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RAPID DETERMINATION OF NAPHTHENES IN HYDROCARBON DISTILLATES USING ON-LINE COLUMN SWITCHING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH DIELECTRIC CONSTANT DETECTION*

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SUMMARY

On-line column switching high-performance liquid chromatography (HPLC) with dielectric constant detection (DCD) can separate and accurately quantify the volume fraction of total cycloparaffins in gasolines and kerosenes having distillation endpoints (ASTM D 2887) of at least 300°C. The three hydrocarbon group-types reported are: acyclic paraffins, cycloparaffins, and unsaturates, *i.e.*, aromatics plus olefins. The HPLC–DCD separations are achieved using an "unsaturate-selective" column, two "naphthenic-selective" columns, two six-port switching valves, and Freon 123 as the mobile phase. Incorporation of one or two additional naphthenic-selective columns could extend the range of samples that can be analyzed to include diesel fuels. The dielectric constant detector ensures a genuine uniformity of response [relative standard deviation $< 2.5\%$] for each hydrocarbon group type independent of the carbon number distribution of the sample. Unity response factors are sufficient for accurate quantitation. On the basis of complex solutions of hydrocarbon standards, the accuracy for each structural group type is within two percent absolute. The chromatographic limit of detection for naphthenes is less than 4.0 vol. % (*ca.* 40 μg) for a kerosene fuel containing a wide carbon number distribution of both mono- and di-cycloparaffins. Sample turnaround time is approximately 40 min.

INTRODUCTION

The abundance of high quality, low cost petroleum crudes and feedstocks is rapidly diminishing. Current feedstocks are incorporating lower grade crudes and off-streams as well as processed liquids from alternate sources of energy, *e.g.*, shale

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oil, tar sands, coal liquids, and biomass materials. The modern petrochemical engineer needs timely and accurate analytical results to optimize refinery operations and monitor product character. Consequently, the analytical chemist must respond faster with more pertinent and accurate compositional detail on samples of a continuously variable nature.

Liquid chromatography (LC) has helped to characterize the group composition of crude oils and hydrocarbon products since the beginning of this century. The kind and relative amount of certain hydrocarbon classes in the matrix can have a profound effect on the quality and performance of the hydrocarbon product. The fluorescent indicator adsorption (FIA) method, ASTM D 1319[1], has served for over 30 years as the official method of the petroleum industry for measuring the paraffinic, olefinic, and aromatic content of gasolines and jet fuels. The technique consists of displacing a sample under isopropanol pressure through a column packed with silica gel, in the presence of fluorescent indicators specific to each hydrocarbon family. Despite its widespread use, FIA has numerous limitations as detailed by Suatoni and Garber[2] and Miller *et al.*[3], and recently by Norris and Rawdon[4].

High-performance liquid chromatography (HPLC), particularly in the normal phase mode, has found great utility in separating different hydrocarbon group types as indicated by Miller *et al.*[3], Chartier *et al.*[5], and Colin and Vion[6]. However, a severe shortcoming of most HPLC approaches to a hydrocarbon group-type analysis is the difficulty in obtaining accurate response factors applicable to different distillate products. Unfortunately, accuracy can be compromised when these response factors are used to analyze hydrotreated and hydrocracked materials having the same boiling range. As Drushel[7] observed, given significant changes in the hydrocarbon distribution within a certain group type, analytical results will be misleading for such samples because of the variation in response with carbon number exhibited by most routinely used HPLC detectors.

Several recent HPLC separation schemes are particularly interesting since they also incorporate detectors not usually associated with conventional hydrocarbon group-type analyses. Matsushita *et al.*[8] employed dual column chromatography with carbon tetrachloride as the mobile phase and infrared detection. Miller *et al.*[3] also investigated the infrared detector but instead used only a single column and Fluorinert FC-72 (perfluoroheptane) as the mobile phase. However, in both cases, the relative response factors spanned a wide range thus limiting the methods to a particular distillate product[3,8]. Norris and Rawdon[4,9] and others[10,11] have reported on hydrocarbon type analyses that employed a supercritical fluid as the mobile phase with flame ionization detection. This method holds great promise owing to the sensitivity and uniformity of response to hydrocarbons that is characteristic of the flame ionization detector.

Thus the ideal detector for a truly versatile and accurate hydrocarbon group-type analysis is one that is sensitive to hydrocarbons, of course, but demonstrates a response that is independent of carbon number. Alfredson and Tallman[12] suggested that a dielectric constant detector, marketed at one time specifically for HPLC[13–18], could offer a viable means of quantitation in a hydrocarbon type analysis of petroleum products. Recent presentations and publications from this laboratory[19–24] have demonstrated the merits of this dielectric constant detector as an integral part of a hydrocarbon group-type analyzer system (patent pending). In one particular appli-

cation of the analyzer system[22–24], a novel method was introduced hitherto referred to as the LC–FIA. This HPLC technique can determine saturates, olefins, and total aromatics in hydrocarbon liquids with distillation endpoints (ASTM D 2887)[1] of at least 400°C. The HPLC separation is achieved using a single, "olefin-selective" columns, a backflush valve, and Freon 123 as the mobile phase. Dielectric constant detection (DCD) ensures a genuine uniformity of response [relative standard deviation (R.S.D.) <2.5%] for each hydrocarbon group-type independent of the carbon number distribution of the sample. Unity response factors are sufficient. On the basis of complex solutions of hydrocarbon standards, the accuracy for each structural group type is within 1% absolute.

More specifically, the accurate determination of cycloparaffins or naphthenes as a group in complex hydrocarbon distillate products of varying distillation ranges that also include kerosenes, has been a formidable analytical task for both spectroscopic and chromatographic approaches. A standard mass spectrophotometric method, ASTM D 2789-81[1], for gasolines uses basic response calibration factors generated using 79 compounds with up to nine carbons. However, kerosenes and jet fuels with a wide boiling range, for example, have hydrocarbons with 15 or more carbon atoms present. To analyze properly these samples, one must include a broader variety of compounds and classes of compounds with overlapping series of molecular ions. Unfortunately, the relative number of possible hydrocarbons available as pure reference compounds diminishes rapidly above nine or ten carbons. Furthermore, introducing a new computer matrix designed for these samples would be both time consuming and expensive. Standards derived from the various fuel types themselves might be a possible solution to the calibration problem.

Although beyond the scope of this paper, most gas chromatographic (GC) routes for measuring total naphthenic content in complex hydrocarbon matrices require intricate column switching and backflushing steps, need identification of individual naphthenes before final summation for reporting, and are limited either to samples without olefins[25] or samples that contain hydrocarbons with less than twelve carbon atoms[26] or both[27,28]. Some clever researchers have even resorted to dehydrogenation microreactors to convert most, but not all, the naphthenes to aromatics for more reliable qualitative identification and subsequent quantitation[29,30].

Miller *et al.*[32,33] submitted that after further optimization, the off-line combination of HPLC and low-resolution GC, *i.e.*, packed GC columns, could provide accurate determination of the hydrocarbon types in gasolines and similar products. Their work was not intended to report the cycloparaffins present, but perhaps incorporation of the proper HPLC column, *i.e.*, one with a selectivity toward naphthenes, could offer a viable, two-dimensional approach for cycloparaffins. Apffel and McNair[33] reported the first on-line coupling of HPLC with capillary GC. However, their system could only admit a small volume of a particular hydrocarbon group type into the capillary column in any one injection. Thus the actual GC profile of any hydrocarbon group type was a function of the sampling time of that peak, due to the molecular sizing that often occurs within an HPLC fraction. Grob, Jr. and Schilling[34] presented an excellent review on the highly attractive advantages of coupled HPLC–capillary GC for total fraction analysis. They advocate the direct and complete transfer of relevant HPLC fractions or peaks from the HPLC into the GC column. However, as before, without an HPLC column that could further fractionate

the saturated hydrocarbons into acyclics and naphthenes, a considerable number of coelutions could occur in the capillary GC separations and thus compromise the accuracy of the total naphthene determination by this coupled technique.

Majors[35], Alfredson[36], and Apffel *et al.*[37] have examined the distinct advantages offered by on-line column switching HPLC particularly as applied to hydrocarbon group-type analyses. By transferring a particular hydrocarbon fraction from one HPLC column operating in one separation mechanism to another column offering different selectivity, the analyst can affect unique separations even on extremely complex hydrocarbon products.

Alfredson[36] introduced a novel HPLC column, henceforth referred to in the present paper as a "naphthenic-selective" column, and a column switching technique that could resolve the cycloparaffins in a wide range of hydrocarbon distillate products[36,38]. However, as noted by Alfredson, accurate quantitation with the refractive index (RI) detector could only be accomplished by using unique response factors laboriously derived for each hydrocarbon product of each different distillation range. As noted above, should the matrix of a new sample vary significantly in carbon number distribution, yet have the same distillation range, the quantitative accuracy for the analysis of that sample could suffer using an RI detector.

Presented herein is a versatile and accurate determination of the naphthenic content of gasoline and kerosene samples distilling up to 300°C that can contain substantial amounts of olefins. The on-line, HPLC column switching method incorporates a novel "unsaturate-selective" column and two naphthenic-selective columns to yield a fractionation of a fuel into acyclic paraffins, naphthenes, and total unsaturates. The fractions are accurately quantitated, without the need of unique response factors, by DCD. This approach is another example of a hydrocarbon group-type analysis using HPLC–DCD.

EXPERIMENTAL

Apparatus

A hydrocarbon group-type analyzer system was configured with the appropriate columns and switching valves to affect a separation of cycloparaffins from complex hydrocarbon matrices. A Varian (Walnut Creek, CA, U.S.A.) Model 4200 liquid chromatograph was used to perform all the analyses in this study. The system has syringe-type pumps and is equipped with a Varian Model 8000 autosampler, a Valco six-port injection valve fitted with a 10-μl sample loop, two Valco six-port backflushing valves, and an Optichrom Model 430 dielectric constant detector (Applied Automations). The electrometer of the dielectric constant detector was set at an amplification range of 1.0 and at an attenuation of 1000 mV full scale. Both the sample cell and the reference cell require flowing environments. However, the flow-rates need not be matched. The reference cell flow-rate was measured to be approximately 0.1 ml/min. The column flow-rate was 1.0 ml/min, but could be increased to significantly reduce the analysis time with minimal deterioration to the separations. A silica guard column (Bio-Rad Labs., Richmond, CA, U.S.A.) preceded the analytical columns to adsorb polar heteroatomic compounds present in the injected samples. The total system backpressure was less than 1000 p.s.i.g. All analyses were performed under ambient conditions.

Dielectric constant detector

Basically, the dielectric constant detector responds to a change in a bulk property (dielectric constant) of the mobile phase. The capacitance of two nearly identical parallel-plate capacitors is monitored. One capacitor (reference cell) has simply pure mobile phase flowing through it. The other capacitor (sample cell) has the HPLC column eluents passing through it. Any difference in capacitance is converted to an analog output signal for data collection and reduction.

When the DCD is used in unison with a mobile phase of high dielectric constant, the detector performs as a universal hydrocarbon analyzer. In this mode, the detector has a high sensitivity for hydrocarbon species. More importantly, the dielectric constant detector responds, on a volume fraction basis, independent of the carbon-number distribution of the sample type or the hydrocarbon group type.

The dielectric constant detector is not commercially available as a laboratory unit. However, Applied Automations is pursuing the re-introduction of the detector to the HPLC market.

Unsaturate-selective column

An experimental, unsaturate-selective HPLC column was used for separating the saturates from the unsaturates. The column was 150 × 4.6 mm I.D. and contained 5-μm silica particles that had been bonded to a strong cation-exchange stationary phase. The silver form of the ion-exchange column was prepared by the *in situ* flushing with aqueous silver nitrate. The lifetime of the column is as yet undetermined but is certainly longer than three months for all the applications examined in this study. The column is regenerated when the saturates are barely baseline resolved from the unsaturates. Versions of the unsaturate-selective column are now under evaluation by two HPLC column manufacturers, *i.e.*, silica-based (Whatman, Clifton, NJ, U.S.A.)[39] and resin-based (Bio-Rad Labs.)[40].

Naphthenic-selective column

Two Varian MicroPak PONA analysis columns[12] were custom packed in Freon 123[41]. These columns have a micro-particulate, organic gel that demonstrates a unique selectivity to saturated hydrocarbons providing separation into normal plus branched or acyclic paraffins and naphthenes. The PONA columns are of preparative size, *i.e.*, 300 × 7.5 mm I.D., and larger injection volumes are required for adequate sensitivity.

Reagents

Freon 123, *i.e.*, 2,2-dichloro-1,1,1-trifluoroethane (Halocarbon Products) was used for the mobile phase since it has both a relatively low solvent strength and a sufficiently high dielectric constant. The mobile phase was filtered to remove any particulates above 0.45 μm in size. Samples were prepared for analysis by diluting them *ca.* 1:15 in Freon 123. This was accomplished by using a micropipetter to deliver approximately 200 μl of sample into an HPLC autosampler vial and diluting with mobile phase (*ca.* 1500 μl total solution). This dilution factor ensured that sample concentrations were still within the linear dynamic range of the detector[20].

Procedure

The combination of Freon 123 with the unsaturate-selective column and the naphthenic-selective columns affected an isocratic separation of gasoline and kerosene into three general group types, *i.e.*, acyclic paraffins, cycloparaffins, and unsaturates. Just what hydrocarbon species eluted in what peak was ascertained from injections of over 100 pure reference standards (Wiley Organics).

A diluted sample of a hydrocarbon distillate was injected into the chromatographic system via a 10-μl sample valve. The actual valve sequencing is illustrated in Fig. 1. In Fig. 1A, the aromatics and olefins were retarded on the unsaturate-selective column while the saturates were eluted and entered the naphthenic-selective columns. Valve A was then rotated. In Fig. 1B, the saturates were separated and eluted from the naphthenic-selective columns and into the dielectric constant detector. Meanwhile, the aromatics and olefins were trapped in the unsaturate-selective column. To better accomodate the analysis of a wide range of distillate products, the predetermined time for switching valve A was set at 120 s at a flow-rate of 1.0 ml/min. After the retention time of *cis*-decalin had elapsed, *i.e.*, 1660 s, Valve B was then turned. In Fig. 1C, the unsaturates were thus back-flushed as a single, sharp peak. Both Valves A and B were then returned to their original positions and the system permitted to reequilibrate prior to the injection of the next sample. Under these conditions, sample turnaround time was approximately 40 min.

Chromatographic runs of complex standard mixtures of known hydrocarbon group-type composition indicated that unity response factors were sufficient to give accurate analytical results. Quantitation was accomplished on a Hewlett-Packard 3357 laboratory automation system. Perpendicular baseline drops displayed in the chromatograms were automatically determined by the computer without operator intervention.

RESULTS AND DISCUSSION

Qualitative analysis

To establish the appropriate elution window for each hydrocarbon group type separated by the HPLC columns, over 100 hydrocarbon reference compounds were chromatographed in the system described in the previous section. Clearly defined elution envelopes were found for the three general group types. Analyzing complex real-world fuel samples, however, can present separation difficulties not realized from the analyses of individual compounds or simple standard solutions. To confirm the integrity of the group-type separations, a complex, real-world jet fuel sample, *i.e.*, 85-POSF-2265, was chromatographed and fractions collected of each hydrocarbon group. Each fraction was subsequently analyzed by on-column, high-resolution capillary GC–mass spectrometry (MS) to determine the extent of overlap of the different group types. At least fifteen major and several minor, randomly selected peaks from each fraction were scanned. Their spectra were compared to the National Bureau of Standards (NBS) library and a local in-house library on the data station. In all cases, the comparisons confirmed that at least 95% if not all of the peaks of each fraction were members of the appropriate hydrocarbon group type.

In general, a molecular sizing of the saturates occurred within the naphthenic-selective columns. For both the acyclic and the cycloparaffinic group types, mole-

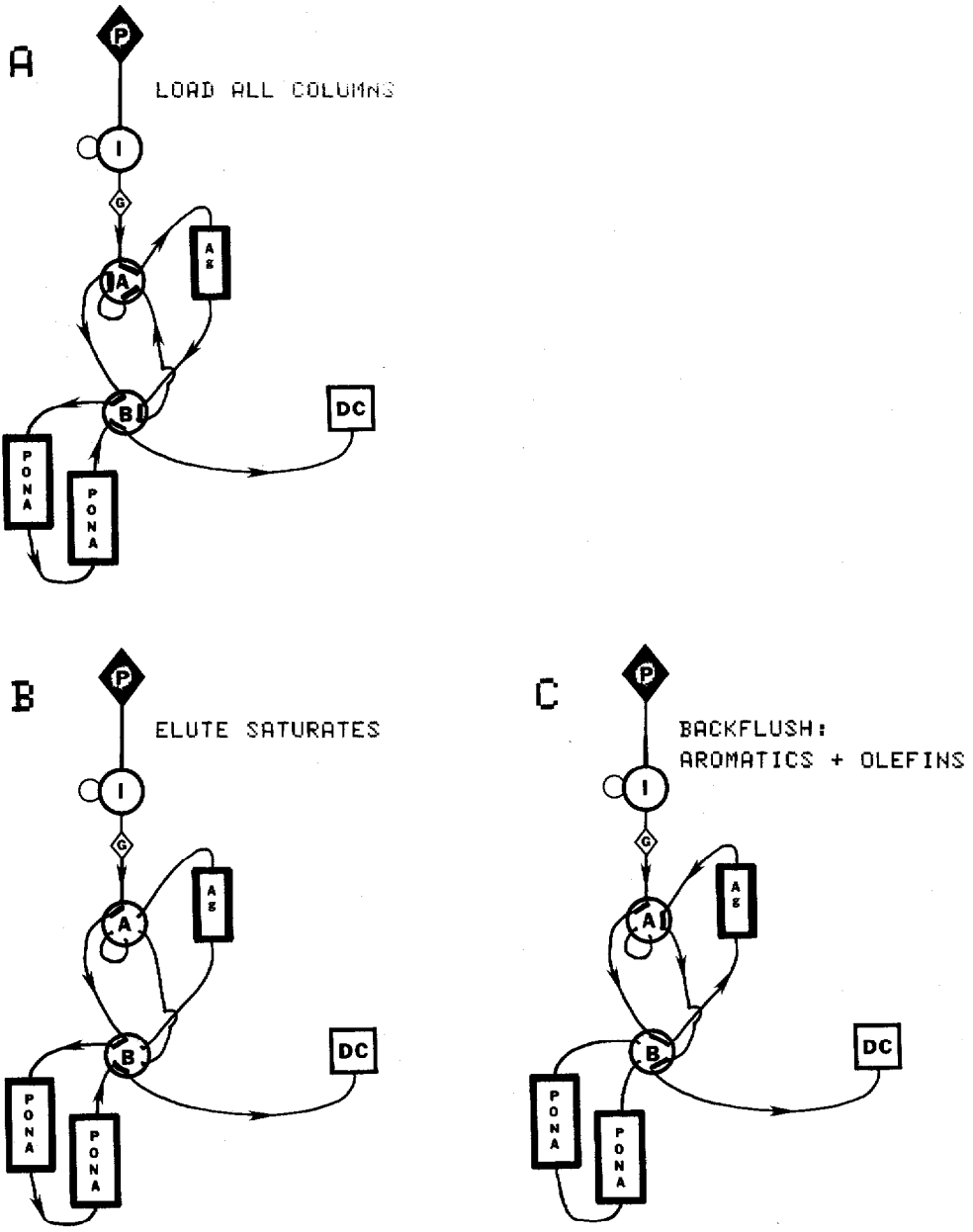

Fig. 1. Multidimensional HPLC–DCD valve-switching configurations. Note that arrows indicate path of flow. P = HPLC pump; I = injector; G = guard column; A, B = switching valves; Ag = unsaturate-selective column; PONA = naphthenic-selective column; DC = dielectric constant detector. (A) Loading Ag column with unsaturates and PONAs with saturates; (B) eluting acyclics–naphthenes; (C) backflushing unsaturates.

cules with a higher degree of alkyl substitution and/or a longer carbon backbone eluted earlier than did smaller molecules. The last acyclic saturates to elute were C_5 and C_6 compounds. The earliest cycloparaffins to elute were the highly substituted alkylcyclohexanes. Employing only two naphthenic-selective columns, some, but not all, cyclohexanes with alkyl substituents containing a total of four or more carbon atoms would coelute with the C_5 and C_6 compounds of the acyclic peak. The last cycloparaffin to elute was *cis*-decalin. Polycyclic saturated hydrocarbons, though not studied extensively in this paper, would elute, again depending on the degree of substitution, after *cis*-decalin. Substituted alkylcyclopentanes eluted somewhere between the alkylcyclohexanes and the alkyldecalins.

It was theorized that for gasoline-range samples, the volume fraction of the C_{10} alkylcyclohexanes would be small and their overlap with the C_5 acyclic paraffins would introduce negligible error. For kerosene-range samples, the smallest acyclic hydrocarbons present would be C_9 and C_{10} compounds. It was found that some, but not all, cyclohexanes with alkyl substituents containing a total of six or more carbon atoms would coelute with a C_8 acyclic paraffin. However, it was theorized that the volume fraction of C_8 acyclic paraffins would be small and their overlap with the C_{12} alkylcyclohexanes would result in negligible error. The most difficult sample for this system to analyze would be a wide-boiling hydrocarbon product with a high volume fraction of C_5 and C_6 acyclics and a correspondingly large amount of C_{10} and larger alkylcyclohexanes. In that case, it is recommended that additional naphthenic-selective columns be added to the system for increased resolution.

For the unsaturate-selective column, the first unsaturated hydrocarbons to elute in the forward flow direction were the largest alkylbenzenes of the sample. For this study, a C_{14} alkylbenzene, *i.e.*, *n*-octylbenzene, was selected. If alkylbenzenes of considerably larger size were present in a distillate product, and the switching time of vale A were not adjusted accordingly, those aromatics might pass through and enter the naphthenic-selective columns. These larger alkylbenzenes would then elute in the middle of the cycloparaffin peak. The last alkylbenzene to elute was benzene, which demonstrated considerable tailing. Higher-molecular-weight alkylnaphthalenes, alkyldiphenyls, and three-ring polynuclear aromatic hydrocarbons would not have eluted from the column in any practical time frame in the forward flow direction. Over 36 olefins having carbon numbers between C_5 and C_{16} were also investigated[24]. Internal and terminal mono-olefins, conjugated and unconjugated di-olefins, cyclo-olefins, and aromatic cyclo-olefins all were not eluted in a practical time frame. However, when the direction of flow was reversed in the unsaturate-selective column, all of the aromatics and the olefins studied were backflushed within the same single, sharp peak.

Until now the discussion has focused solely on the hydrocarbon matrix, ignoring the potential interference from polar additives and impurities. Over, 30 heteroatomic compounds that have a high probability of occurring as polar material in a hydrocarbon distillate product were chromatographed as a composite mixture[24]. The vast majority of polar compounds are either irreversibly adsorbed on the silica guard column or elute outside the retention windows of the hydrocarbon group types. It is possible, though, that a few polar compounds could elute with or adjacent to a hydrocarbon group. However, polar species usually have high dielectric constants, *i.e.*, close to that of the mobile phase, and the detector, as a result, would be insen-

sitive to their presence. Apparently, a large amount of polar materials in a hydrocarbon distillate product should have no interference in the determination of the hydrocarbon ratios.

Quantitative analysis

To establish the quantitative accuracy of the hydrocarbon group-type analyzer system, a series of complex solutions of known group-type composition were chromatographed[24]. Blending solvents were used wherever applicable to increase sample complexity and more closely mimic different product types. The composition of a typical standard solution, *i.e.*, the "simulated" high density kerosene JP-8X mix is presented in Table I. As indicated, besides including decalins (*cis,trans*), the cycloparaffins varied markedly in carbon number and ring size. The individual naphthenes used in the composite mixture were as follows: 1,2-dimethylcyclohexane (*cis,trans*), methylcycloheptane, *cis*-1-ethyl-2-methylcyclopentane, 1,1-dimethylcyclohexane, *cis,trans,trans*-1,2,4-trimethylcyclohexane, *cis,cis,trans*-1,3,5-trimethylcyclohexane, 1,2,3,4-tetramethylcyclopentane (mixed isomers), *tert.*-butylcyclohexane, *cis*-1-methyl-4-isopropylcyclohexane, *trans*-1,1,3,5-tetramethylcyclohexane, 1,2,3,5-tetramethylcyclohexane (mixed isomers), 1-*tert.*-butyl-4-methylcyclohexane, (2-methylbutyl)-cyclohexane, 1,1,3,3,5-pentamethylcyclohexane, 1-methyl-2-*n*-butylcyclohexane, 1-isobutyl-2,5-dimethylcyclohexane, 1,2,4-trimethyl-4-isopropylcyclohexane, 1,2-di-*n*-propylcyclohexane. This standard solution was analyzed by capillary GC–MS and shown to contain several hundred compounds. The exact amount of each compound in each blending solvent is not known. However, mass spectrometric analysis found each solvent to be 99+ wt.% pure relative to the hydrocarbon group type it was meant to represent.

TABLE I

PREPARATION OF STANDARD MIX: "SIMULATED" HIGH DENSITY KEROSENE JP-8X

Hydrocarbon group-type	*Blending stocks/pure components*	*Vol.%*
Saturates	–	92.0
normal + branched	–	12.0
	"Isopar C" (Exxon isoparaffinic solvent, b.p. = 98–106°C)	6.0
	"Isopar M" (Exxon isoparaffinic solvent, b.p. = 207–254°C)	6.0
cycloparaffins	–	80.0
	Decalins (*cis,trans*)	60.0
	Composite mixture of C_8–C_{12}	20.0
Aromatics	Composite blend: xylene bottoms (C_8–C_{10} benzenes) + tetralin	8.0
Olefins	–	0.0

The relative amounts of each of the hydrocarbon group types were deliberately varied from one standard solution to the next. Overall, the different hydrocarbon group types covered a wide range of volume fractions as follows: aromatics from 8 to almost 50 vol.%, olefins from 0 to 10 vol.%, and naphthenes from 10 to 80 vol.%. The standard solutions were then chromatographed on the HPLC–DCD system. The absolute errors found for each group type are displayed in Table II. The results

TABLE II

ABSOLUTE ERROR OF HPLC–DCD METHOD FOR NAPHTHENES

Standard solution	*Hydrocarbon group-type*	*Known vol.%*	*Found vol.%*
VN-82-216	Acyclics	26.6	28.8
	Naphthenes	24.5	22.5
	Aromatics	48.9	–
	Olefins	0.0	–
	Total unsaturates	48.9	48.7
Synthetic gasoline	Acyclics	56.0	54.4
	Naphthenes	10.0	11.2
	Aromatics	24.0	–
	Olefins	10.0	–
	Total unsaturates	34.0	34.4
Synthetic JP-8X (kerosene jet fuel)	Acyclics	12.0	12.8
	Naphthenes	80.0	79.0
	Aromatics	8.0	–
	Olefins	0.0	–
	Total unsaturates	8.0	8.2

clearly indicate the excellent quantitative accuracy afforded by the HPLC–DCD method. The most significant feature of the quantitative analysis of hydrocarbon group types by HPLC–DCD is that unity response factors yield accurate results regardless of the carbon number distribution of a particular group type or sample.

The repeatability of the HPLC–DCD system was determined over a two-month period using a high-density kerosene jet fuel sample (POSF-2265) as shown in Table III. Again, the quantitative repeatability for this sample was excellent.

The limit of chromatographic detection is crucial in evaluating any new HPLC technique. This limit of detection incorporates the band broadening contributions of the sample injection loop (10 μl), the guard column, the analytical columns, all the interconnecting tubing, the switching valves, and the dead volume of the detector (*ca.* 23 μl). For the hydrocarbon group type of particular interest in this analysis, *i.e.*, the naphthenes, serial dilutions of the kerosene sample (POSF-2265) were made. The chromatographic limit of detection for naphthenes was found to be less than 4.0

TABLE III

HPLC–DCD REPEATABILITY STUDY

Analyses performed over a two-month period. Sample: kerosene JP-8X sample (POSF-2265).

Hydrocarbon group-type	*Mean vol.% HPLC–DCD (MS)*	*n*	*S.D.*	*R.S.D.(%)*	*Range*
Acyclics	8.7 (9.3)	5	0.4	4.4	0.8
Naphthenes	68.6 (70.6)	5	0.4	0.6	0.9
Unsaturates	22.8 (20.0)	5	0.5	2.2	1.4

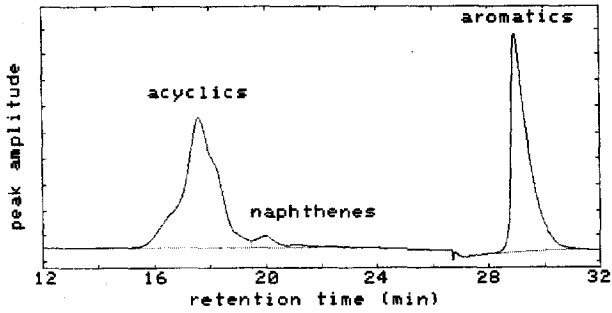

Fig. 2. HPLC–DCD profile of unleaded gasoline sample (B).

vol.% (*ca.* 40 μg). This is a worse case example since the naphthenes found were actually a wide carbon number distribution of mono- and di-cycloparaffins. These naphthenes included alkylcyclopentanes, alkylcyclohexanes, and alkyldecalins. Part of the reason the naphthenes peak was so broad was that partial separation was occurring by ring number.

A gasoline sample and three kerosene jet fuel samples having widely different aromatic, olefinic, and naphthenic contents were examined. These samples were also comparatively analyzed by several techniques. Typical HPLC–DCD profiles of these sample types are displayed in Figs. 2 and 3. The corresponding comparative analyses are provided in Table IV. The first method listed in Table IV, *i.e.*, HPLC–DCD, is the new, proposed column switching technique for determining total naphthenes. The second method listed in the tables is MS, which is a standard mass spectrometric method, ASTM D 2789[1], for measuring cycloparaffins but which had not, however, been calibrated specifically for kerosene samples. The third method given is LC–FIA which is the HPLC–DCD method for measuring the saturates, olefins, and aromatics in hydrocarbon products[22–24]. The final method provided, *i.e.*, FIA, is the standard liquid displacement method, ASTM D 1319[1], that reports the same hydrocarbon groups as LC–FIA.

The proposed column switching technique for measuring the total naphthenic content of gasolines and kerosenes has a fundamental advantage over MS techniques.

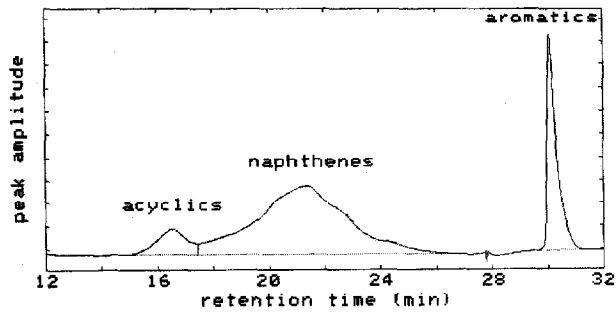

Fig. 3. HPLC–DCD profile of experimental kerosene jet fuel sample (POSF-2265).

TABLE IV

COMPARATIVE ANALYSES OF VARIOUS HYDROCARBON DISTILLATE PRODUCTS BY HPLC–DCD (Vol.%)

Sample code	*Hydrocarbon group-type*	*HPLC–DCD*	*MS*	*LC–FIA*	*FIA*
Unleaded gasoline (B)	Acyclics	53.3	47.0	–	–
	Naphthenes	3.6	16.7	–	–
	Total saturates	56.9	63.7	57.6	52.0
	Olefins	–	(10.0)	11.0	10.0
	Aromatics	–	26.3	31.4	38.0
	Total unsaturates	43.1	36.3	42.4	48.0
Kerosene (POSF-2264)	Acyclics	8.8	10.7	–	–
	Naphthenes	39.6	44.9	–	–
	Total saturates	48.4	55.6	49.8	45.9
	Olefins	–	(0.6)	0.0	0.6
	Aromatics	–	43.8	50.2	53.5
	Total unsaturates	51.6	44.4	50.2	54.1
Kerosene (POSF-2265)	Acyclics	8.2	9.3	–	–
	Naphthenes	69.0	70.6	–	–
	Total saturates	77.2	79.9	77.8	74.2
	Olefins	–	(0.5)	0.0	0.5
	Aromatics	–	19.5	22.2	25.3
	Total unsaturates	22.8	20.0	22.2	25.8
Kerosene (POSF-2268)	Acyclics	7.7	5.3	–	–
	Naphthenes	89.0	92.1	–	–
	Total saturates	96.7	97.4	97.2	95.1
	Olefins	–	(0.0)	0.0	0.0
	Aromatics	–	2.6	2.8	4.9
	Total unsaturates	3.3	2.6	2.8	4.9

All MS methods can directly analyze only low-olefinic distillates because of an inherent inability to differentiate between olefinic and naphthenic moities. For those samples containing significant levels of olefins, the standard FIA method is often performed and the olefins found are then subtracted from the appropriate MS data to ascertain total naphthenic content. The data enclosed in parentheses in Table IV under the MS column designate olefinic results determined by the FIA. Obviously, any inaccuracies present in the FIA determinations for olefins are thus incorporated into the MS results for cycloparaffins. In addition, it is believed that the LC–FIA results for total unsaturates are extremely accurate. Note that the HPLC–DCD results for total unsaturates closely match the LC–FIA results. However, the MS determinations for total unsaturates are consistently too low, compared to the results of all the other analytical methods shown in Table IV. This means that a substantial error could exist in the saturates portion of the MS results. Consequently, the absolute accuracy of the total naphthenes reported for all the samples analyzed by MS is in doubt.

CONCLUSIONS

The hydrocarbon group-type analyzer system described in this paper can accurately measure the naphthenic content of gasoline and kerosene products without operator intervention. Diesel fuels and light oils could also be analyzed if one or two additional naphthenic-selective columns are incorporated. The quantitative results are directly determined in volume percent. The presence of light hydrocarbons (C_4 and C_5), highly colored species, and/or polar heteroatomic compounds does not affect the hydrocarbon ratios. Use of unity response factors gave analytical results within one to two percent absolute for complex standard solutions.

Any isocratic HPLC system can perform this analysis with minor modification, if any, to accommodate the volatile Freon 123 (b.p. = 27°C). The mobile phase required for this application is rather expensive, *i.e.*, US $ 310/gallon, but can be recycled several times without special treatment to significantly reduce the actual solvent cost per run. A simple, one-plate distillation can readily purify the mobile phase, if desired.

Future work will substitute analytical size versions of the PONA column, *i.e.*, 300 × 4.6 mm I.D., and employ at least four of them in series. The lower dispersion offered by the analytical size columns could significantly sharpen the peaks eluting in the saturates time window, thus lowering the chromatographic limit of detection for naphthenes. Furthermore, twice as many PONA columns in series could also improve the resolution of the acyclics from the naphthenes to the point that diesel fuels and light cycle oils could also be analyzed.

Total automation can be achieved with an autosampler, electronically controlled switching valves, and a computing integrator. The adaptability of this method to on-line process stream analysis may be fairly easy, since the detector is already an integral part of a commercially available process liquid chromatograph (Applied Automations).

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