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HYDROCARBON GROUP ANALYSIS OF GASOLINES WITH MICROBORE SUPERCRITICAL FLUID CHROMATOGRAPHY AND FLAME IONIZATION DETECTION

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SUMMARY

Hydrocarbon group separation of gasoline was performed with supercritical fluid chromatography and flame ionization detection. Silica microbore (1 mm I.D.) columns were used in conjunction with sulfur hexafluoride (SF_6) to affect separation between paraffins and olefins. Aromatics were eluted, without backflushing, by means of a simultaneous step-program of pressure, flow and temperature. A conventional flame ionization detector was used, except that the collector was gold-plated in order to prevent corrosion and a special adapter was used to connect the column to the detector via a fused-silica restrictor (10 μm I.D.). This interface design was shown to cause minimal extra-column band broadening. The lower flow-rates inherent to microbore columns required no flow-splitting, neither at the injector nor at the detector side. Control over the activity of the packing material resulted in excellent short- and long-term precision of retention times. This was accomplished by means of an in-line guard column or by using SF_6 with a very low water content. This supercritical fluid chromatographic method offers an attractive alternative to the classical fluorescent indicator adsorption method and to proposed liquid and gas chromatographic methods in that specific advantages of the latter techniques are combined. Analysis time is *ca.* 15 min.

INTRODUCTION

The analysis of hydrocarbons in petroleum samples has long been a challenging problem for analytical chemists. In addition to physical data, *e.g.* boiling range, density, fuel ignition properties, etc., knowledge of the chemical composition of specific fractions and individual components within the fractions can provide important information on feedstock material, and products, and may ultimately contribute to process control and quality assurance. At present, capillary chromatographic methods permit several hundreds of components to be determined in one analysis. While a detailed composition profile of a particular sample may be required in some cases, a knowledge of the relative amounts of specific hydrocarbon groups is of more practical interest.

For over 30 years, the fluorescent indicator adsorption (FIA) method has been

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used for the determination of paraffins, olefins annd aromatics in gasoline and jet fuels. This method, ASTM D1319[1], involves the use of fluorescent dyes in conjunction with classical liquid-displacement chromatography, followed by detection of the various zones (corresponding to hydrocarbon groups) under UV light. The limitations of the FIA method are well documentated in the literature[2]: relatively long analysis time, poor precision and limited applicability to materials containing significant amounts of pentane or lighter fractions, or to materials with end points above 315°C.

A recent review covers the analytical chemistry of gaseous and liquid petroleum fuels[3], while gas chromatographic (GC) methods are summarized by Smith and Paulsen[4]. Both high-performance liquid chromatography (HPLC) and capillary GC have been employed to overcome the difficulties encountered with the FIA method. Dedicated capillary GC and HPLC instruments, including software packages for the analysis of paraffins, olefins, naphthenes and aromatics ("PONA"), are currently commercially available. For state-of-the-art GC/HPLC methodology, as well as for an excellent historical overview of hydrocarbon group analysis, the reader is referred to a series of articles by Johansen, Ettre and Miller[5–7]. Briefly, the authors concluded that with capillary GC, the identity of virtually every peak must be known to achieve accurate quantitation; this necessitates extensive calibration and use of software in order to reduce analysis time. Therefore, combined HPLC–GC was proposed to facilitate identification[7].

HPLC does have the potential advantage of true group fractionation. Suatoni *et al.*[8] employed a low-polarity fluorocarbon (FC-78) as mobile phase for separations on silica columns. Matsushita *et al.*[9] described a dual-column system for obtaining group separations. One column consisted of silica and the other of silver-impregnated silica, which selectively retains the olefins. This principle, also known in the literature as "argentation chromatography", was recently utilized by Norris and Rawdon[10] for work with supercritical fluid chromatography (SFC). Alfredson[11] described a PONA separation on a polystyrene–divinylbenzene packing using hexane as the mobile phase. Apfel and McNair[12], Alfredson[13] and Miller[14] used multidimensional column-switching techniques for the analysis of gasoline, oil and solvent-refined coal samples. Backflushing techniques were employed by Dark[15] to separate polar compounds from saturates and aromatics and, more recently, by Miller *et al.*[5] to separate paraffins, olefins, and aromatics with a fluorocarbon mobile phase. However, a major concern in HPLC is detection.

A flame ionization detector (FID) would be a logical choice for use in HPLC, since in GC the response factors for individual hydrocarbon components are almost equal[4,5]. Although a commercial detector for HPLC has been introduced recently, it appears that this detector is not suitable for lighter petroleum fractions such as gasolines[16]. In contrast to the flame ionization detector, a refractive index (RI) detector does not provide equal response for individual components[6,8], as the RI detector varies considerably for each component. Consequently, the (relative) peak area is not proportional to concentration, and the detector must be calibrated. Infra-red (IR) detection is reported to yield more uniform response factors and has been suggested as a useful alternative[6,9]. However, the IR detector suffers from poor detection limits.

The use of SFC with conventional HPLC columns and flame ionization de-

tectors for hydrocarbon group analysis was demonstrated by Norris and Rawdon[10]. Clearly, SFC shows potential for those analyses that are too difficult to perform with either HPLC or GC. From a chromatographic perspective, the low viscosity, high diffusivity and solvating power of supercritical fluids are attractive features. Design constraints make few HPLC instruments directly compatible with SFC. For example, pressure programming requires a software control that is not available on many conventional HPLC systems[17]. Recently, we have demonstrated the use of a dual syringe Micropump for SFC[18,22]. Like Matsushita *et al.*[9], Norris and Rawdon have used a silver-impregnated silica column to affect the paraffin/olefin separation, with carbon dioxide as the mobile phase. Our initial efforts to duplicate this work suffered from rather poor column-to-column reproducibility, presumably due to difficulties in controlling the homogeneity and amount of silver in the packing. Currently, the method of Rawdon and Norris is under investigation by an ASTM study group.

In HPLC, microbore columns (*i.e. ca.* 1 mm I.D.) have the advantage of low solvent consumption, while interfacing to GC-type (*e.g.* mass spectrometric, flame photometric, etc.) detectors is facilitated[19,20]. For example, a recent paper has shown that when conventional HPLC columns are employed with SFC–FID, flow splitting is required prior to detection[21]. On the other hand, the extremely small dimensions of capillary columns necessitate an inlet splitter in the SFC system to follow the injection valve[17].

The purpose of this paper is to determine whether SFC–FID, combined with packed microbore columns and minimal instrument modifications, can provide a valid approach to the hydrocarbon group analysis of gasolines. The key to group separation is the selection of a novel solvent with low solvent strength, sodium hexafluoride (SF_6). Optimized temperature and pressure conditions are selected to fine-tune the analysis. Finally, the results of the analysis of gasoline samples by SFC are compared with the results obtained by the FIA method.

EXPERIMENTAL

Instrumentation

A Model G micropump (Brownlee Labs, Santa Clara, CA, U.S.A.) with software REV F was used for fluid delivery. Only one of the two syringes of the micropump was used, and the pump was operated in the constant-pressure mode. The liquified gas, SF_6 (minimum purity 99.8%), was supplied from a small 7-lb. cylinder. The cylinder was positioned upside down and connected by means of a stainless-steel tube (12 cm × 1/8 in. O.D.) and a Swagelok (1/4–1/8 in.) female connector (Sunnyvale Valve and Fittings, Sunnyvale, CA, U.S.A.) to the micropump. The pump was easily filled with liquified gas, without cooling the pump, as previously described[18].

A Model 5890 gas chromatograph (Hewlett-Packard, Avondale, PA, U.S.A.) with flame ionization detector was used for maintaining supercritical temperatures (oven temperature 50°C) in the column and detector. The hydrogen flow-rate for the detector was 75 ml/min, the air flow was 370 ml/min, and the temperature was maintained at 250°C. The FID was equipped with a capillary liner and jet, and was connected, without flow-splitting, via a 7 cm × 10 μm I.D. fused-silica restriction tube (Scientific Glass Engineering, Austin, TX, U.S.A.) to the microbore column. For

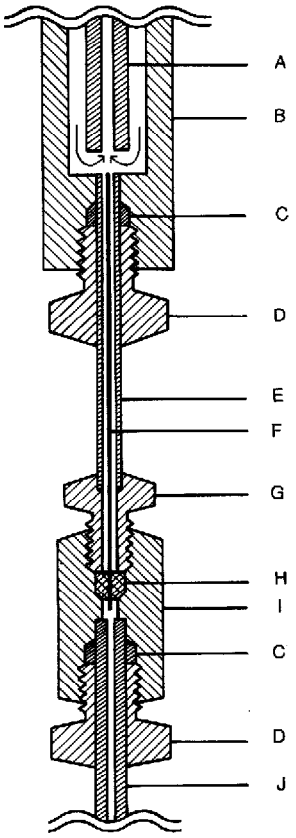

Fig. 1. Diagram of column–flame ionization detector interface. A = capillary jet; B = capillary liner (see text); C = 1/16 in. stainless-steel ferrule; D = 1/16 in. nut; E = 1/16 in. O.D. × 0.02 in. I.D. capillary tube; F = 50 μm O.D. × 10 μm I.D. fused-silica restrictor; G = 1/32 in. nut; H = 0.4 mm vespel/graphite ferrule; I = 1/16–1/32 in. reducing union; J = 1/16 in. O.D. × 0.007 in. I.D. connecting tube to column.

some experiments (*cf.* Fig. 3), the capillary restrictor lengths were 0.7, 2, 4 or 14 cm. A 10-μm I.D. restrictor was found ideally suitable for microbore columns. No clogging of the restrictor was experienced during the course of this work. A diagram of the column–detector interface is given in Fig. 1. The rather fragile fused-silica restrictor was protected from breaking by means of an outer "jacket", consisting of a 0.02-in. I.D. piece of capillary tubing (E in Fig. 1). The liner adaptor constructed was similar to the one used for capillary columns in the Model 5890 gas chromatograph, except that the bottom part was designed to fit a 1/16-in. nut and ferrule. The present interface is convenient in that microbore columns can be interchanged easily without disconnecting the restrictor–detector assembly.

The column inlet pressure was directly observed on the display of the pump. The outlet pressure was determined by installing a second pressure transducer (Sensometric, Simi Valley, CA, U.S.A.) between the column and the restrictor.

Modifications of the gas chromatograph

The hydrogen–air flame of the flame ionization detector caused decomposition

of SF_6, yielding hydrogen fluoride. Venting of hydrogen fluoride gas was accomplished by an in-house vacuum system, which was connected to a plastic hose and funnel. The funnel (*ca.* 15 cm in diameter) was placed entirely over the detector housing. It also proved necessary to protect the collector of the detector from the corrosive action of hydrogen fluoride. This was achieved by plating the 304-stainless-steel collector with a 100-μin. thick layer of gold and a thin nickel underlayer (Precision Nickel & Gold, Sunnyvale, CA, U.S.A.). Operation of this gold-plated collector required only occasional cleaning with a cotton swab, but severe corrosion problems were encountered with the stainless-steel collector, which required cleaning on a daily basis with sandpaper and hot soapy water.

A low-dispersion Model 7520 (0.2 μl volume) injection valve (Rheodyne, Cotati, CA, U.S.A.) was employed to inject samples without dilution. The valve was mounted above the oven of the Model 5870 gas chromatograph, with the outlet stator flow-passage facing downward into the oven. In this fashion, the capillary connecting tube (4 cm × 0.007 in. I.D.) from the valve to the microbore column was embedded in the thermal insulation material of the GC oven.

Columns

The analytical microbore column (25 cm × 1 mm I.D.) packed with Spheri-5 (5 μm) silica particles (Brownlee Labs), was slightly curved in order to fit into the GC oven. The microbore column was preconditioned at 120°C for several hours prior to use. A small guard cartridge column (3 cm × 2 mm I.D.; Brownlee Labs) was filled with 30-μm silica particles and connected with 0.01-in. I.D. capillary tubing to the pump outlet and injection valve. The function of this guard column was to protect the analytical column from particulates and other fluid impurities, and to remove traces of water. Like the analytical column, the guard column was preconditioned at 120°C. Several ready-to-use guard columns were kept in an oven and substituted periodically.

Data acquisition

For some experiments, a Model 3390 integrator (Hewlett-Packard) was used for the integration of chromatographic peaks. Digitized chromatograms were stored on floppy disks by means of the computer data acquisition system described in a previous publication[22]. This made it possible to recall the raw data for evaluation of integration methods and peak variances. A special software program was written for area calculations of the hydrocarbon groups. The integration limits (start and end of each hydrocarbon group) were set by visual inspection of the chromatogram, taking into account the retention data of reference compounds (Table I). After establishment of the baseline, the areas corresponding to each hydrocarbon group in the chromatogram were integrated. For all samples investigated, the results thus obtained were in excellent agreement with the results obtained with the HP 3390 integrator.

Chemicals and standards

Standards were purchased from Aldrich (Milwaukee, WI, U.S.A.) or from Chem Service (West Chester, PA, U.S.A.). The calibration gases, methane and propane (Scott Speciality Gases, Plumsteadville, PA, U.S.A.), were used for column

TABLE I

RETENTION DATA FOR STANDARD COMPOUNDS

Conditions: inlet pressure, 3400 p.s.i.; temperature, 50°C; 7 cm × 10 μm restrictor; t_0 = 2.71 min (see Experimental). Decane was used as reference for α calculations.

Compound	t_R *(min)*	k'	α
Hexane	3.85	0.42	0.60
Cyclopentane	3.87	0.43	0.61
Methylcyclopentane	3.97	0.46	0.66
2,2,4-Trimethylpentane	3.99	0.47	0.67
Cyclohexane	4.06	0.50	0.71
Octane	4.17	0.54	0.77
Methylcyclohexane	4.20	0.55	0.79
1-Pentene	4.45	0.64	0.91
Decane	4.61	0.70	1.00
1-Hexene	4.76	0.76	1.09
cis-2-Pentene	4.91	0.81	1.16
2-Methyl-1-butene	4.94	0.82	1.17
1-Heptene	5.10	0.88	1.26
Dodecane	5.22	0.93	1.33
2-Methyl-2-butene	5.25	0.94	1.34
Benzene	9.06	2.34	3.34
Toluene	13.30	3.90	5.57

dead-volume and extra-column variance measurements, as described below. Sulfur hexafluoride, minimum purity 99.8%, was obtained from (Linde/Union Carbide, South San Francisco, CA, U.S.A.); for some experiments, "SFC-grade" sulfur hexafluoride was used (Scott Speciality Gases). Gasoline standards were kindly supplied by C. Calkin and J. Veal (Shell Development, Houston, TX, U.S.A.) and were cooperatively analyzed via the FIA method by twenty participating laboratories of the Pacific Coast Exchange Group.

Column hold-up time (t_0)

For retention and selectivity measurements, the column hold-up time or dead-time must be known with sufficient accuracy. In the GC and HPLC literature, t_0 determination has been the subject of many discussions[23,24]. In the present paper, we have opted for a linearization method, extensively discussed by Kaiser and co-workers for GC[26,27]. This procedure involves the measurement of the retention times of a homologous series (see Fig. 2) and assumes a semilogarithmical relationship between the corrected retention time ($t_R - t_0$) and homolog number (n). Retention times were calculated from the center of gravity of chromatographic peaks, as the first statistical moment[28]. The hold-up time (t_0) can be determined by first taking an estimate of t_0, and subsequently reiterating the procedure so as to maximize the regression coefficient (r^2). A BASIC computer program was written for calculation of t_0.

Extra-column effects with microbore columns

When working with microbore columns, it is important to consider the instru-

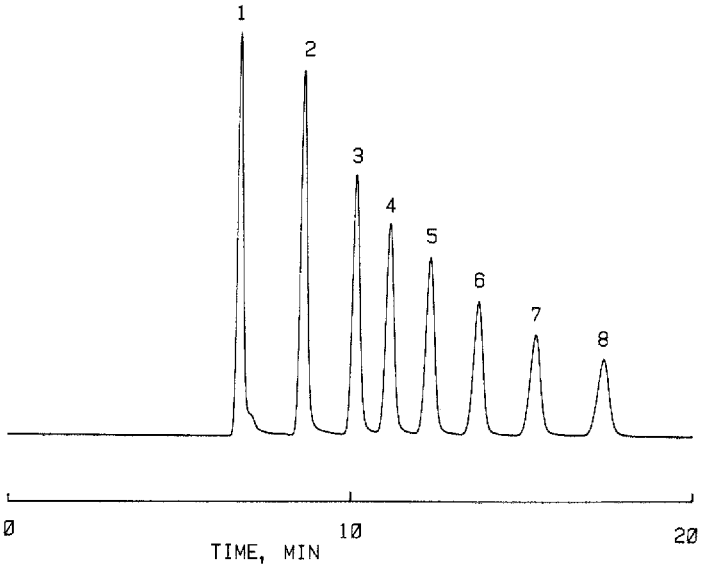

Fig. 2. Chromatogram of a test mixture of alkanes to determine extra-column effects and t_0. Peaks: 1 = pentane; 2 = nonane; 3 = undecane; 4 = dodecane; 5 = tridecane; 6 = tetradecane; 7 = pentadecane; 8 = hexadecane. Column: 25 cm × 0.1 cm I.D., Spheri-5 silica. Detector: FID. Mobile phase: SF_6. Inlet pressure: 1000 p.s.i. Column temperature: 50°C. Restrictor: 4 cm × 10 μm I.D.; alkane concentrations 20 μl/ml in dimethyl formamide.

mental of "system" variance (σ_S^2), especially at low k' valves. Because the observed or measured peak variance (σ_M^2) is linearly related to t_R^2, σ_S^2 can be determined by linear extrapolation of the peak variance and retention data. This method was recently discussed in several papers[29–31].

Fig. 2 shows the chromatogram of a homologous series of *n*-alkanes, eluted in the k' range 0.84–2.72. Peak variances and plate counts were calculated with the statistical "moments" analysis[28]. Selecting peaks nos. 2, 4, 5, 6, 7 and 8 (Fig. 2), a σ_S^2 of 6.4 s was calculated. Based on this value for σ_S^2, it was concluded that extra-column effects do not significantly degrade the performance of the microbore column. Only a small loss in plate count (5–8%) was apparent in the lower k' range. Correcting for the extra-column variance, an average ("true") column plate count of 10511 was obtained, a satisfactory result for hydrocarbon group separations.

RESULTS AND DISCUSSION

Hydrocarbon group selectivity

Table I lists the retention data under isobaric/isothermic conditions for representative standards separated in the present system with SF_6 as the mobile phase and with a silica microbore column. It can be seen that, under these conditions, most of the selected paraffin standards are separated from the olefins. Only 1-pentene could potentially cause a problem, because it is eluted before decane. However, literature data suggests that 1-pentene, like decane, is present in only minor concentrations (< 0.1%) in typical gasoline samples[4]. It is worth mentioning that all of the cyclo-

paraffins present in appreciable amounts in gasoline are eluted before decane. Therefore, decane was chosen to serve as a reference for expressing selectivity in the SFC system:

$$\alpha = \frac{k' \text{ (standard)}}{k' \text{ (decane)}}$$

where α is the selectivity factor, and the capacity factor $k' = (t_R - t_0)/t_0$. The t_0 determination is discussed in the experimental section. The selectivity of the present olefin/paraffin separation is quite similar to literature data of SFC[10] and HPLC[8,9,32] systems. Table I shows that benzene, the first of the aromatic fractions to be eluted, has a considerably longer retention time under isobaric/isothermic conditions. As will be described, the retention times of the aromatic fraction can be substantially reduced by implementing a stepwise pressure and temperature program.

Column activity

Control over the water content of the mobile phase is very important, as water and other modifiers can deactivate the silica surface yielding changing retention times and irreproducible results. The activity of the silica column can be controlled by taking the following precautions:

(1) Inserting a silica guard column before the injector. The volume of the guard column must be large enough to retain all the water present in the SF_6 supply-cylinder and small enough not to interfere with steady flow. A 3 cm × 4.6 mm I.D. column, dry-packed with 60–200 μm silica particles, was found suitable for this purpose. Prior to use, the guard column was conditioned under helium flow at 120°C.

(2) Keeping the analytical column overnight at 120°C. It was found unnecessary to maintain solvent flow during this period.

(3) Using dry SF_6. Supercritical-grade SF_6, with a specified water content (< 0.5 ppm) is now commercially available (*cf.* Experimental).

Table II shows the effect of column activity on retention and selectivity. When none of the above-described precautions were taken, 1-hexene was eluted between

TABLE II

EFFECT OF COLUMN ACTIVITY ON RETENTION TIME AND SELECTIVITY FACTOR

Conditions: inlet pressure: 3400 p.s.i.; temperature, 50°C; 14 cm × 10 μm restrictor.

Compound	*Wet system**		*Dry system***	
	t_R *(min)*	α	t_R *(min)*	α
Hexane	7.54	0.42	7.73	0.41
Octane	8.15	0.67	8.36	0.66
Decane	8.95	1.00	9.22	1.00
Dodecane	9.98	1.42	10.38	1.45
1-Hexene	7.99	0.61	9.47	1.10
1-Heptene	8.36	0.76	10.13	1.36

* No column or mobile phase conditioning.

** With in-line guard column; column preconditioned at 120°C.

TABLE III

PRECISION DATA FOR THE MICROBORE SFC SYSTEM

Conditions: as in Table I.

Compound	*Relative standard deviation (%)*			
	t_R *(min)**	t_R *(min)***	*Area**	*Area (%)**
Hexane	0.00	0.54	1.7	0.86
Octane	0.09	0.56	2.3	0.39
Decane	0.10	0.54	2.6	0.50
Dodecane	0.15	0.64	2.3	0.48
1-Hexane	0.00	1.43	0.5	0.35
1-Heptene	0.09	1.75	0.9	0.38

* Eight consecutive runs.

** Six runs in a one-week period, measured at the beginning of each day.

hexane and octane. When precautions nos. 1 and 2 were taken, 1-hexene was eluted after dodecane. Thus, selectivity is best with a dry solvent system. Similar retention and selectivity were achieved when dry SF_6 (precaution No. 3) without a guard column was used. Table II also shows that the column activity only affects the selectivity for olefins and not for paraffins. Typically, only a 2–3% decrease in α and a 1–2% decrease in retention time was experienced for the olefins during the course of 1 day. No drop in retention was noticed for the paraffins.

Precision

Table III summarizes the precision data achieved with selected standards and with the pump operating in the constant-pressure mode. The activity of the column was controlled by taking the precautions described above. In eight consecutive analyses, the relative standard deviation (R.S.D.) in retention time was *ca.* 0.1%, an excellent result by both GC and HPLC standards. As for peak quantitation, slightly better precision was achieved with relative area calculations (area %) than with absolute area calculations. A R.S.D. of 1% in the area percent measurements is typical of precision data obtained with state-of-the-art HPLC instrumentation under thermostatted conditions[33]. The second column of Table III shows the R.S.D. obtained in six analyses over a 1-week period and gives an indication of the long-term reproducibility of the SFC system. Each chromatographic experiment was run at the beginning of the day, after the oven temperature had been decreased from 120°C (conditioning temperature) to 50°C (operating temperature). No upward or downward trend was observed in the retention times (not shown). Although the precision is slightly inferior to that obtained with consecutive measurements, it certainly is acceptable for quantitative purposes.

Restrictors

A capillary restrictor at the end of the column is necessary to maintain supercritical conditions over the entire column length and to prevent premature solute condensation[17]. By varying the length of restrictor tubing at a constant inlet pressure, the inlet flow-rate and the outlet pressure, *i.e.* the pressure at the end of the column,

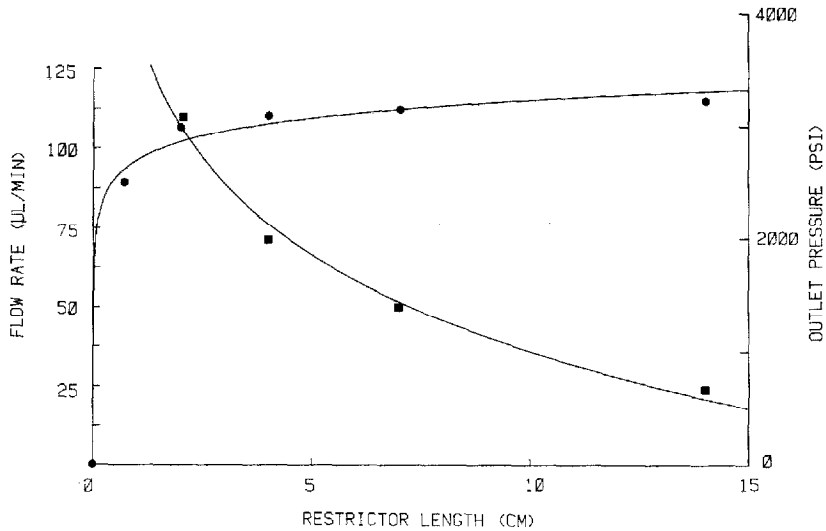

Fig. 3. Plot of flow-rate (■) and outlet pressure (●) *vs.* restrictor length. Column, mobile phase and temperature conditions as in Fig. 2. The left-hand scale is used for plotting flow-rate, the right-hand scale is for outlet pressure.

can be varied. Fig. 3 shows that with the selected restrictor dimensions, most of the 3400-p.s.i. pressure drop is due to the restrictor. Even the short, 2-cm restrictor contributes 88% of the total pressure drop. Increasing the I.D. of the restrictor tubing would increase the pressure drop over the column under constant inlet pressure conditions. In general, this would be unfavorable, because very high volumetric flow-rates would result and lead to unstable flame conditions and noisy baselines. Short pieces of 10-μm I.D. restrictor tubing were found to be compatible with packed microbore columns. No clogging of the restrictors, which would result in decreased flow-rates and irreproducible results, was experienced in the course of this work. Fig. 3 shows that the use of 2–14 cm × 10 μm I.D. restrictor tubing and an inlet pressure of 3400 p.s.i. resulted in inlet flow-rates ranging from 24 to 110 μl/min of liquid SF_6 at room temperature. These flow-rates were experimentally determined by operating the pump in the constant-flow mode while adjusting the flow-rate setting to match the inlet pressure. It may be noted that a flow-rate of 20–100 μl/min is typical for 1-mm microbore columns in HPLC[20]. When the length of the restrictor tubing was decreased from 14 to 4 cm, retention times for the olefins and paraffins were found to decrease roughly proportionally. However, the selectivity was not found to be dependent on restrictor length and remained approximately constant.

Inlet pressure

As expected, increasing the inlet pressure while using a fixed restrictor length would decrease retention. Fig. 4 shows a plot of α *vs.* column inlet pressure. It can be seen that while α is increasing with column inlet pressure for the olefins, α decreases for dodecane. Consequently, higher column inlet pressures would yield more favorable conditions for the paraffin–olefin group separation. A column inlet pressure of 3400 p.s.i. was selected for further experiments.

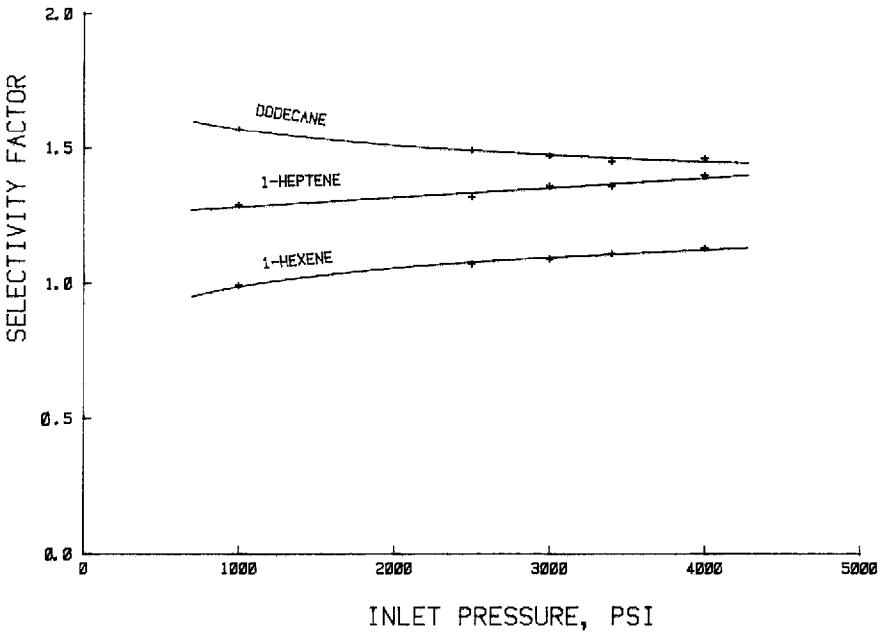

Fig. 4. Plot of selectivity factor *vs.* inlet pressure. Conditions: column and temperature as in Fig. 2; restrictor: 7 cm × 10 μm I.D.

Temperature

The effect of temperature on α is shown in Fig. 5. At an inlet pressure of 3400 p.s.i., α sharply decreases with increasing temperature for the olefins, while the change in α is less drastic for the paraffins studied. In fact, dodecane shows a slight decrease in α with increasing temperature, while octane and hexane show a slight increase in α. We also studied the effect of temperature at an inlet pressure of 1700 p.s.i. Again, α decreases with increasing temperature for the olefins, but now, in contrast to the results in Fig. 5A, α increases with increasing temperature for dodecane while α decreases for octane and hexane. No satisfactory theoretical explanation for this behavior has been found so far. It is clear from Fig. 5 that relatively low temperatures yield favorable conditions for separating olefins from paraffins.

Analysis of gasoline samples

In the previous sections, the focus was primarily on deriving optimal conditions for the olefin–paraffin separation. We will now examine gasoline samples containing aromatics. Fig. 6A shows the separation of a gasoline sample under the conditions of Table I, *i.e.* isobaric at 3400 p.s.i. and isothermic at 50°C. While adequate separation of paraffins and olefins is obtained, peaks eluted after 10 min tail badly, and the analysis time is fairly long (*ca.* 25 min). The peak shapes for the aromatic compounds are probably due to non-linear isotherms in this particular SFC system, and not to inferior column efficiency, as symmetrical peaks were obtained for selected *n*-alkanes (Fig. 2).

Analysis time can be reduced by increasing the inlet pressure to 5000 p.s.i.

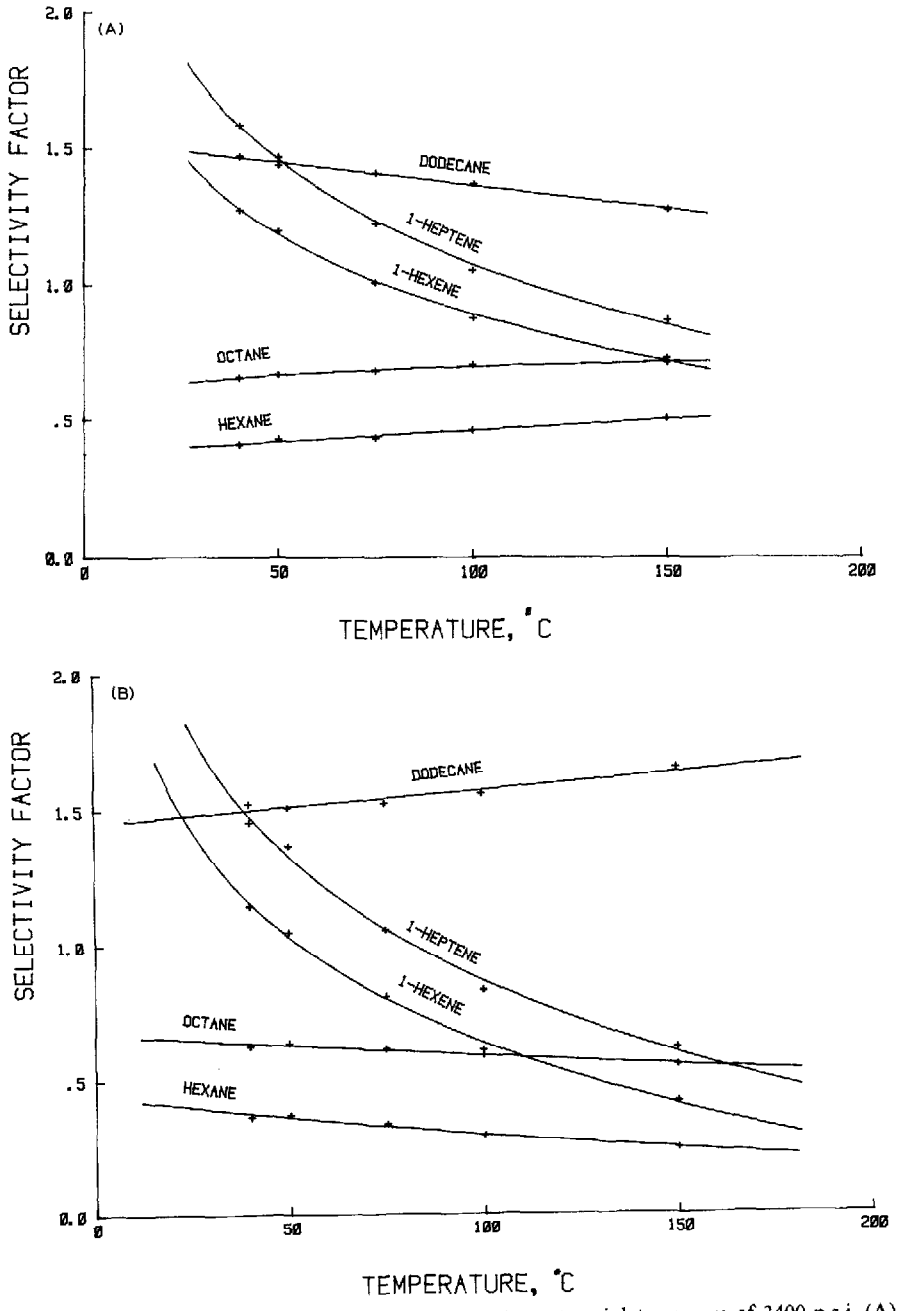

Fig. 5. Plot of selectivity factor *vs.* column temperature at an inlet pressure of 3400 p.s.i. (A) and 1700 p.s.i. (B). Conditions: column and restrictor as in Fig. 4.

after 7 min. This effect is shown in Fig. 6B. In addition to a step in pressure, the pump was programmed to initiate a step in flow from 100 to 1000 μl/min. Since supercritical SF_6 is highly compressible, this step in flow-rate was made to reach the 5000 p.s.i. pressure limit in the shortest possible time. After the pressure limit was reached (*ca.* 20 s), the flow-rate was reduced to 100 μl/min to avoid overshooting the pressure unnecessarily.

A dramatic improvement in peak shape and analysis time can be achieved by increasing the temperature from 50 to 150°C. This is shown in Fig. 6C. Finally, Fig. 6D shows the chromatogram obtained by simultaneously increasing pressure, flow-rate and temperature, which resulted in the shortest analysis time (*ca.* 15 min).

Four gasoline samples, obtained from the Pacific Coast Exchange Group and varying widely in hydrocarbon composition, were examined next. Fig. 7 shows the

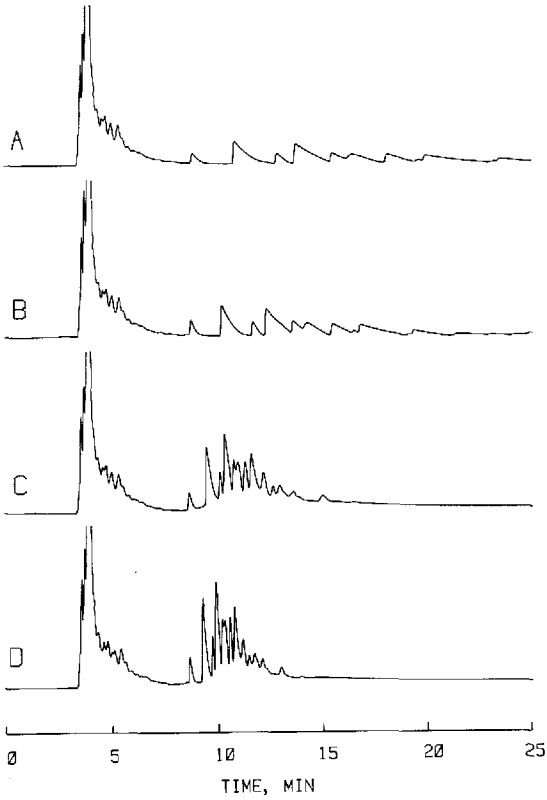

Fig. 6. Chromatogram of a gasoline sample under various experimental conditions. Column, mobile phase and detector as in Fig. 2. Restrictor: 7 cm × 10 μm I.D. (A) Isobaric at 3400 p.s.i. and isothermic at 50°C. (B) Initially as A; after 7 min a step in pressure to 5000 p.s.i. and a step in flow to 1000 μl/min was initiated. (C) Initially as A; after 7 min a step in temperature to 150°C was initiated. (D) Initially as A; after 7 min temperature, pressure and flow were stepped as in B and C. Column and restrictor as in Fig. 4. Paraffins elute between 3.20 and 4.49 min, olefins between 4.49 and 7.00 min. Aromatics elute after 8.00 min.

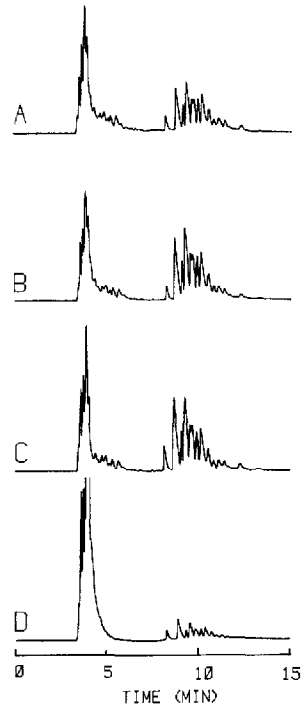

Fig. 7. Chromatograms of gasoline samples under optimized conditions. The composition of samples A, B, C and D is detailed in Table V. Conditions as in Fig. 6D. Paraffins elute between 3.20 and 4.49 min, olefins between 4.49 and 7.00 min and aromatics between 8.00 and 14.00 min.

chromatograms for these samples under the same conditions as indicated in Fig. 6D. Samples A, B and C contained appreciable amounts of olefins (confirmed by FIA analysis) while sample D, a fully hydrogenated sample, contained no olefins and a significantly lower percentage of aromatics. Clearly, no peaks could be discerned in the region where olefins are expected to elute according to the retention times of Table I. The chromatograms of Fig. 7 will be examined in more detail in the section dealing with the FIA and SFC comparison.

Detector linearity and relative response factors

Important considerations in quantitative analysis are the detector linearity and the relative response to various compounds. As was illustrated in Fig. 7, with gasoline samples, the ratios of the hydrocarbon groups may vary widely. For GC it is well known that the flame ionization detector is among the detectors with the largest linear range. This finding was verified for the SFC system used in this work. It was found that the detector was linear over at least three orders of magnitude in the weight range typically expected for gasoline samples.

One of the drawbacks of HPLC in hydrocarbon group analysis is the lack of a suitable universal detector yielding approximately equal detector response. In GC–FID, an equal weight of individual hydrocarbons yields an equal response in the detector, assuming their carbon number does not vary too much[34]. To verify this finding for the present SFC–FID system, a test mixture of eight compounds was used for the determination of relative response factor (f). 2,2,4-Trimethylpentane was chosen as a reference ($f = 1.00$), consistent with the literature[7,35]. The data in Table IV shows that the paraffins and olefins have equal f values to within 5%. However, benzene and toluene gave consistently higher response values. This was also found by Miller, Ettre and Johansen[6], although, in this work, lower f values were determined (*ca.* 1.12–1.08 for selected aromatics).

Quantitation; comparison of SFC with FIA

Four gasoline samples, cooperatively analyzed by the FIA method by twenty participating laboratories of the Pacific Coast Exchange Group, were used to evaluate

TABLE IV

RELATIVE RESPONSE FACTORS FOR SELECTED COMPOUNDS WITH FID AND SF_6

Conditions: as in Figs. 6D and 7. Injected, 0.2 μl of a solution of 50 μl of solute per ml dimethylformamide.

Compound	*Volume in test mixture (μl)*	*Relative* response factor*
Pentane	200	0.95
2,2,4-Trimethylpentane	400	1.00
Nonane	200	0.96
1-Heptene	200	0.97
1-Nonene	200	0.95
Benzene	200	1.24
Toluene	200	1.24
tert.-Butylbenzene	200	1.06

* Relative to 2,2,4-trimethylpentane; average of two determinations.

TABLE V

COMPARISON OF SFC WITH FIA RESULTS FOR GASOLINE SAMPLES

Sample		*SFC (wt.%)*	*FIA (vol.%)**
A	Paraffins	45	55
	Olefins	13	13
	Aromatics	42	32
B	Paraffins	39	55
	Olefins	8	6
	Aromatics	53	39
C	Paraffins	40	54
	Olefins	8	6
	Aromatics	52	40
D	Paraffins	88	94
	Olefins	–	0.5
	Aromatics	12	6

* Average of twenty determinations.

the results of the present method. The chromatograms of these samples are shown in Fig. 7. Table V gives the percentage composition of the three hydrocarbon groups as determined by both SFC and FIA. It is important to establish the integration limits for each hydrocarbon group. In the present work, the end of the paraffin group and the beginning of the olefin group is of particular importance. The limits were defined on the basis of retention data of reference compounds (Table I). Any errors due to this approach would have a small impact on the relative proportions of the hydrocarbon groups.

Improper establishment of the baseline in the chromatogram may lead to quantitation errors. This problem is accentuated when groups are not completely resolved or when one group is eluted in the presence of a large excess of another. We agree with Miller, Ettre and Johansen[6] that the establishment of the baseline is a fairly arbitrary decision. However, as retention times are highly reproducible (Table III), the area determinations outlined in the experimental section should be suitable for routine work.

The FIA numbers represent the average values of the results obtained by the twenty participating laboratories. As pointed out by Norris and Rawdon[10], a direct comparison of the FIA and SFC results is not possible because the FIA results are expressed in volume percent (vol. %), while the SFC–FID method yields weight percent (wt. %). Unless the densities of the three fractions are known (they vary from sample to sample according to compositional differences), it is impossible to convert weight percent into volume percent. Norris and Rawdon used an empirical calibration plot of volume percent (based on FIA) *vs.* weight percent (based on SFC) to convert the aromatic weight percent to volume percent; subsequently, the paraffins and olefins were adjusted to make up the difference, while keeping the paraffin/olefin ratio constant. This method is only reliable when a large number of data points are used. In our case, only four known samples were available for analysis. Since the

slope and intercept of the Norris and Rawdon calibration plot (0.88 and −3.80, respectively) are very similar to the ones obtained by linear regression of SFC and FIA data (0.82 and −3.63) from our results, it appears that our SFC method is in good agreement with Norris and Rawdon's SFC method[36].

The inadequacies and inaccuracies of the FIA method are well documented[2,4]. Therefore, the FIA results in Table V should only serve as a rough guideline, and any comparisons between this method and others must be made with extreme care.

CONCLUSION

In summary, this work has demonstrated that:

(1) Supercritical SF_6, by virtue of its low polarity, yielded group separation of paraffins and olefins on silica columns. No special silver-loaded columns were necessary, which is advantageous in terms of column-to-column reproducibility. Aromatics can be eluted with a step program of temperature, pressure and flow, which obviates the use of a back-flush system.

(2) No flow splitting was necessary because of the use of microbore columns.

(3) Excellent short- and long-term precision in retention times can be obtained by control over the activity of the silica column.

(4) Quantitative results obtained by SFC were consistent with results obtained by FIA.

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