Paraffin, Olefin, Naphthene, and Aromatic Determination of Gasoline and JP-4 Jet Fuel with Supercritical Fluid Chromatography

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Abstract

A method that uses supercritical fluid chromatography (SFC) with flame-ionization detection (FID) to determine naphthenes (cycloparaffins), paraffins, olefins, and aromatics in gasoline and JP-4 jet fuel is developed. Four packed silica columns in series are used to isolate the aromatics and provide ring number distribution. In addition, the silica columns provide separation of paraffins from the coeluting olefins and naphthenics. The olefins are trapped on a silver-loaded strong cation-exchange silica gel column and removed by back-flushing. Good agreement is found between gas chromatographic hydrocarbon analysis and the SFC method. A relative standard deviation of 0.4% is found for a jet fuel with a naphthene content of 21.6 wt%. At a low naphthenic content of 1.0 wt%, a relative standard deviation of 3.0% is achieved for gasoline. Analysis times are typically 22 min.

Introduction

Supercritical fluid chromatography (SFC) with flame-ionization detection (FID) has been established for hydrocarbon type analysis of light and middle distillates such as gasoline, jet fuel, and diesel fuel. Currently, SFC–FID is being used as an American Society for Testing and Materials method (ASTM D5186) for the determination of aromatics in diesel fuel (1). SFC–FID breakdown of aromatics into mono-, di-, and tri-rings has been achieved in gasoline, jet, and diesel fuels (2–5). FID provides a nearly uniform response for different hydrocarbon types, which makes calibration unnecessary.

The determination of alkenes in gasoline is important because high olefin content can plug injection nozzles and valves. Aromatic content is of interest because of concerns for pollution and performance. Fluorescent indicator adsorption (ASTM D1319) (6) is a common industry method for the determination of saturates, olefins, and aromatics in fuels. It has been found, however, to suffer from poor precision and reproducibility, and it is time consuming (7). High-performance liquid chromatographic (HPLC) methods for hydrocarbon type analysis of fossil fuels require extensive calibration with commonly used detec-

tors such as ultraviolet or refractive index. Calibration is necessary with these detectors because of the lack of a uniform response to various hydrocarbon classes and the varying molecular structures and molecular weights within these classes.

It has been reported that olefins as well as saturates and aromatics could be quantitated in gasoline, jet fuel, and diesel fuel through the use of an SFC–FID fitted with silica columns and a silver ion cation-exchange column (3,8). Saturates eluting from the silica column pass almost unretained through the cation-exchange column, while the olefins are trapped. Aromatics retained on the silica column are passed directly to the detector. Olefins are back-flushed from the cation-exchange column. CO_2 or 10% CO_2 in SF_6 has been used as the mobile phase.

This work describes the use of four silica columns in series and a silver ion cation-exchange column to obtain a separation of paraffins from naphthenes (cycloparaffins) for gasoline and JP-4 jet fuel. Naphthenic determination is important for the monitoring of catalytic reforming processes which are used for raising the octane number in gasoline. The analysis can be carried out with satisfactory quantitative results even though complete baseline separation between paraffins and naphthenics was not achieved. Olefins and aromatics were also determined. Aromatics can be separated by ring number.

Experimental

Materials

SFC-grade CO_2 was purchased from Matheson (La Port, TX). Standards were obtained from Chem Services (West Chester, PA), Wily Organics (Coshocton, OH), and Aldrich (Milwaukee, WI).

Instruments

A Hewlett-Packard Model G1205A supercritical fluid chromatograph equipped with FID and diode array detection (in split effluent mode) was used. The internal flow configuration was such that one portion of the effluent passed to an integral fused-silica restrictor connected from a tee to the FID. The

other portion of the flow went to the HP Model 1050 multi-wavelength photodiode array detector. The FID was operated at a temperature of 300°C, and the air and hydrogen flow rates were 411 and 48 mL/min, respectively. The CO_2 expanded flow rate from the FID was 6.50 mL/min. The injection valve used was a Rheodyne Model 7410-077 with a 0.5-μL sample loop. Three Rheodyne 7000 6-port valves were used for back-flushing and flow path change. The valves were operated manually. The CO_2 outlet pressure was maintained at a constant 148 atm. The oven temperature was maintained at 29°C.

Four 250-mm × 4.6-mm i.d. columns packed with 5-μm silica particles (HP Aromatic Hydrocarbon Group Separation columns) and a 30-mm × 4.6-mm column packed with Selectosil (5-μm i.d. particle size) silver-loaded strong cation-exchange from Phenomenex (Torrance, CA) were used for this method. Connecting lines were 0.12-mm i.d. tubing.
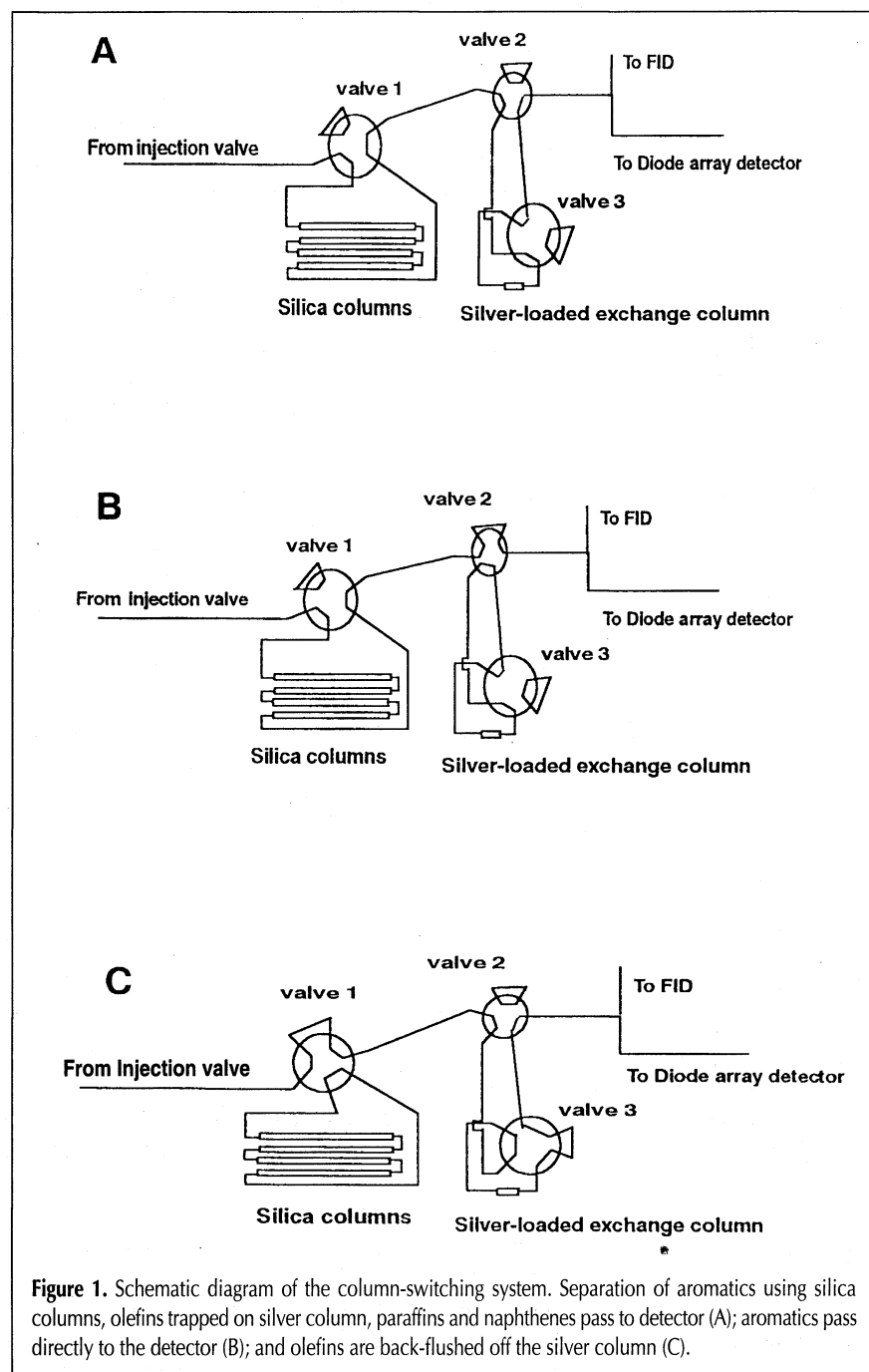
Chromatographic procedure

A multidimensional system with column switching was utilized, as shown in Figure 1. The method does not require any sample preparation, as neat samples can be directly injected. The initial flow rate was 2.5 mL/min. The samples were injected into the silica column series. Paraffins followed by naphthenics with coeluting olefins emerged from the silica column onto the silver ion cation-exchange column where the olefins are retained. Paraffins followed by naphthenics passed through to the FID and ultraviolet detectors (Figure 1A). Valve 2 was switched, and the subsequently eluting separated mono- and di-aromatics passed to the detectors (Figure 1B). Valve 1 then switched the silica columns out of flow and valve 2 opened flow to the cation-exchange column. Valve 3 was switched, and flow to the cation exchange column was reversed (Figure 1C). The mobile phase flow rate was increased to 3.2 mL/min, and the olefins were removed. The ultraviolet diode-array detector confirmed no detectable aromatics eluting with the olefins. The total time of analysis was approximately 22 min.

Preparation of standards used for method validation

Reference standards consisting of several hydrocarbons from the classes studied were mixed together and used to verify the accuracy of the SFC method. The n-paraffins reference standard consisted of 8 compounds in the range of 5–16 carbon atoms. The iso-paraffins standard consisted of 53 compounds in the range of 6–20 carbon atoms. The cycloparaffins consisted of 44 compounds in the range of 5–16 carbon atoms. The olefins, both normal and branched, consisted of 19 compounds in the range of 5–12 carbon atoms. The aromatic standard consisted of 21 alkylated and unalkylated mono-, di-, and tri-nuclear aromatics.
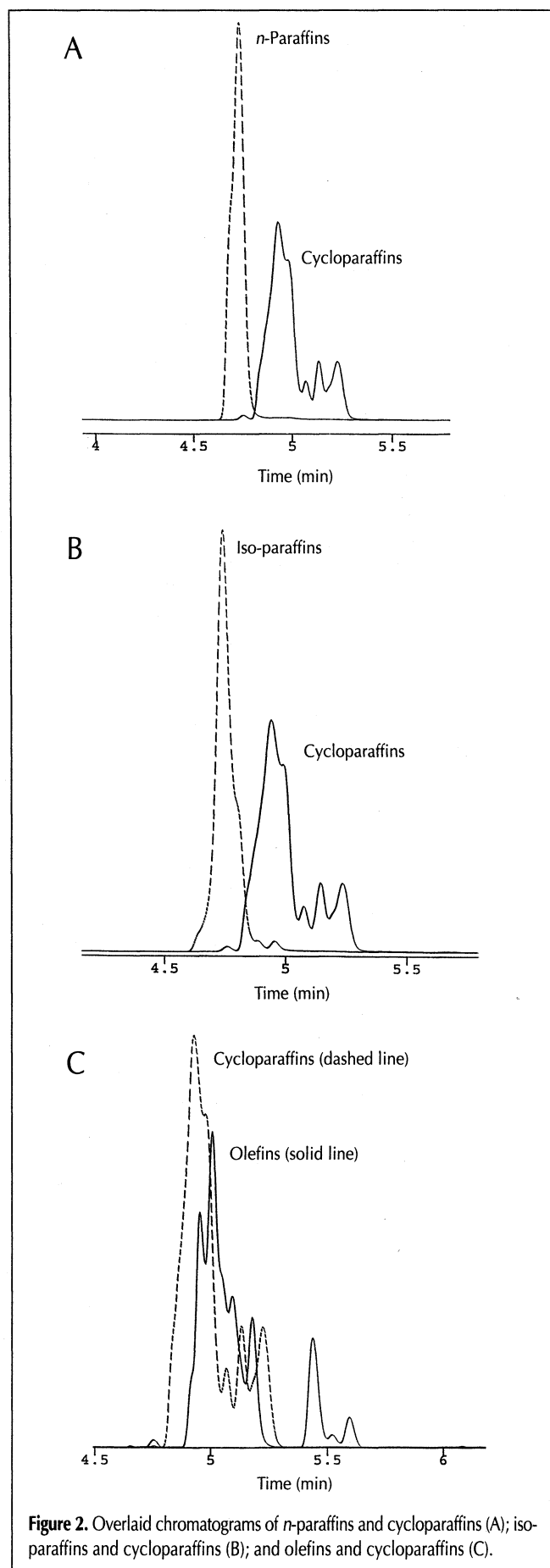
GC analysis

The gas chromatographic quantitation of hydrocarbon types for comparison with the SFC data was accomplished using a single-column PIONA method. A HP 5890 with flame-ionization detection was used with a 100-m x 0.25-mm Supelco Petrocol DH column (Bellefonte, PA). The initial oven temperature was 35°C, and then it was programmed to 220°C with multiple ramp rates. Peak identification was made by comparison to standards and a reference library.

Figure 1. Schematic diagram of the column-switching system. Separation of aromatics using silica columns, olefins trapped on silver column, paraffins and naphthenes pass to detector (A); aromatics pass directly to the detector (B); and olefins are back-flushed off the silver column (C).

Figure 2. Overlaid chromatograms of *n*-paraffins and cycloparaffins (A); iso-paraffins and cycloparaffins (B); and olefins and cycloparaffins (C).
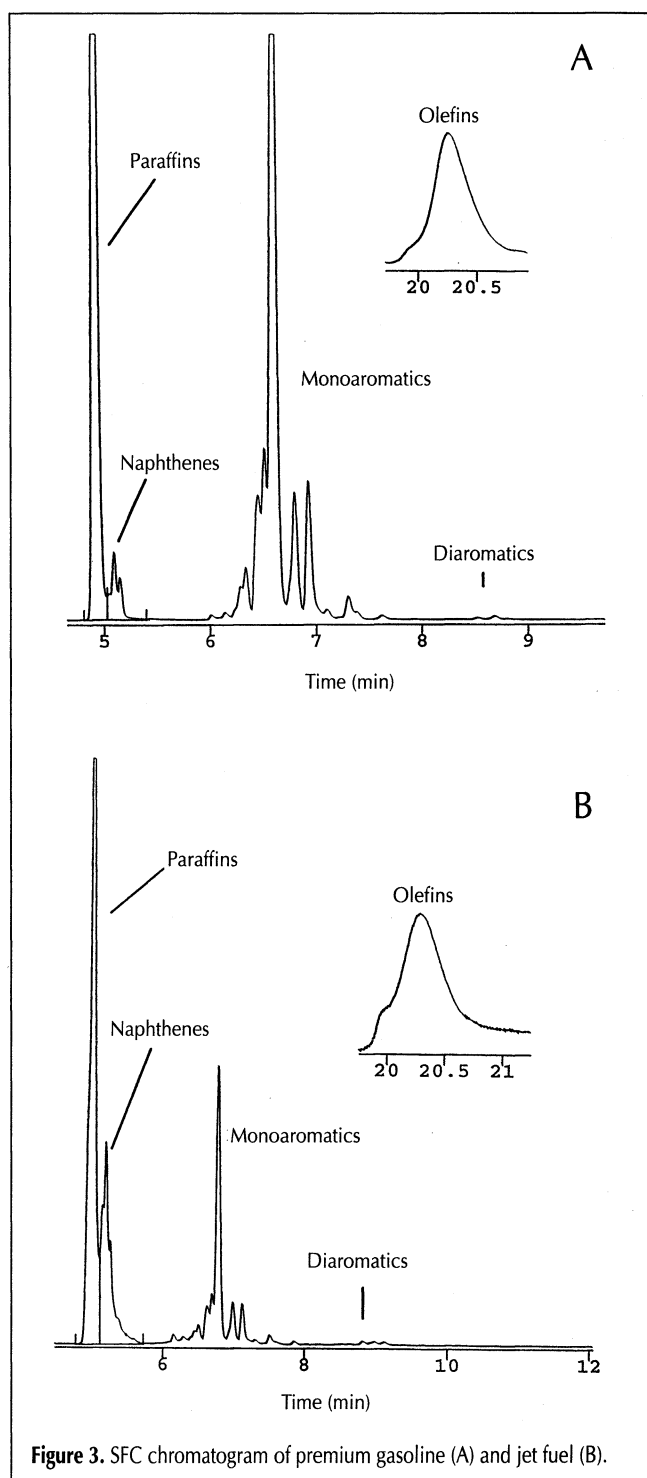
Results and Discussion

The HPLC elution of cycloparaffins as a shoulder after *n*- and iso-paraffins for hydrotreated light cycle oil was noted by Carbognani (9). Four columns in series, the first being dinitroanilinopropyl derivatized silica and the last three being underivatized silica, were used, and Freon 123 was used as the mobile phase.

Carbognani found that cyclopentane and cyclohexane had greater retention times than *n*-alkanes with carbon numbers ranging from 5–28. A sizing effect was also observed for satu-

Figure 3. SFC chromatogram of premium gasoline (A) and jet fuel (B).

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rates and olefins with larger members of a group having increasingly shorter retention times (9,10). For SFC with CO_2 as the mobile phase, packed silica columns were found to give longer retention times for decalin, cyclohexane, and cholestane relative to n-alkanes (7,11).

The following retention times for normal, iso, and cyclic C_{10} compounds were obtained using four HP hydrocarbon silica columns in series: decane, 5.21; 3,5-dimethyloctane, 5.25; 4,4-dimethyloctane, 5.23; n-butylcyclohexane, 5.45; iso-butylcyclohexane, 5.43; tert-butylcyclohexane, 5.50; cis-decalin, 5.78; and trans-decalin, 5.68. The iso-alkane retention times vary little (less than 0.04 min) from the retention time of n-decane. The cycloalkanes, however, show greater retention time differences from n-decane. A retention time difference of close to a half minute was found for both decalins (cis and trans) and paraffins. The magnitude of the separation could suggest a size-exclusion mechanism because the difference in polarity between alkanes and cycloalkanes is small. Optimum separation conditions of alkanes and cycloalkanes were found at an oven temperature of 29°C, a flow rate of 2.5 mL/min, and a constant pressure of 148 atm. At higher temperatures, separation was found to be increasingly governed by compound boiling point.

At temperatures as low as 0°C, a substantial decrease in resolution that was due to peak broadening was observed. The addition of a fifth column did not noticeably improve the naphthenic–paraffinic or aromatic–saturate separation. Other types of silica, nucleosil (5 μm, 120Å), and partisil (10 μm, 85Å) did not give hydrocarbon class separation to the same extent. The HP hydrocarbon silica column pore size was unavailable.

n-Paraffins, iso-paraffins, cycloparaffins, and olefin standards were injected individually into the four silica column series. Figure 2A shows the overlaid chromatograms of n-paraffins with cycloparaffins. A shorter average retention time for n-paraffins was observed. Iso-paraffins show a retention time difference similar to cycloparaffins (Figure 2B). Olefins and naphthenics elute in a similar retention time range as shown in Figure 2C.

Quantitative Analysis

Figure 3 shows the chromatograms of a premium gasoline and commercial JP-4 jet fuel. Because baseline separation was not achieved between paraffins and naphthenics, integration was done by drawing a line from the lowest valley between the two groups to the baseline. Jet fuels with higher boiling ranges than JP-4 (293–518°F) did not give adequate separation of naphthenics and paraffins for quantitative analysis.

Response factors determined from hydrocarbon standards were found to be 1.05, 1.03, 0.93, and 0.96 for paraffins, naphthenes, olefins, and aromatics, respectively. Integrator responses were assumed to represent weight distribution because of the close agreement between these factors. The limit of chromatographic detection was determined to be 0.01 wt% for the tri-aromatic anthracene. The limit of chromatographic detection for olefins and naphthenes was determined with serial dilutions of JP-4 jet fuel. The limits were found to be 0.1 wt% for olefins and 0.2 wt% naphthenics.

Accuracy verification of naphthenic detection and olefin recovery was accomplished by spiking a premium gasoline with a known amount of hydrocarbon and determining the percent recovery. Methylcyclopentane and 1-octene were added to gaso-

Table I. Comparative Analysis of Gasoline Using the SFC and GC Methods*

Fuel		SFC	GC[†]
Premium A	Paraffins	31.46	32.92
	Naphthenics	1.12	1.8
	Olefins	1.58	1.5
	Aromatics	65.83	63.64
Premium B	Paraffins	39.69	42.84
	Naphthenics	3.21	3.56
	Olefins	0.74	0.25
	Aromatics	56.35	53.28
Regular A	Paraffins	39.46	42.7
	Naphthenics	3.36	3.56
	Olefins	0.72	0.23
	Aromatics	56.46	53.35
Regular B	Paraffins	45.11	47.55
	Naphthenics	3.08	3.48
	Olefins	1.22	1.16
	Aromatics	50.58	47.71
Regular C[‡]	Paraffins	26.44	29.5
	Naphthenics	3.3	2.65
	Olefins	39.22	35.2
	Aromatics	31.04	32.9
Regular D	Paraffins	43.59	45.66
	Naphthenics	1.37	2.18
	Olefins	0.77	0.34
	Aromatics	54.26	50.73

* Unidentified compounds account for the remainder of the samples.
[†] Gasoline analysis was done by 100-m capillary GC.
[‡] GC–PIONA was used.

Table II. Comparative of Weight Percent and SFC–FID Area Percent for Standards

	Known wt%	SFC area%
Paraffins	50.19	47.8
Naphthenes	20.12	19.73
Olefins	1.35	1.45
Aromatics	29.08	30.97
Paraffins	33.03	31.79
Naphthenes	7.53	7.24
Olefins	10.72	10.33
Aromatics	48.62	50.63
Paraffins	34.51	32.37
Naphthenes	5.03	4.95
Olefins	0.81	0.95
Aromatics	59.74	61.73

Table III. SFC Repeatability Study

	Paraffins	Naphthenes	Monoaromatics	Diaromatics	Olefins
Gasoline, n = 10					
Average wt%	35.35	1.00	61.22	1.58	0.85
Standard deviation	0.20	0.03	0.20	0.05	0.03
Jet fuel, n = 8					
Average wt%	49.56	21.60	27.10	1.28	0.46
Standard deviation	0.14	0.08	0.09	0.15	0.03

the SFC method are shown in Table II. Reasonable agreement was found between SFC and the known standard mixtures.

Repeatability

Repeatability of the method is shown on Table III for both premium gasoline and jet fuel. Analyses were performed over a 1-month period. A gasoline sample with 1.0 wt% average naphthenics had a relative standard deviation of 3.0%. A jet fuel with 21.6 wt% average naphthenics had a relative standard deviation of 0.4%.

line at both low and high concentrations. The percent recoveries were calculated according to Equation 1:

$$\%Recovery = 100\left(\frac{A-[100-B]C}{B}\right) \qquad Eq\ 1$$

where A is the SFC determined weight percent of the spiked hydrocarbon class, B is the weight percent of added hydrocarbon, and C is the SFC determined fraction of the hydrocarbon class of interest in the original (unspiked) fuel. The original gasoline composition was 35.71 wt% paraffins, 0.98 wt% naphthenes, 61.01 wt% monoaromatics, 1.47 wt% diaromatics, and 0.82 wt% olefins. After being spiked with high and low weight percents of methylcyclopentane (2.1 and 8.5 wt%) and octene (1.13 and 8.9 wt%), the percent recoveries were 107.2 (low) and 98.6 (high) for methylcyclopentane and 112.0 (low) and 110.0 (high) for octene. Jet fuel was also spiked individually with high and low concentrations of known amounts of *t*-decalin (7.18 and 14.3 wt%), dodecene (1.7 and 7.09 wt%), ethylbenzene (6.12 and 12.99 wt%), and 1-methylnaphthalene (1.13 and 3.24 wt%). The percent recoveries were 101.5 (low) and 100.6 (high) for *t*-decalin; 110.0 (low) and 105.6 (high) for dodecene; 98.0 (low) and 101.5 (high) for ethylbenzene; and 112.0 (low) and 108.0 (high) for 1-methylnapthalene. The original jet fuel composition was 50.15 wt% paraffins, 21.27 wt% naphthenics, 27.00 wt% monoaromatics, 1.12 wt% diaromatics, and 0.44 wt% olefins.

The SFC method was compared with gas chromatography (GC) for the analysis of paraffins, olefins, naphthenics, and aromatics. A single column, detailed hydrocarbon analysis by 100-m capillary GC–FID was obtained for regular and premium gasoline samples. The results were compared with the SFC method (Table I). For the high olefin gasoline, (regular unleaded C), difficulties with identifying, separating, and quantitating large numbers of olefin isomers can occur (12). A GC–PIONA analyzer (Analytical Controls; Bensalem, PA) was used in this case. There was good agreement between the GC and SFC methods for paraffins, naphthenics, and aromatics. For olefin samples of less than 1.0 wt%, agreement was off by a factor of 3 in some cases. Better agreement was found for the gasoline samples with olefin concentrations greater than 1.0 wt%.

To further establish the accuracy of this method, the *n*-paraffin, iso-paraffin, cycloparaffin, olefin, and aromatic standards were mixed together at various quantities. The composition in weight percent of the mixtures and the weight percents determined by

Conclusion

The SFC–FID method described here provides a way to determine naphthenics, paraffins, olefins, and aromatics (including aromatic ring distribution). Although complete separation is not obtained between paraffins and cycloparaffins, quantitation seems possible. A size-exclusion mechanism appears to be the mode of separation for paraffin and naphthenic classes, although more work is needed to determine this conclusively. Work is in progress to determine a method that includes the analysis of reformulated gasoline.

Acknowledgment

References

1. *Annual Book of ASTM Standards,* Vol. 05.03. American Society for Testing and Materials, Philadelphia, PA, 1991, Method ASTM D5186.
2. F.P. DiSanzo and R.E. Yoder. Determination of aromatics in jet and diesel fuels by supercritical fluid chromatography with flame ionization detection (SFC–FID): a quantitative study. *J. Chromatogr. Sci.* **29:** 4–7 (1991).
3. P.E. Andersson, M. Demirbuker, and L.G. Blomberg. Quantitative hydrocarbon group analysis of gasoline and diesel fuel by supercritical fluid chromatography. *J. Chromatogr.* **595:** 301–11 (1992).
4. E.N. Chen, Jr., P.D. Cusatis, and E.J. Popiel. Validation of the aromatic ring distribution in diesel fuel refinery streams by supercritical fluid chromatography and mass spectrometry. *J. Chromatogr.* **637:** 181–86 (1993).
5. B.J. Fuhr, L.L. Klein, C. Reichert, and S.W. Lee. Determination of aromatic types in middle distillates by supercritical fluid chromatography. *LC–GC* **8:** 800–804 (1990).
6. *Annual Book of ASTM Standards,* Vol. 05.02. American Society for Testing and Materials, Philadelphia, PA, 1991, Method ASTM D1319.

7. T.A. Norris and M.G. Rawdon. Determination of hydrocarbon types in petroleum liquids by supercritical fluid chromatography with flame ionization detection. *Anal. Chem.* **56:** 1767–69 (1984).

8. R.M. Cambell, N.M. Djordjevic, K.E. Markides, and M.L. Lee. Supercritical fluid chromatographic determination of hydrocarbon groups in gasolines and middle distillate fuels. *Anal. Chem.* **60:** 356–62 (1988).

9. L. Carbognani. Group-type separation of middle petroleum distillates by adsorption and charge-transfer liquid chromatography with dielectric constant detection. *J. Chromatogr.* **663:** 11–26 (1994).

10. P.C. Hayes, Jr. and S.D. Anderson. Hydrocarbon group type analyzer system for the rapid determination of saturates, olefins, and aromatics in hydrocarbon distillate products. *Anal. Chem.* **58:** 2384–88 (1986).

11. E. Lundanes and T. Greibrokk. Group separation of oil residues by supercritical fluid chromatography. *J. Chromatogr.* **349:** 439–46 (1985).

12. R.E. Pauls. Chromatographic characterization of gasolines. *Adv. Chromatogr.* **35:** 294–95 (1995).