Determination of Hydrocarbon Types in Petroleum Liquids by Supercritical Fluid Chromatography with Flame Ionization Detection

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Supercritical fluid chromatography using packed columns and carbon dioxide as the mobile phase provides an alternate to the fluorescent indicator adsorption method (FIA) for determining saturates, olefins, and aromatics in petroleum liquids boiling below 350 °C. Silica and silver nitrate impregnated silica columns are used in series. Standard deviation is in the 0.4 to 0.8 wt % range, depending on sample type. Unlike the FIA method, this technique is suitable for colored samples and for samples containing material lighter than hexane. The separation requires 4 min per sample.

Since its development by Conrad (*1*) and Criddle and LeTourneau (*2*), the fluorescent indicator adsorption (FIA) method, ASTM D 1319 (*3*) has been used by the petroleum industry for the determination of saturated, olefinic, and aromatic hydrocarbons in gasoline and jet fuel. The method uses a specially designed glass column packed with activated silica gel. A narrow band of silica gel near the head of the column contains a mixture of dyes which fluoresce under ultraviolet light. The sample, added to the top of the silica gel, is desorbed down the column with isopropyl alcohol. The hydrocarbons are separated into saturate, olefin, and aromatic bands along with the dyes which separate selectively to leave the saturates colorless while coloring the olefins yellow, the aromatics blue, and the alcohol front red. The volume percent of each hydrocarbon type is calculated by measuring the length of each colored zone in the precision bore glass tubing which makes up the analyzer section of the column.

The FIA method has been an industry standard for over 30 years, primarily because it is the only direct method of measuring saturates, olefins, and aromatics in gasoline and jet fuel, but it does have several problems. The most obvious is that it depends upon the operator's ability to consistently distinguish the first sharp yellow, blue, or red front. Certain types of gasoline range materials, especially cracked stocks, yield poor separation of olefin and aromatic components leading to erroneous results (*4*).

Since colored samples interfere with detection of the dyed zone boundaries, sometimes making them impossible to see, the method is not useful for highly colored shale or coal-derived fractions. The scope of the method excludes samples containing significant amounts of pentane and lighter hydrocarbons or those with end points over 315 °C (600 °F). Over the years problems have arisen with variations in dye composition or quality and with availability of the proper grade and activity of silica gel. Finally, the precision of the method is rather poor.

A number of studies have been reported on modification of the silica gel (*4–6*), the dyes (*7*), and the mobile phase (*8*) in an attempt to improve the precision of the method. In an effort to reduce the human error introduced by visually selecting the start of each colored zone, attempts have been made to instrumentalize the method by using HPLC (*9, 10*) and GC (*11*) for hydrocarbon type analysis. HPLC is hampered by the lack of a suitable universal detector. UV detectors do not respond to saturated hydrocarbons, are not generally useful in the short wavelength region where olefins absorb, and give widely varying response for aromatics.

Refractive index detectors, while less selective, require calibration for "typical" saturates, olefins, and aromatics. The use of two columns (silica plus silver nitrate impregnated silica) was reported for HPLC (*12*) using an IR detector to detect saturates, olefins, and aromatics in gasoline. The wide range of the response factors required suggests that this method is best limited to a given sample type, e.g., gasoline. Transport type FID detectors which require mobile phase evaporation are not suitable for volatile samples. Gas chromatography, on the other hand, needs a column which provides compound class separations over a wide boiling range. The common technique of using a long capillary column to separate all the sample components requires extensive calibration and is limited to light samples, containing little or no olefin.

We have tried many of the suggested approaches to improve upon the FIA method with limited success. Recently we have been evaluating supercritical fluid chromatography (SFC) as a routine technique (*13*). One of the early problems investigated was the analysis of fuels for saturates, olefins, and aromatics. Our main objective was to determine if SFC with FID detection could provide a satisfactory alternative to the FIA technique. In addition we wanted to see if some of the limitations of the FIA method (presence of C_4s and C_5s, colored material, high boilers, etc.) could be overcome by using the instrument.

EXPERIMENTAL SECTION

The supercritical fluid chromatograph used is a modified high-performance liquid chromatograph (Hewlett-Packard 1082B). The modification has been described by Gere, Board, and McManigill (*14*) and, with the exception of the detector, has been used as described by them. A description of the modified gas chromatographic flame ionization detector used (Gow Mac 12-800) has been reported by Rawdon (*15*) and will not be repeated here. Columns are 25 × 4.6 mm i.d. 5-μm silica (Alltech Associates, Deerfield, IL) and 25 cm × 4.6 mm i.d. packed with 20% silver nitrate coated RSil-5 (Alltech Associates). This packing is prepared by slurrying the silica in a methanol solution of the silver nitrate. After the methanol is removed under vacuum and the packing gently heated, the column is slurry packed using 50:50 toluene:chloroform. After purging excess solvent, the column is activated in carbon dioxide at 3000 psi and 65 °C for 1 h.

Carbon dioxide (air-free or bone dry grade, AGL Welding Supply, Clifton, NJ) is supplied in siphon tube cylinders and dried through activated silica gel. Reference compounds were used as received (Chem Service, West Chester, PA). Samples were analyzed as 2-μL injections without dilution. Reference compounds were injected likewise either neat or in a suitable solvent. The mobile phase flow rate was controlled by the chromatograph. While repeatability of this flow is entirely sufficient for our purposes, the compressibility of carbon dioxide causes the listed flow rate to be incorrect. Further, the linear velocity of the mobile phase is a function of operating pressure and temperature as well as flow rate. Under conditions of this analysis, a listed flow of 3 mL/min corresponds to a velocity of 0.46 cm/s.

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Table I. Comparison of SFC and FIA Results for Gasoline Range Samples

sample	SFC wt %	SFC vol % (calcd)	FIA vol %
A saturates	24.9	33.0	29.5
olefins	0.7	0.8	2.0
aromatics	74.4	66.2	68.5
B saturates	55.7	61.4	63.5
olefins	4.8	5.3	7.0
aromatics	39.5	33.3	29.5
C saturates	59.9	64.0	59.5
olefins	17.2	18.4	22.0
aromatics	22.9	17.6	18.5
D saturates	53.0	57.3	58.0
olefins	16.9	18.3	18.0
aromatics	30.1	24.4	24.0
E saturates	32.3	38.1	35.5
olefins	8.3	9.8	13.5
aromatics	59.5	52.1	51.0
F saturates	19.6	21.8	19.0
olefins	38.2	42.4	45.0
aromatics	42.2	35.8	36.0
G saturates	83.2	88.1	85.5
olefins	0.0	0.0	0.5
aromatics	16.8	11.9	14.0

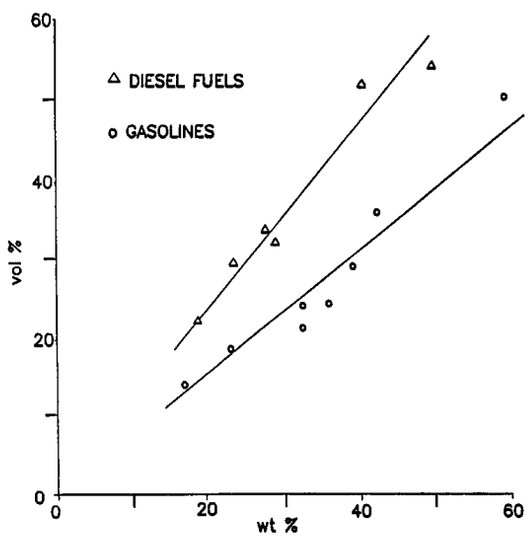

Figure 1. Correlation of FIA (D 1319) and SFC results for aromatic hydrocarbons.

RESULTS AND DISCUSSION

Our initial efforts in hydrocarbon type analysis by SFC with a silica column and a UV detector at 190 nm demonstrated that we could separate olefins and aromatics in gasoline range samples. Addition of the FID to the system showed that saturates were coeluting with the olefins. Addition of the silver nitrate column in series provided the saturate/olefin separation.

Direct comparison of FIA results with SFC is not possible since FIA gives volume percent while the SFC flame detector gives results in weight percent. The SFC results obtained on a number of gasoline range samples were converted to volume percent in the following manner for purposes of comparison: A calibration plot was constructed of weight percent vs. volume percent for aromatics in samples which had been analyzed by SFC and FIA. This plot is then used to correct aromatic weight percent data to volume percent, while the saturates and olefins are adjusted to make up the difference, keeping the saturate/olefin ratio constant. This assumes a common density for these two fractions. The results obtained for several samples are given in Table I and show good agreement between the two methods.

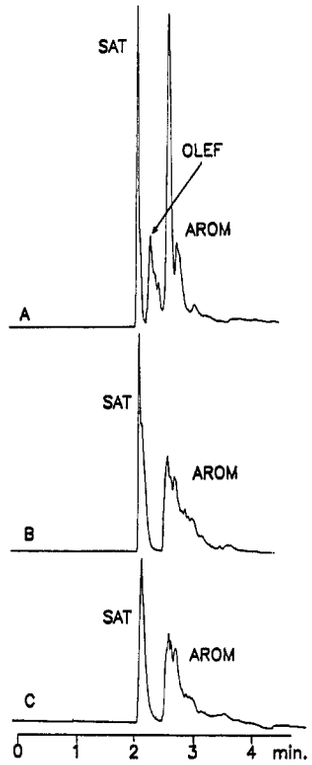

Figure 2. Chromatograms of gasoline (A), kerosene (B), and diesel fuel (C). Saturates are attenuated 8×. Conditions: column temperature, 35 °C; inlet pressure, 3600 psi; outlet pressure, 2600 psi; mobile phase, 3 mL/min of dry carbon dioxide; FID flows, 120 mL/min hydrogen, 600 mL/min air.

Table II. Retention Times of Model Compounds

compound	time, min	compound	time, min
n-dodecane	2.06	1,3-cyclohexadiene	2.44
cyclohexane	2.11	*n*-octylbenzene	2.48
1-heptene	2.17	xylene	2.52
decalin	2.18	tetralin	2.83
1-dodecene	2.21	2-octyne	2.87
cyclohexene	2.28	naphthalene	3.25

Table III. Repeatability of Five Consecutive Determinations, All Results in Weight Percent

sample	saturates	olefins	aromatics	std dev
gasoline	57.7	21.7	20.6	0.44
kerosene	81.1	0.0	18.9	0.74
no. 2 diesel	86.4	0.0	13.6	0.80

Figure 1, which plots weight vs. volume percent aromatics for gasoline and diesel fuel, illustrates that different conversion factors will be required for each different sample type. Conversion of weight to volume percent, in our opinion, serves no useful purpose and would, in fact, reduce the precision of the method. We have obtained excellent agreement for total aromatics and saturates plus olefins between our SFC method and an in-house HPLC procedure which uses a refractive index detector and response factors to determine weight percent in the diesel fuel boiling range.

Figure 2 compares the chromatograms of typical petroleum products. Gasolines may be analyzed directly, without the depentanization required for FIA, since all saturates in the four to twenty carbon range elute together. Table II gives retention times for a number of model compounds. The only "problem" compounds are decalin, a fused ring dicycloparaffin,

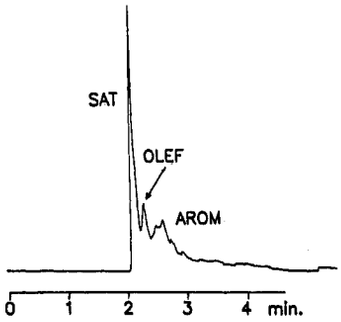

Figure 3. Shale oil (NBS Standard Reference Material 1580). Conditions are given in Figure 2.

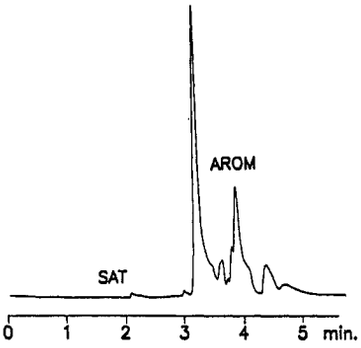

Figure 4. Creosote oil (National Solvents Inc.). Conditions are given in Figure 2.

and octyne. The amount of acetylenic or fused dicyclo-paraffinic material present in samples for which this method is intended is likely to be quite small and should not contribute significant errors to the results. Repeatability of the method for petroleum products is given in Table III. This compares favorably with the FIA method.

This procedure is useful for samples beyond the scope of D 1319 as well. Distillation end points may extend beyond 315 °C, as illustrated by the diesel fuel example (end point 340 °C). Highly colored samples are no problem, allowing coal and shale derived liquids to be analyzed. Figures 3 and 4 show chromatograms of these types of sample. These materials contain polar heteroatomic components not found in petroleum fuels. These are not detected in this analysis, being either irreversibly adsorbed or eluting very slowly. Gasoline frequently contains light alcohols or ethers as fuel extenders and octane enhancers. These oxygenates are not eluted from the columns in this procedure, but their presence in the sample does not affect the observed ratios of saturates, olefins, and aromatics.

CONCLUSIONS

SFC offers a viable alternative to the FIA technique for determining saturates, olefins, and aromatics in gasoline and kerosene and can easily be extended to include the diesel fuel range. This method complements GC and HPLC for characterization of petroleum liquids. In addition, the technique lends itself to materials such as shale and coal derived liquids. The use of an easily modified, commercial FID should open the door to a number of applications of SFC for samples which are too heavy for GC or too light for HPLC or for which desired resolution is not currently available.

Registry No. Silver nitrate, 7761-88-8.

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