6-mm-inside-diameter, 5-μm reversible Hi-Chrom aminosilane column (Regis Chemical Company); 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 aminosilane column is used.

Preparative chromatograph.—A model 830 liquid chromatograph (Du Pont Company) equipped with a model 837 spectrophotometer and a model 845 refractometer, which had been converted to a high-performance preparative liquid chromatograph (HPPLC), was used to produce class standards from each fuel. This chromatograph used a 25-cm by 21.2-mm-inner-diameter aminosilane column in place of the analytical column. A fraction collection system, a dead-volume tee, and a needle valve were also part of the HPPLC. The valve was adjusted so that a fuel component was discharged at the same time its presence was indicated by a response on the refractive index detector.

Chromatographic Methods

Analysis.—The analytical chromatograph indicated in figure 1 can be used for several types of fuel analysis: aromatic class-type analysis, group-type analysis, and identification of components of the miscellaneous polycyclic class. Group-type and aromatic class-type analyses need only one column (the amino column) in the system. Group-type analyses require backflushing to be started after elution of the saturated hydrocarbons and olefins and prior to elution of any aromatic hydrocarbons. On the other hand, class-type analyses require no backflushing. Identification of the components of the miscellaneous polycyclic fraction generally requires the use of all three columns. Details of the identification methods are presented in the section DATA TREATMENT.

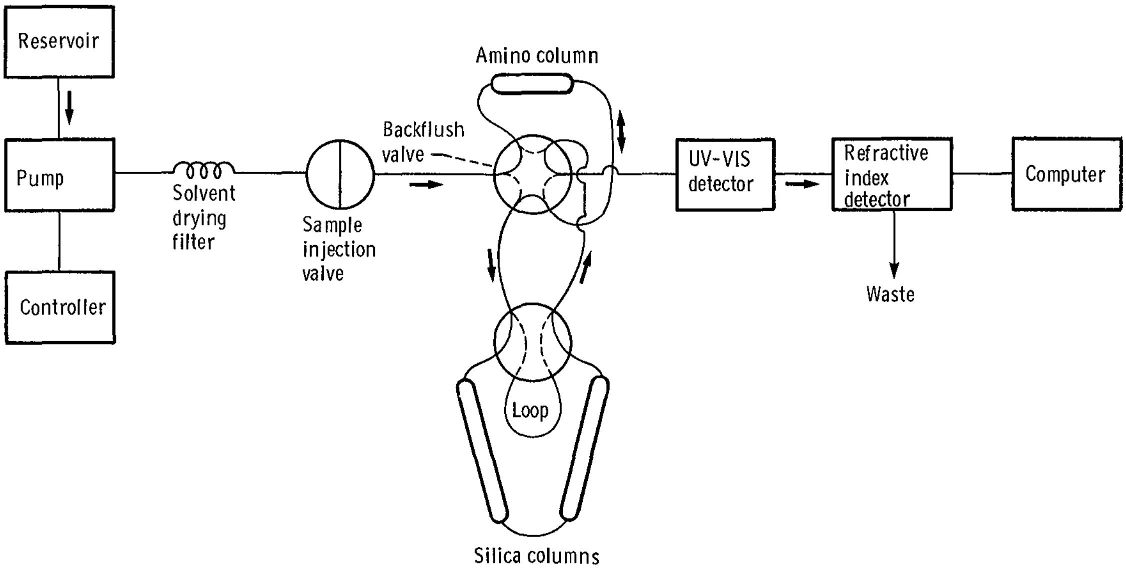

Figure 1.—Diagram of high-performance liquid chromatograph.

Several chromatographic conditions are the same for all three types of analysis. The eluent is hexane with a flow rate of 1.00 ml/min. The sample volume is 1 μl. The responses of the refractive index detector are used to obtain quantitative results. The UV/VIS detection systems provide information to facilitate identification of some of the various fuel components. The chromatogram is generally completed in about 10 or 15 min.

Normalized elution times are used to identify the class to which the responses belong. Normalization is the adjustment of data to values that would have been obtained at a constant flow rate. Normalized elution times for each class are included in table I. All of the components of the saturated hydrocarbon class elute as one peak as do those of the monocyclic aromatic class. Components of the other three classes may elute as multiple peaks. The components of the miscellaneous polycyclic aromatics can include such diverse compounds as acenaphthenes, acenaphthylenes, biphenyls, bibenzyls, fluorene, and even a few dimethyl-substituted naphthalenes (table II). Spectra were obtained for the predominate peak in this class in attempts to identify the major components in some fuels. Tentative identification suggested the presence of dimethylnaphthalenes and biphenyls in diesel fuel 2 as well as some unidentified components. Even though identification of the components might improve the accuracy of the analysis, the improvement would not be significant in comparison with the errors inherent in the method. Large errors can be expected when one set of standards or one set of refractive indices is used to quantitate HPLC data for many types of fuel. Hence, greater efforts to identify these minor fuel components were not made.

Standards production.—Standards for the accurate determination of aromatic classes in fuels are difficult to produce. The sensitivity of the standard must be the same as that of the class whose concentration is to be determined. Inasmuch as fuels differ widely in composition, many standards may be required to achieve accurate results. Results that were deemed to be accurate were obtained by using standards that were produced for each fuel by preparative chromatography of that fuel (PC standards). Other standards were also prepared for this study.

Preparative chromatography.—The procedure to produce standards by preparative chromatography involved (1) the separation of the various fuel classes, (2) evaporation of most of the eluent by using the Kuderna-Danish evaporator, and (3) removal of the last traces of the eluent by using a rotating evaporator. The last step was carried out only when a chromatogram indicates that the particular class of the standard is virtually free from contamination by any other class. Several days of operator time were required to prepare a set of standards for each fuel.

The flow of the eluent, pentane, was adjusted to 20 ml/min. When the responses of the refractive index and the spectrophotometer set at 280 nm were constant, 1.0 ml of fuel was injected. Each fraction was collected during the time the presence of a class was indicated by the detector response. Cross-contamination was indicated when the response did not go to baseline between fractions. All components were generally eluted in about 15 or 20 min. About ten 1-ml portions of each fuel were used to obtain enough material to use as standards for monocyclics and fused dicyclics. All

TABLE I.—REFRACTIVE INDICES OF FUEL COMPONENTS AT 23 °C

(a) Fractions obtained by preparative chromatography

Fuel	Fraction				
	Saturated hydrocarbons	Monocyclic aromatics	Fused dicyclic aromatics	Miscellaneous polycyclic aromatics	Fused tricyclic aromatics
	Measured refractive index, n_D				
Diesel fuel	1.4473	1.5123	1.5907	------------	------------
Middistillate blend 1[a]	1.4436	1.5035	------	------------	------------
Middistillate blend 2[b]	1.4396	1.5104	1.5844	------------	------------
Blend stock	1.4445	1.5048	1.6045	------------	1.6600
ERBS 1	1.4365	1.5171	1.6036	------------	1.7353
JP-5	1.4365	1.5073	1.5767	------------	------------
JP-5 (derived from shale)	1.4285	1.5088	1.5962	------------	------------
ERBS 2	1.4374	1.5110	1.6047	------------	------------
Average	1.4396 ± 0.0061	1.5092 ± 0.0042	1.5926 ± 0.0110	------------	1.70
Elution time, min	3.1 ± 1	4.0 ± 0.01	5.4 to 5.7	6.3 to 8.2	>8.2

(b) Compounds

Compound	Refractive index, n_D	Information obtained from
Hexane	1.3732	Ref. 13
Monocyclic aromatics		
Toluene	1.4945	Ref. 14
Mesitylene	1.4958	Ref. 14
Monocyclic standard	1.5054	Measurement (100 percent)
Fused dicyclic aromatics		
Naphthalene	1.6256	Measurement (24.4 percent in toluene)
1-Methylnaphthalene	1.6145	Ref. 15
1-Methylnaphthalene	1.6074	Measurement (10 percent in $C_{12}H_{26}$)
Dicyclic standard	1.6104	Measurement (100 percent)
Miscellaneous polycyclic aromatics		
Biphenyl	1.5696	Measurement (5 percent in $C_{12}H_{26}$)
4-Pentylbiphenyl	1.5727	Measurement (9.9 percent in $C_{12}H_{26}$)
4-Pentylebiphenyl	1.5706	Measurement (100 percent)
Diphenylmethane	1.6004	Measurement (7 percent in $C_{12}H_{26}$)
Triphenylmethane	1.6297	Measurement (4 percent in xylene)
Bibenzyl	1.5687	Measurement (10 percent in $C_{12}H_{26}$)
Acenaphthene	1.6347	Measurement (5 percent in xylene)
Acenaphthene	1.6363	Measurement (6.9 percent in $C_{12}H_{26}$)
Fluorene	1.6690	Measurement (8.1 percent in xylene)
Average	1.6057 ± 0.0377	
Fused tricyclic aromatics		
Anthracene	1.7347	Measurement (1 percent in xylene)
Phenanthrene	1.7047	Measurement (5 percent in xylene)
1-Methylphenanthrene	1.6847	Measurement (4 percent in xylene)
9-Methylanthracene	1.7287	Measurement (5 percent in xylene)
2-tert-Butylanthracene	1.6707	Measurement (5 percent in xylene)
2-Ethylanthracene	1.6467	Measurement (5 percent in xylene)
9,10-Dimethylanthracene	1.7107	Measurement (2.5 percent in xylene)
Average	1.6973 ± 0.0317	

[a] Low naphthalene content.

[b] High naphthalene content.

TABLE II.—COMPOSITION OF SYNTHETIC AROMATIC STANDARDS

Monocyclic aromatics standard		Fused dicyclic aromatics standard	
Compound[a]	Concentration, wt %	Compound[b]	Concentration, wt %
Ethylbenzene	0.18	Naphthalene	3.45
Xylene	.18	2,6-Dimethylnaphthalene	↓
Mesitylene	12.77	2,3-Dimethylnaphthalene	
1,2,4-Trimethylbenzene	3.76	2-Methylnaphthalene	
Isopropylbenzene	5.47	1,3-Dimethylnaphthalene	16.93
1,2,3,4 Tetramethylbenzene	5.71	2-Ethylnaphthalene	8.62
1,2,3,5 Tetramethylbenzene	5.64	1-Methylnaphthalene	43.10
m-Diethylbenzene	5.47		
p-Diethylenzene	3.64		
tert-Butylbenzene	5.49		
sec-Butylbenzene	3.64		
n-Butylbenzene	5.45		
Pentamethylbenzene	4.22		
Hexamethylbenzene	4.22		
Indan	6.11		
tert-Dibutylbenzene	2.11		
1-Phenyltridecane	9.30		
Tetrahydronaphthalene	9.30		
Tetrahydronaphthalene	10.29		

[a] Average refractive index n_D^{24}, 1.5054.

[b] Average refractive index n_D^{24}, 1.6101.

fractions from different runs that eluted in the same time period were combined. Most of the pentane was evaporated on the Kuderna-Danish evaporator. Those fractions which were cross-contaminated were again chromatographed, and the pentane was evaporated.

When the chromatograms indicated little or no cross-contamination of a fuel fraction, the rest of the pentane was removed by using a rotating evaporator. The evaporation conditions for this operation were critical. The pentane was evaporated for 1 hr at room temperature at a pressure of 5338 to 6000 N/m^2 (40 to 45 mm Hg). Preliminary tests indicated that pentane could be completely removed from a fuel fraction without losing enough of its components to cause significant change in test results. The volumes of some fuel classes were so small that they were either combined with other classes or diluted with a hydrocarbon from another class in order to obtain a usable standard. The concentrations of these standards had to be established by other means.

Standards whose volumes were insufficient for analysis were generally diluted with hexadecane. If measurable volumes of the fraction were available, the dilution factor was used to calculate the concentration of the class in the standard. If the volume of the fraction could not be measured, its concentration in the standard was estimated by an indirect method. That is, the concentration of the hexadecane was determined by HPLC, and its concentration in percent was then subtracted from 100 percent to estimate the class concentration.

Synthetic standards.—Several synthetic standards were used to quantitate the HPLC data that were obtained for each fuel. The standard for monocyclic aromatics is a mixture of 19 substituted benzenes (table II). The standard for dicyclic aromatics includes naphthalene and is a mixture of eight substituted naphthalenes (table II). Mixtures containing known amounts of the monocyclic and the dicyclic standards were used to establish the sensitivities.

Data Treatment

Measurement of refractive indices.—An Abbe refractometer was used to measure the refractive index at room temperature of those substances for which literature values could not be found. Those substances included hydrocarbons that are solid at room temperature and fuel fractions isolated by preparative chromatography.

The refractive indices of solids were obtained by an indirect method which involves the refractive index of a solution containing a known concentration of the solid in a liquid whose refractive index is known. The refractive index of the solid is calculated by using an equation derived from one given in Partington (ref. 12) by assuming that the solution is ideal. The derived equation is

$$n_m = n_1 f_1 + n_2 f_2 \tag{1}$$

where n_m is the measured refractive index, n_1 and n_2 are the refractive indices of the two components of the solution, and f_1 and f_2 are their volume fractions. Inasmuch as both concentrations and n_m and n_2 are known, the value of n_1 can be calculated. Table I lists the values obtained for the refractive index of 17 solids obtained in this manner, as well as literature values for some fuel components (refs. 13 to 15). The accuracy of these values is better for those solutions with higher solids concentrations than for those with very low concentrations. In the latter case the concentrations were limited by the low solubility of the solid. In spite of this, the accuracy that was achieved is adequate for this method. This becomes evident during the discussion of the recommended method.

The refractive indices of the aromatic classes are given in table I(a). Fuel fractions were produced by preparative chromatography, their refractive indices were measured, and these values were used to calculate the refractive index of the class that was the major component of the fraction. In the event that the fraction contained only one class (as indicated by a chromatographic analysis) the value measured was assumed to be the refractive index of that class. If more than one class was present, an iteration procedure was used to estimate the refractive index of the major class.

The iteration procedure involves the estimation of approximate concentrations of the classes in a fuel fraction first by using the refractive index method and then by using equation (1) to determine the refractive index of the major class of the fraction. This method for the estimation of the concentration uses refractive indices to quantitate chromatographic data obtained with a refractive index detector. In the initial step of the iteration, the measured refractive index of each fuel fraction is assumed to be that of its major component. Values of concentration obtained in this step are then used in equation (1) to calculate a more accurate value of the refractive index for the major component in the fuel fraction. For this calculation the measured refractive index is used correctly as that of the fuel fraction. The refractive index for the major component obtained in this way is then used to estimate more accurate concentrations of the classes in the fuel fraction. Repetitions of these calculations are then carried out by using the calculated refractive index and concentration values until the values are equal to those obtained in the previous calculation.

Normalization of HPLC data.—During the course of this research, methods were developed to reduce the error due to two types of sensitivity fluctuation (ref. 16). One type was short-term variations in flow rate, and the other was day-to-day fluctuations due to unspecified causes. Corrections for both involved normalization of the data. Errors due to fluctuations in flow rate were normalized by adjusting the data to values they would have had at a uniform flow rate. Normalization for day-to-day sensitivity fluctuations is needed only when data obtained on two different days are used in calculations. Normalization in this case is done by adjusting the data obtained on one day to values they would have had if the sensitivity were the same as that of the other day. The normalization equation is

$$R_n = \frac{D_n}{D_o} R_o \tag{2}$$

where R_o and R_n are the observed and normalized responses respectively, D_o is the observed elution time (or sensitivity of a standard), and D_n is elution time (or sensitivity of the same standard) to which the responses are to be normalized (ref. 16).

Quantitation of HPLC data.—The HPLC data which were obtained for each fuel were quantitated by two methods by using several parameters for each method. The first method used several types of standards. The most accurate results were deemed to be those that were obtained by using standards produced by preparative chromatography of the fuel being analyzed (PC standards). The other standards were synthetic standards which were used with all the fuels. The second method of quantitation, which is new, uses refractive indices to quantitate the HPLC data. It is discussed in the next section.

Derivation of an equation to quantitate HPLC data using refractive indices.—The derivation of an equation to quantitate HPLC data using refractive indices is based on two equations. One is an identity that states that the sum of the concentrations (in percent) of all fuel components C_j is equal to 100 percent:

$$\Sigma_j C_j = 100 \tag{3}$$

The other equation is the relation between a response R_i of the refractive index detector for a substance and its concentration C_i:

$$R_i = k_i C_i = \varphi_i (n_i - n_e) C_i \tag{4}$$

where k_i and φ_i are constants, and n_i and n_e are the refractive index of a fuel component and the eluent, respectively. Preliminary investigations indicated that the accuracy would be improved by using only the data for the aromatic classes. These investigations included the determination of φ_i for representative compounds of various fuel classes and groups and quantitative calculations involving data for all fuel components as well as for only the aromatic classes. Inasmuch as a rapid method is available to determine concentrations of aromatic classes, equation (1) is modified to

$$C_a = \Sigma_i C_i \tag{5}$$

where i refers only to the aromatic components. Dividing a rearranged form of equation (4) by equation (5) gives the following:

$$\left.\begin{aligned} \frac{C_i}{C_a} &= \frac{\dfrac{R_i}{\varphi_i(n_i-n_e)}}{\Sigma_i C_i} = \frac{\dfrac{R_i}{\varphi_i(n_i-n_e)}}{\dfrac{R_i}{\Sigma_i \varphi_i(n_i-n_e)}} \\ &\text{or} \\ C_i &= \frac{\dfrac{R_i}{\varphi_i(n_i-n_e)}}{\Sigma_i \dfrac{R_i}{\varphi_i(n_i-n_e)}} C_a \end{aligned}\right\} \tag{6}$$

If φ_i has the same value for all aromatics, then

$$C_i = \frac{\dfrac{R_i}{n_i-n_e}}{\Sigma_i \dfrac{R_i}{n_i-n_e}} C_a \tag{7}$$

Calculations using this equation can generally be made in a few minutes.

Let us now consider the errors that are introduced by the assumption that φ_i's are equal. Experimental investigations indicate that values of φ_i can vary as much as 5 percent for those monocyclic and fused dicyclic aromatics that are apt to be present in middistillate fuels. This suggests that the use of an average value of φ_i could cause an uncertainty of 2 or 3 percent in the reported concentration. The values of φ_i for fused tricyclic aromatics can be as much as 17 percent higher and show greater variations than for the two classes mentioned previously. Generally, the errors which are introduced by the assumption that the values of φ_i for tricyclics are the same as those of the other aromatic classes have negligible effect on the results for the other aromatic classes because the concentrations of the fused tricyclic aromatics are rarely greater than 1 percent. Corrections can be made for those fuels with higher concentrations of fused tricyclic compounds by including the appropriate values of φ_i in equation (6).

Similar considerations help us to understand why the accuracy of aromatic class determinations decreases when equation (7) also includes data for the saturates group. This group is generally at least 70 percent of the fuel. Hence, a small relative difference of 3 percent in the value of φ_i for saturated hydrocarbons would produce a 2-percent absolute error in total aromatics. This is significantly greater than the differences reported in table III (maximum 0.9 percent) between results for total aromatics using preparative chromatography standards (considered to be the most accurate results) and those using sulfuric acid prepared standards. Hence, a method which uses data for the saturates group is expected to produce aromatic class concentrations that are more erroneous than those from the method which uses concentrations of the aromatics obtained by using sulfuric acid prepared standards.

Results and Discussion

Aromatics Class Analysis

Data which were used to evaluate various methods of quantitation are presented in tables III and IV. Table III compares the concentrations obtained for the aromatic group (i.e., total aromatic classes) by all methods considered. These data were used to indicate those methods which are sufficiently accurate to merit further consideration. The concentrations of the aromatic classes obtained by these selected methods are presented in table IV.

Two types of results are presented in table III. They are the sum of the concentrations of all fuel groups obtained by using standards produced by preparative chromatography (PC standards) and the sum of the concentration of all aromatic classes in a fuel obtained by the quantitation methods being studied. The sums of the concentrations of all fuel groups in each of seven fuels are presented in the first row of the table. All sums were within 1.6 percent of 100 percent. This strongly implies that the relative errors in these analyses were not more than 2 percent. It also suggests that the errors for the aromatic class concentrations obtained by using PC standards should also be in the same range.

Two quantitation methods produced results for the aromatic class concentrations which agreed with the results based on PC standards with an average difference of 0.7 percent. The methods included the use of standards prepared by reaction of each fuel with sulfuric acid (H_2SO_4 standards) and the use of synthetic standards. The maximum differences were 1.1 percent by using H_2SO_4 standards and 1.8 percent by using synthetic

TABLE III.—DATA FOR PRELIMINARY COMPARISON OF METHODS OF QUANTITATION

Method of quantitation	Fuel						
	Diesel 2	Middistillate blend 1[a]	Middistillate blend 2[b]	Blend stock	ERBS 1	JP-5	JP-5 derived from shale
	Sum of concentrations for all components, vol%						
Preparative chromatography standards	99.60	100.5	100.3	98.4	101.1	99.3	98.7
	Sum of concentrations for all aromatics classes, vol%						
Preparative chromatography standards	20.0	30.2	28.3	77.4	28.1	18.5	21.3
Synthetic standards[c,d]	19.9	28.4	27.7	74.1	29.0	18.7	20.4
Toluene and naphthalene standards[d]	21.5	33.7	31.3	84.0	31.7	28.8	23.6
Mesitylene and 1-methylnaphthalene standards[d]	21.0	31.1	30.0	80.8	30.7	17.2	22.1
Standards by fuel and H_2SO_4 reaction[e]	20.3	30.1	28.0	78.8	27.8	18.9	21.6
Mass spectroscopy (ref. 17)	21.4	30.8	28.6	73.4 [f](76.0)	28.7	----	----
Fluorescence indicator analysis FIA (ASTM-D1319)	17.8, 21.0, 26.0	32.4	31.6	61.7	31.1	18.5	21.3

[a] Low naphthalene content.

[b] High naphthalene content.

[c] Compositions of synthetic standards can be found in table I.

[d] Values obtained by using preparative chromatography derived standards for miscellaneous polycyclic and for fused tricyclic classes were included in these totals.

[e] Data from table V.

[f] Corrected value based on blendstock blend analyses (ref. 17).

standards. Examination of the data suggests that the accuracy of the aromatic group concentrations obtained by using H_2SO_4 standards was better than indicated. In every case, the aromatic group concentrations obtained by using H_2SO_4 standards and those obtained by using PC standards differed in the same direction as the correction that is needed for the sum of the concentrations of all fuel components to equal 100 percent. The values reported in this table for aromatic group concentrations obtained by using H_2SO_4 standards are the corrected values listed in table V. The corrections are discussed in connection with that table.

It can be observed in table III that the aromatic group concentrations obtained by mass spectroscopy (MS) were higher than those obtained by using PC standards except for the blend stock. In this case, mass spectrometric results for the aromatic group concentration were suspect (ref. 17). Aromatic group concentrations obtained by using a toluene and naphthalene standard, a mesitylene and 1-methylnaphthalene standard, and the FIA method (ASTM-D1319) are also presented in this table. Aromatic group values obtained by using these three quantitation methods indicate that these methods produced aromatic class results with large errors, so they were not considered further. It should be noted that the FIA (ASTM-D1319) method yielded values which agreed with most of the values obtained by using PC standards, synthetic standards, the H_2SO_4 method, and mass spectrometry within the reproducibility limits specified for the FIA method.

Table IV presents values for the concentrations of four aromatic classes which were obtained by the three most accurate quantitation methods using the same HPLC data, as well as by other analytical techniques. The four classes are monocyclic aromatics (alkyl-substituted benzenes), fused dicyclic aromatics (alkyl-substituted naphthalenes), miscellaneous polycyclic aromatics, and fused tricyclic aromatics (alkyl-substituted anthracenes and phenanthrenes). Miscellaneous polycyclic aromatics are those compounds which elute after most of the fused dicyclics and before fused tricyclics. They include acenaphthene, acenaphthylenes, fluorenes, some methylated naphthalenes, biphenyls, diphenylmethane, etc. This class often appears as several peaks. Identification of the components responsible for any of these peaks would permit estimation of their concentrations. Two components of this class have been tentatively identified in diesel fuel 2. They are methylnaphthalenes and substituted biphenyls. Other components have not been identified. This class could be

TABLE IV.—CONCENTRATIONS OBTAINED FOR AROMATIC CLASSES BY THREE MOST ACCURATE QUANTITATION METHODS

Fuel	Quantitation method					
	Ratio with standard sample		Refractive index method using–		Mass spectroscopy (ref. 17)	Ultraviolet spectra ref. (4)
	Preparative chromatography	General synthetic	n_i values obtained for fuel	Average n_i values		
	Concentration, vol%					
Monocyclic aromatics						
Diesel 2	13.1	14.1	13.8	13.7	13.4	----------
Middistillate blend 1[a]	29.2	27.5	29.3	29.3	29.2	----------
Middistillate blend 2[b]	21.2	21.8	20.9	21.1	20.5	----------
Blending stock	54.9	53.8	55.6	54.4	46.5	----------
ERBS 1	15.0	16.5	15.0	15.1	14.0	----------
JP-5	17.6	17.1	16.9	17.0	----	----------
JP-5 derived from shale	17.2	17.8	18.7	18.7	----	----------
Fused dicyclic aromatics						
Diesel 2	5.6	4.2	5.0	5.1	5.0	7.0,10.6,12.6
Middistillate blend 1[a]	1.0	.86	.95	.96	1.3	.7
Middistillate blend 2[b]	5.9	5.1	5.6	5.4	5.5	6.3
Blending stock	20.1	17.7	20.1	21.5	18.3	17.0
ERBS 1	11.9	11.3	11.1	11.1	9.8	11.6
JP-5	1.6	1.5	1.7	1.6	----	1.7
JP-5 derived from shale	2.8	2.4	2.8	2.7	----	3.1
Miscellaneous polycyclic aromatics						
Diesel 2	0.56	----	0.91	0.91	3.01	----------
Middistillate blend 1[a]	.003	----	.05	.06	.16	----------
Middistillate blend 2[b]	1.1	----	1.0	1.0	1.96	----------
Blending stock	1.2	----	1.2	1.2	6.29	----------
ERBS 1	.71	----	.71	.66	3.72	----------
JP-5	.07	----	.06	.08	----	----------
JP-5 derived from shale	.05	----	.05	.05	----	----------
Fused tricyclic aromatics						
Diesel 2	0.83	----	0.59	0.51	1.0	----------
Middistillate blend 1[a]	0	----	0	0	.07	----------
Middistillate blend 2[b]	.40	----	.49	.52	.70	----------
Blending stock	1.3	----	1.5	1.4	2.4	----------
ERBS 1	.42	----	.64	.72	1.2	----------
JP-5	0	----	0	0	----	----------
JP-5 derived from shale	.06	----	.004	.003	----	----------

[a] Low naphthalene content.

[b] High napthalene content.

TABLE V.—CORRECTION OF ERRORS IN GROUP-TYPE DETERMINATIONS DUE TO EXCESSIVE LOSS OF POLYCYCLIC AROMATIC HYDROCARBONS DURING PREPARATION OF STANDARDS BY REACTION OF FUELS WITH SULFURIC ACID

[Ref. 18]

Fuel	Total polycyclics, vol%	R_{ar}/R_a	Correction factor	Total aromatics, vol%		
				Not corrected	Corrected	By other methods
Diesel 2	6.6	0.4708	1.186	17.7	20.4	[a]19.6
		.3979	1.2184	17.8	20.1	[b]17.8, [b]21.0, [b]26.0
		.3786	1.2192	17.9	20.1	[c]20.8
		.3347	1.2404	18.3	20.4	------------
Diesel	3.2	0.4280	------	16.9	----	------------
		.3452	1.1465	17.4	18.5	------------
		.3394	1.1675	17.0	18.3	------------
Middistillate blend 1	1.9	0.4183	[d]1.0147	30.1	30.3	[a]30.2, [b]32.4
Middistillate blend 2	6.8	0.2631	1.1044	27.3	28.0	[a]28.3
Blend stock	22.8	0.9475	[e]1.0061	77.9	79.9	[a]77.6
		.9475	[e]1.0006	77.9	78.1	[b]67.2, [c]75.1
		.1116	1.1294	78.2	78.5	------------
ERBS 1	12.4	0.5014	1.0619	26.3	27.6	[a]28.1
		.396	1.2079	25.6	27.0	[b]31.1
		.375	1.0931	26.6	27.7	[c]27.8
		.196	1.1951	26.6	27.5	------------
		.0534	1.2421	27.2	27.5	------------
ERBS-blend (11.8 hdyrogen)	22.6	0.5165	1.0630	44.8	46.6	------------
		.2815	1.1295	45.2	46.5	------------
		.1847	1.1536	45.6	46.5	------------
JP-5	1.66	0.5006	1.0286	18.5	18.9	[a]18.5
		.1614	1.0527	18.4	18.5	------------
JP-5 derived from shale	2.88	0.2451	1.0610	21.3	21.6	[a]21.3

[a] Value obtained by using PC standards.

[b] Value obtained by fluorescence indicator analysis.

[c] Value obtained by mass spectroscopy.

[d] Maximum correction (assumed that all polycyclic aromatics were removed by sulfuric acid treatment).

[e] Calculated by using data from chromatograms of same standard. Shows magnitude of error that can occur when only a small portion of aromatics react with H_2SO_4 to produce standard.

included with fused dicyclics. However, it is reported separately in this work in order to suggest some of the potential of the method.

Different sections of table IV are used to present data for each aromatic class. The data are concentrations which were obtained by two methods of quantitation of the HPLC responses. One method of quantitation involved the use of standards. The most accurate results were assumed to be those obtained by using PC standards. These results were used to evaluate the accuracy of the results obtained by using other standards. The results obtained by using synthetic mixtures as standards for all fuels are also reported for the major components. The other methods of quantitation are referred to as the refractive index methods. They involved the use of equation (7). Two sets of data that employed refractive indices are reported here. In one set, the refractive index of each class of a fuel was measured and used to calculate the concentrations for only that fuel (specific refractive index method). In the other set, average values of the refractive indices of each class were obtained by averaging the values found for each fuel and were used in the calculation of the concentrations for all fuels (general refractive index method). The average value of the refractive indices for mixed polycyclics was the average of the values listed for the compounds in this category in table I(b). Published results from two other sources are included in table IV. They are mass spectrometry (ref. 17) and ultraviolet spectroscopy (ref. 4). The latter was developed to estimate the fused dicyclic aromatic concentrations only. Other refractive index values were used to quantitate these HPLC data. They merely indicated that the refractive indices could be varied by ±0.03 for both the miscellaneous polycyclic and the fused tricyclic classes without causing any significant change in the results.

The concentrations of the monocyclic aromatics and of the fused dicyclics (table IV) indicated that the general refractive index method could produce more accurate results for all fuels than the method that used one set of synthetic standards for the same fuels. A change in the composition of these standards could improve the accuracy of the method but not the large variation in results. The data also confirmed the view that the general refractive index method was less accurate than the specific refractive index method. The maximum relative error for both refractive index methods was 9 percent for monocyclic aromatics. For fused dicyclics, the maximum relative error was 10 percent for the general refractive index method and 7.3 percent for the specific refractive index method.

The data for miscellaneous polycyclic aromatics and for fused tricyclic aromatics (table IV) include values obtained by using PC standards, the two refractive index methods, and mass spectrometry.

Results obtained by the use of synthetic mixtures as standards for these two classes are not included. All the concentrations of both classes were within the range of 0 to 1.55 percent. Hence, the methodology for these substances did not warrant a detailed study at this time. The data were similar for both classes; that is, the accuracy of both refractive index methods were about the same. However, the general refractive index method caused slightly greater error than did the specific refractive index method. The maximum absolute error was about 0.3 percent for either of these classes. The errors for these minor classes appeared to be associated primarily with the errors in the concentrations of the two major aromatic classes. This was supported by the observation that relatively large variations in the refractive indices used in the calculation of concentrations of the minor classes caused only slight variation in the results. Apparently greater accuracy in the results for the minor classes could be achieved by the use of a synthetic standard.

Group-Type Analysis

The concentration of the aromatic group in a fuel can readily be determined by HPLC using an H_2SO_4 standard (ref. 18). In general, over half of the aromatic group and none of the saturates group are removed in this method. The equation to quantitate the HPLC data is

$$1-F_a=\frac{1-\dfrac{k_a}{k_{ar}}\dfrac{R_{ar}}{R_a}}{\dfrac{R_{sr}}{R_s}-\dfrac{k_a}{k_{ar}}\dfrac{R_{ar}}{R_a}} \tag{8}$$

where F, R, and k are the concentration (volume fraction), the response, and the sensitivity of the substances indicated by the subscripts, respectively. The subscripts a, ar, s, and sr indicate that the value is that obtained for the aromatic or saturates groups before or after reaction of the fuel with H_2SO_4, respectively. Heretofore, it has been assumed that $k_a=k_{ar}$ (i.e., the aromatic fraction does not vary in composition as the fuel is reacted with sulfuric acid). Aromatic group-type results obtained by using this assumption generally agreed with FIA (ASTM D1319) values within the ASTM limits. However, when these data were correlated with results obtained by using PC standards, the differences in the results from these two methods were greater for those fuels with relatively large polycyclic aromatic concentrations. Since polycyclic aromatics react with sulfuric acid more rapidly than monocyclic aromatics (ref. 19), the concentration of polycyclics in the aromatic group would be expected to decrease when the fuel reacts with sulfuric acid. The refractive index of this group would also decrease because the refractive indices of polycyclic aromatic compounds are generally greater than those of monocyclic aromatic compounds (refs. 12 to 14). Therefore, the assumption that $k_a=k_{ar}$ is not true, and the errors resulting from its use should be evaluated for these fuels.

This was done for this investigation by generating correction factors for each of the fuels. Correction factors are ratios of the sensitivities of the aromatic fraction before reaction with sulfuric acid to those after reaction. The refractive index n_i of the i^{th} substance is related to its sensitivity when a refractive index detector is used in the following manner:

$$k_i=\varphi_i(n_i-n_e) \tag{9}$$

where φ_i is a constant related to the i^{th} substance (see eq. (4)). Hence we may write

$$\text{Correction factor}=\frac{k_{ar}}{k_a}=\frac{\varphi_a(n_a-n_e)}{\varphi_{ar}(n_{ar}-n_e)} \tag{10}$$

The correction factors listed in table V were calculated by using this equation and assuming $\varphi_a=\varphi_{ar}$. The values for

n_a and n_{ar} were calculated by using methods described in this report. That is, the concentrations of the four classes in the aromatic group were estimated for both the unreacted and the reacted fuel by using the average refractive index that was found for each class and their HPLC response in equation (7). These concentrations and refractive indices are used in the following equation:

$$n_a = \frac{\Sigma_i C_i n_i}{\Sigma_i C_i} \qquad (11)$$

in which the summations include all aromatic components. This equation is the general form of equation (1).

Table V presents data concerning the correction of errors. The first two columns list the fuel and the total aromatic polycyclic concentrations (i.e., all aromatic classes except monocyclics). The next two columns list the ratio of the responses for the total aromatics in the reacted fuel and the unreacted fuel and the correction factor obtained for that standard. The ratio of responses is an approximation of the fraction of the original aromatic concentration that remains after reaction. The next two columns present the uncorrected and corrected values for the aromatic concentration found by using an H_2SO_4 standard. The last column presents values for this concentration obtained by other methods. The value for the aromatic group obtained by adding the concentrations of the aromatic classes found by using PC standards is listed first in this column.

The data presented in table V indicated that these corrections could improve the precision and accuracy of aromatic group determinations. They also suggested that these corrections were trivial for those fuels with low polycyclic aromatic concentration. This suggestion was easily confirmed by the data for middistillate blend 1 and the two JP-5 fuels. Data for the JP-5 fuel derived from shale indicated that the corrected result was not as accurate as the uncorrected value. This conclusion might be wrong because the value assumed to be correct was very probably erroneously low. This possibility was suggested by the fact that only 98.7 percent of the fuel could be accounted for by the results obtained by using PC standards.

The improved precision resulting from these corrections was observed in table V for diesel 2, ERBS 1, and ERBS blend (11.8 percent of hydrogen). The concentrations of the polycyclic aromatics in these fuels were all greater than 6.5 percent. The data for blend stock which contains more than 20 percent polycyclic aromatics should not be included in this consideration. The decrease in the aromatic concentration of only 5 percent resulting from a mild sulfuric acid reaction caused the corrections to be erroneous. This could be deduced from the fact that the two correction factors for this treatment were almost identical (1.0061 and 1.0006).

Improved accuracy due to these corrections could be observed with diesel fuel 2, middistillate blend 2, and with ERBS 1. Of the fuels with high polycyclic aromatic concentrations, only the blend stock showed a decrease in accuracy caused by this type of correction. In this case, both the corrected and the uncorrected results were higher than the value obtained by using a PC standard which was assumed to be correct. Only 98.4 percent of the blend stock was accounted for upon adding the values for all of its components obtained by using PC standards. Hence, the actual value for the total aromatic concentration could be greater than the value obtained by using this method by more than 1 percent. In the event that it was only 0.8 percent greater, these data would be consistent with all the other data obtained for fuels with a high polycyclic concentration. That is, this type of correction would also improve the accuracy for this fuel.

Concluding Remarks

This study has showed that HPLC can be used to estimate the concentrations of four aromatic classes in middistillate fuels in about 15 or 20 min. The classes were:

(1) Monocyclic aromatics (alkyl-substituted benzenes)
(2) Fused dicyclic aromatics (alkyl-substituted naphthalenes)
(3) Miscellaneous polycyclic aromatics (specific dimethylnaphthalenes, fluorenes, acenaphthenes, biphenyls, etc.)
(4) Fused tricyclic aromatics (alkyl-substituted anthracenes and phenanthrenes)

In the rapid HPLC method developed, the concentration of each aromatic class, C_i, was calculated by using the following equation:

$$C_i = \frac{\dfrac{R_i}{n_i - n_e}}{\Sigma_i \dfrac{R_i}{n_i - n_e}} C_a$$

where R_i is the response of the refractive index detector due to the i^th^ class; n_i and n_e are the refractive indices of the i^th^ class and the eluent, respectively; and C_a is the concentration of the total aromatic group.

Average values of the refractive index for each class were used in the calculations for all the fuels that were tested.

The precision of the results was generally very good, but the accuracy fluctuated because the sensitivities varied from fuel to fuel. The relative errors determined for the refractive index ranged from 0.3 to 8.8 percent for monocyclic aromatics and 0.6 to 10.1 percent for fused dicyclics. The absolute errors for the miscellaneous polycyclics and the fused tricyclics were all less than 0.3 percent. Significant improvements in accuracy could be expected by limiting the method to a specific fuel type. Hence, the method could then be considered to be a determination rather than an estimation.

This work also indicated that polycyclic aromatics could adversely affect with group-type analyses in which the fuel was reacted with sulfuric acid to produce standards. The resulting changes in concentration of the components of the aromatic fraction was employed to evaluate correction factors. The use of these factors improved both the precision and the accuracy of group-type analysis.

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16. Abstract

An HPLC method to estimate four aromatic classes in middistillate fuels is presented. Average refractive indices are used in a correlation to obtain the concentrations of each of the aromatic classes from HPLC data. The aromatic class concentrations can be obtained in about 15 min when the concentration of the aromatic group is known. Seven fuels with a wide range of compositions were used to test the method. Relative errors in the concentration of the two major aromatic classes were not over 10 percent. Absolute errors of the minor classes were all less than 0.3 percent. The data show that errors in group-type analyses using sulfuric acid derived standards are greater for fuels containing high concentrations of polycyclic aromatics. Corrections are based on the change in refractive index of the aromatic fraction which can occur when sulfuric acid and the fuel react. These corrections improved both the precision and the accuracy of the group-type results.

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