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Quantitative hydrocarbon group analysis of gasoline and diesel fuel by supercritical fluid chromatography

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ABSTRACT

A two-dimensional supercritical fluid chromatographic system is described for the determination of saturates, alkenes and mono-, di- and tri-aromatics in gasoline and diesel fuel. Aromatics were isolated from saturates/alkenes and group separated according to the number of aromatic rings on a capillary column packed with silica of particle size 4 μm. The alkenes were separated from saturates on a 38-mm capillary column packed with a silica-based cation exchanger which had been modified *in situ* with silver nitrate. Elution of alkenes was facilitated by the use of a relatively high column temperature, 65°C, and operation in the back-flush mode. Carbon dioxide was used as the mobile phase. Relative standard deviations were generally in the range 0.4–20.0%. At a low content of alkenes, 0.5%, a relative standard deviation of 8.4% was achieved. The analysis time was under 8 min. The utility of the method is demonstrated by the analysis of feedstock before and after hydration.

INTRODUCTION

The determination of saturates, alkenes and aromatics in petroleum products has for many years been performed by the fluorescent indicator adsorption (FLIA) method [1]. However, this method suffers from the problems [2] that manual detection leads to low precision, the applicability is limited for samples containing significant amounts of pentane or lighter fractions, or materials with an end-point above 315°C, and the analysis times are relatively long.

In recent years, appreciable efforts have been made to develop procedures that could replace the FLIA method [3]. Mass spectrometry and nuclear magnetic resonance have been applied [4–6]. Recently, a method utilizing near-infrared spectrometry was presented [7]. It is evident that greater opportunities for improvement are offered by introducing greater instrumentation, making use of high-performance liquid chromatography (HPLC). Various types of separation columns have been used. Suatoni *et al.* [8,9] achieved the separation of saturates, alkenes and aromatics from a heavy gasoline distillate by the use of a silica column and a low-polarity perfluorocarbon mobile phase. This method was further investigated by Miller *et al.* [10]. Separation of saturates and alkenes was obtained also by Matsushita *et al.* [11] using a dual-column system consisting of a silica column followed by a silica column impregnated with silver nitrate. The latter column type is unstable, silver nitrate gradually being rinsed from the column. A much higher stability is achieved when a silica-based cation exchanger is used as the support for the silver ions. Such columns have been used in more recent work [12,13]. Further, in an IP method, amino columns are recommended for the separation of aromatic hydrocarbons in diesel fuel [14]. In this method, separation takes *ca.* 30 min. An amino-bonded silica column followed by a silica column was used in an HPLC–capillary gas chromatographic (GC) system for the characterization of diesel fuels [15]. Separation of the saturates into the acyclic and cyclic alkane groups on columns packed with polystyrene–divinylbenzene copolymer particles in LC [13,16] and molecular sieve 13X in GC [17,18] has been demonstrated. Further, an HPLC–

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GC system containing a molecular sieve 13X GC column for paraffins, olefins, naphthenes and aromatics (PONA) analysis has recently been introduced by Chrompack (Middelburg, Netherlands).

Separation of the different hydrocarbon groups is generally obtained by HPLC, the analysis greatly hampered, however, by the lack of suitable universal detectors. Refractive index (RI) and UV detectors have been used, but extensive calibration of these detectors is required owing to their specificity to certain types of compounds. Use of RI and UV detectors in tandem has also been reported [16,19]. The IR detector has also been employed [10,11]; the relative response factors of this detector spanned a wide range, thus limiting the methods to a particular distillate product. Dielectric constant detection (DCD) has been used in the HPLC analysis of fuels [12–13,20–22). DCD was reported to have a uniform response when used in connection with mobile phases having high dielectric constants. However, the Freon mobile phase is expensive.

Flame ionization detection (FID) gives an almost equal response for a wide range of hydrocarbons, and is therefore ideal for the analysis of petroleum products. However, FID is not suitable for HPLC of lighter fractions, but can readily be used in connection with compressed fluids, *e.g.*, when carbon dioxide, in a supercritical or subcritical state, is employed as the mobile phase. A number of papers on the analysis of fuels by means of supercritical fluid chromatography (SFC)–FID have appeared [2,3,6, 23–32]. The columns used for SFC have largely been of the same type as those employed in HPLC. Column types and conditions have been selected according to the aim of the analysis. Separation on a silica column has been shown to be sufficient for the determination of alkanes and mono-, di- and triaromatics. When it is of interest to determine alkenes, *e.g.*, in gasoline, diesel and jet fuel, silica–silver-loaded cation exchangers have been employed [29]. For group separation of crude oils, a system consisting of two cyano columns and one silver-loaded cation exchanger has been used [3]. Asphaltenes and resins were eluted from the first column by back-flushing.

There is a clear connection between the composition of the fuel and the exhaust gas of automobiles. Currently, there is interest in developing new fuels which on combustion will emit compounds that are less toxic. Alkenes may cause coating of injection nozzles and valves, which leads to impaired combustion and more toxic exhaust gases. It is therefore of interest that the content of alkenes in the fuels is low. In this connection, analytical methods for the determination of low levels ($< 2\%$) of alkenes in fuels would be needed. Few methods for the determination of alkenes in gasoline and diesel fuels at these concentration levels have appeared [29,33].

The aim of this work was to develop a method, based on packed capillary SFC using neat carbon dioxide as the mobile phase, for the quantitative analysis of petroleum distillation fractions used for fuels.

EXPERIMENTAL

Analyses were performed on a Lee Scientific (Salt Lake City, UT, USA) 600 Series SFC system connected to an ELDS (Kungshög, Sweden) data system. The columns were connected to the injector, two Valco (Houston, TX, USA) N6W six-port switching valves and detector by means of fused-silica capillary tubing (50 μm I.D.). Transfer lines were connected to the columns and to the restrictor by capillary mini-unions with MVSU/004 and MDGF/005 ferrules (SGE, Ringwood, Victoria, Australia). The tops of the FS.25 polyimide ferrules (Valco) that were used in these unions were filed flat. A frit restrictor (Lee Scientific) (50 μm I.D.), adjusted to give a linear flow-rate of *ca.* 5.5 mm/s, was used. A diagram of the column-switching system is shown in Fig. 1. Carbon dioxide of SFC grade, (Scott Specialty Gases, Plumsteadville, PA, USA) was used as the mobile phase. Samples were introduced without dilution using a 60-nl internal sample loop valve (Valco). A splitting ratio of 1:1 and a timed split of 0.2 s were used.

Columns were prepared from fused-silica capillary tubing of 250 μm I.D. and 430 μm O.D. (Polymicro Technology, Phoenix, AZ, USA). The packed bed was supported by a glass-fibre filter [34].

All columns were prepared using a slurry packing technique as described previously [34]. Superspher Si 60 (4 μm) (Merck, Darmstadt, Germany) and Nucleosil 5 SA (Macherey–Nagel, Düren, Germany) were used as packing materials. Impregnation with Ag^+ was carried out as described previously [35].

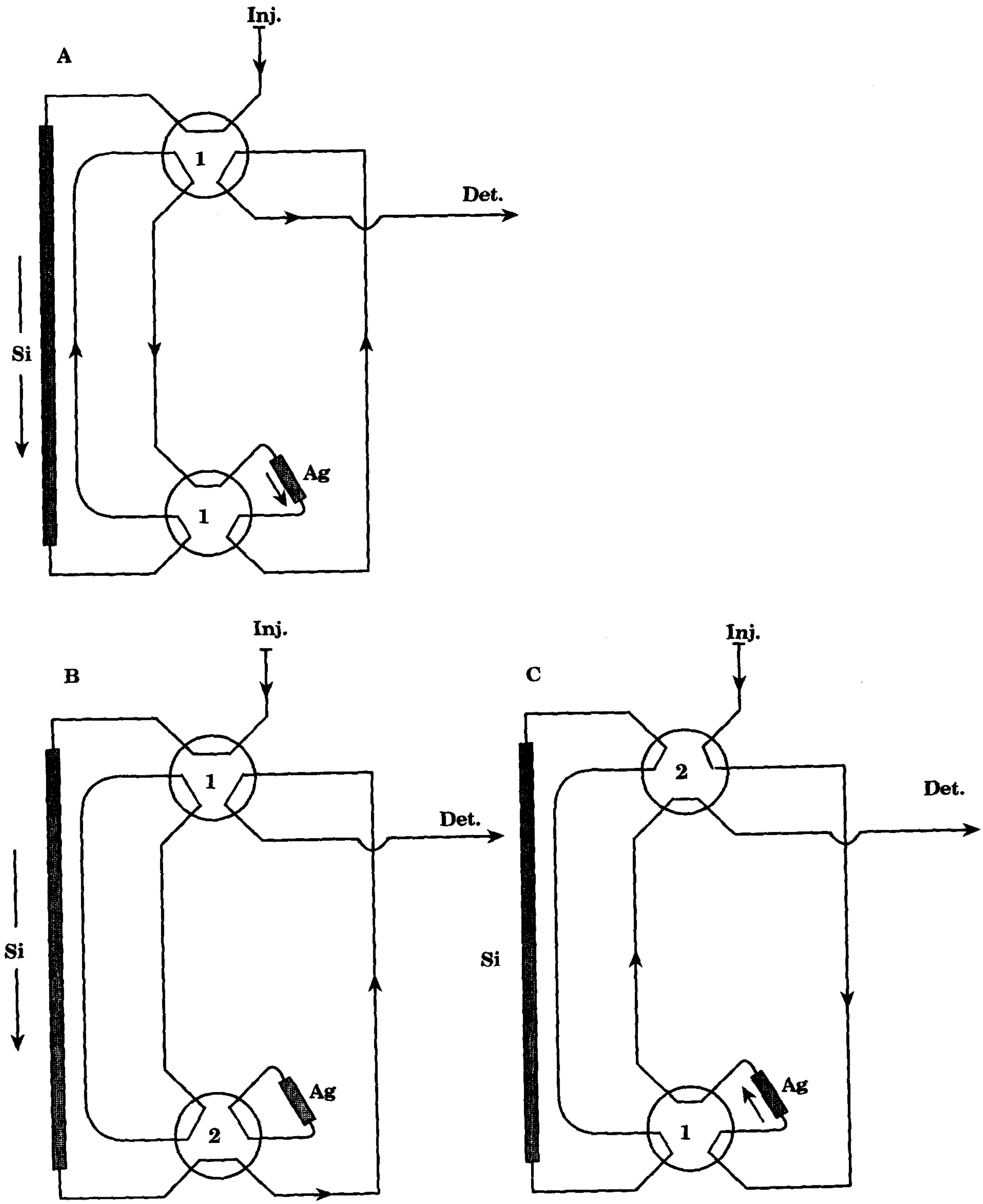

Fig. 1. Schematic diagram of the column-switching system. (A) Separation on the Si column, saturates and alkenes transferred to the Ag column; (B) aromatics transferred from Si column to flame ionization detector; (A) saturates eluted from the Ag column; (C) alkenes

A series of fuels was analysed. The compositions of the lead-free gasolines F1–F4 and the diesel fuels D1, D2 and D4–D9 have been described elsewhere [36,37]. Samples of feedstock were obtained from Neste (Porvoo, Finland).

Separations were performed at 300 atm and 65°C. Injection of the sample was made on the silica column, where the aromatics were retained. The saturates and alkenes were transferred to the silver-loaded cation-exchange column. This column was then switched out of the system and the aromatics were eluted from the silica column directly to the flame ionization detector. The saturates were then eluted from the argentation column and detected by FID. Finally, the alkenes were back-flushed from the argentation column and detected. In addition, the system allows back-flushing of the silica column.

RESULTS AND DISCUSSION

Separation on the silica column

Performance under different conditions was investigated. First, it was found that the retention of alkanes was influenced to a much greater extent than that of aromatics by the mobile phase density. At a density of 0.67 g/cm^3, tetracosane and benzene co-eluted. This was observed at 100°C and 300 atm and also at 65°C and 184 atm. At 130°C and 200 atm, density 0.38 g/cm^3, benzene was eluted before heptadecane. At higher densities, 0.82 g/cm^3, which here was obtained at 65°C and 300 atm, the alkanes and alkenes eluted as a single peak. Lee *et al.* [24] found that in the range 0.88–0.93 g/cm^3, at 35°C, the retention was only slightly influenced by mobile phase density. However, at a density of 0.58 g/cm^3, which was obtained at 90°C and 221 atm, severe overlap between saturates and aromatics was observed.

The second factor to be considered concerns the pressure drop over the column. Such a pressure drop creates a density gradient over the column, which can be significant at temperatures close to critical, where density is highly pressure dependent. Further, the pressure drop will, of course, increase with increasing column length and decreasing particle size. Finally, the restriction over the column would be so high that, in order to maintain a sufficiently high mobile phase flow-rate, only a small restriction can be attached to the column end. Further, the degree of restriction applied is decreased with decreased inlet pressures and increased mobile phase flow-rates. Adverse combination of the above-mentioned factors resulted in decreased performance; the mobile phase density was too low for elution of solutes that have low mobile phase solubility. The conditions used were 30°C and 115 atm with a mobile phase velocity of 5.5 mm/s, using a 320-mm column, packed with 4-μm silica particles. The performance was, however, much improved when a restrictor giving a mobile phase velocity of 1.8 mm/s was used. Low temperatures for separation of fuels on silica columns were used by Di Sanzo and Yoder [32] and Lee *et al.* [24], *viz.*, 30°C and 115 atm and 35°C and 245 atm, respectively. No adverse effect of pressure drop was observed with the columns and flow-rates applied; the columns were 250 mm long, packed with 5-μm particles, and the mobile phase velocity was 0.6 mm/s [32] and 1.3 mm/s [24].

The use of low column temperatures may lead to some complications. Relatively long equilibration times are required to attain stable conditions at 30°C. Moreover, heat from the detector may destabilize the conditions. Further, in the region close to the critical temperature, the density, and thereby retention, changes drastically with temperature. In this work, separation was performed at 65°C and 300 atm, density 0.82 g/cm^3, on a 320-mm microcolumn packed with 4-μm silica particles. The mobile phase velocity was 5.5 mm/s. An optimum velocity of *ca.* 5 mm/s has been reported for a similar column system [38]. The conditions have thus been traded to advantage to give separations of the groups of interest and a high speed of analysis. In comparison with previous work [24,32], our method results in better resolution and shorter analysis times.

The requirements on the silica column are more stringent for the separation of diesel fuel samples than for gasoline samples as shown by the separation of commercial fuels shown in Figs. 2 and 3. Separation of saturates and alkenes from aromatics can be difficult for heavy commercial diesel fuels. Highly alkylated aromatics have relatively short retention times, *e.g.*, triethylbenzene is eluted before benzene (Table I). Such aromatics may elute relative close to peak 1. The improved separation

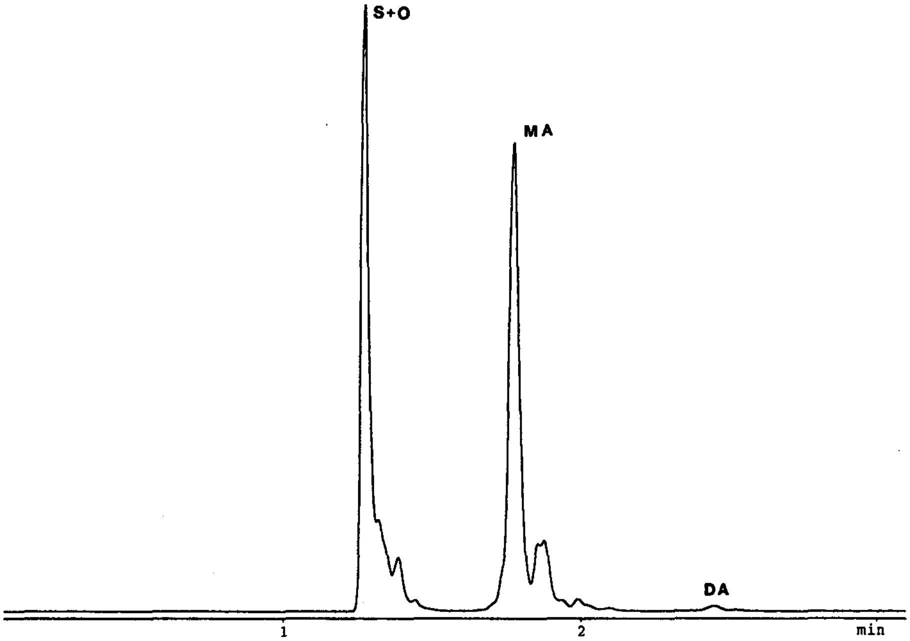

Fig. 2. Supercritical fluid chromatogram (FID) of gasoline F4 on a fused-silica column (320 mm × 0.25 mm I.D.), packed with Superspher Si 60, 4 μm. Mobile phase, carbon dioxide; 65°C and 300 atm. Peaks: S = saturates; O = alkenes; MA = monoaromatics; DA = diaromatics.

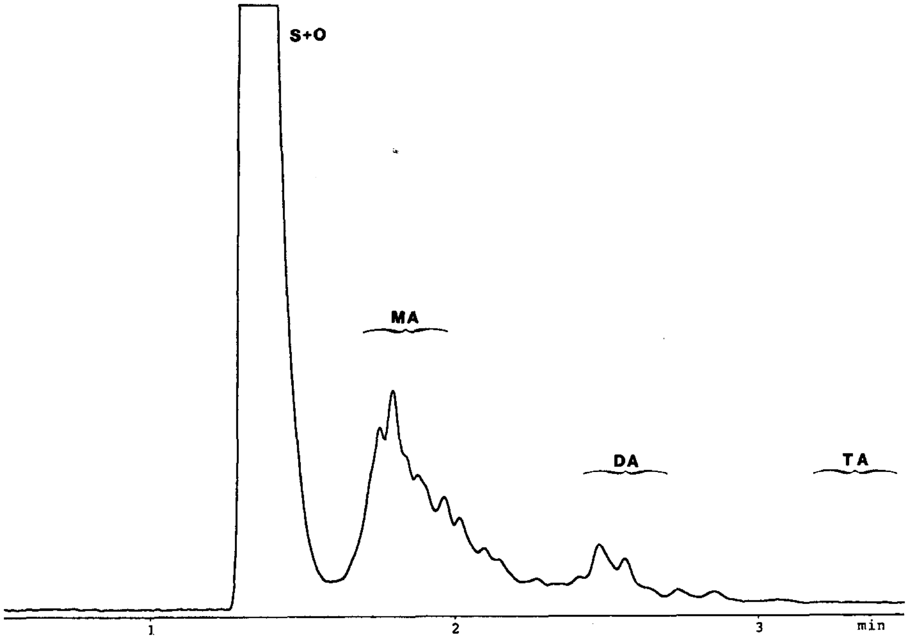

Fig. 3. Supercritical fluid chromatogram (FID) of diesel fuel D6. Column, conditions and peaks as in Fig. 2, TA = triaromatics.

TABLE I

RETENTION OF STANDARD COMPOUNDS ON A MICROCOLUMN PACKED WITH SILICA PARTICLES

Compound	Retention time (min)
Hexane	1.03
Decane	1.03
Tetracosane	1.07
Cyclohexane	1.07
2-Methyl-2-butene	1.08
1-Hexadecene	1.08
Decahydronaphthalene	1.13
Triethylbenzene	1.35
Benzene	1.39
Propylbenzene	1.39
Naphthalene	1.88
Anthracene	2.80

achieved in this work is due mainly to the use of small spherical silica particles having a high surface area; some improvement was obtained by increasing the column length. The chromatographic performance of the silica column was maintained throughout this investigation.

In the present system, it is possible to reverse the mobile phase flow on the silica column. The elution of triaromatics and polar compounds is thereby improved.

Separation on the silver-loaded cation-exchange column

The group separation of petroleum liquids by SFC and a dual-column system consisting of a silica column and a silica column impregnated with silver nitrate was first reported by Norris and Rawdon [2]. Later, Campbell *et al.* [29] reported that they were unable to reproduce this work. The observed irreproducibility may be explained by the fact that silver nitrate is successively leached out from the impregnated column. The chromatograms presented by Norris and Rawdon [2] therefore ought to have been produced on partially impregnated silica.

TABLE II

RETENTION OF STANDARD COMPOUNDS ON A MICROCOLUMN PACKED WITH A SILVER-MODIFIED CATION EXCHANGER

Compound	Retention time (min)
Hexane	0.38
Decane	0.38
Tetracosane	0.38
Benzene	0.64
2-Methyl-2-butene	0.84
1-Hexadecene	4.0

Fused-silica capillaries, packed with a silica-based cation exchanger, and modified *in situ* with Ag^+, have been used for the separation of triacylglycerols [34,35]. These columns were highly stable under SFC conditions, and maintained their retention properties even after heat treatment to 130°C. The strength of the silver–alkene complexes formed in silver-loaded columns decreases with increasing temperature, and excessive retention times can easily be avoided by the use of increased column temperatures.

Alkenes and aromatics are selectively retained on an Ag^+-containing argentation column (Table II). In our system, the aromatics will however, never enter this column, but are switched directly to the flame ionization detector from column 1. Further, an argentation column is farily sensitive towards non-elutable compounds, and is therefore protected by column 1. With such protection, the chromatographic properties of the silver column did not change even after more than 100 fuel injections.

Branched alkenes are much less retained than linear alkenes [39], and co-elution of long *n*-alkanes and short isoalkenes may occur in gasoline analyses. Such co-elution was not observed with the columns used here (Table II). Diesel fuels consist of more high-boiling fractions, and it seems that the separation of saturates and alkenes can be achieved relatively easily in this instance. A large difference in retention was, for example, observed for *n*-tetracosane and 1-hexadecene (Table II).

Alkenes present in diesel fuels have, in general, a relatively high molecular weight and often occur in concentrations less than 2 vol.% [22]. It may therefore be difficult to elute them from the silver column as measurable peaks. Two steps were taken to make elution feasible. First, a relatively high column temperature, 65°C, was applied, the strength of the olefin–silver complex thereby becoming weakened. Second, alkenes were eluted from the silver column in the back-flush mode immediately after the straight elution of the saturates. Further, the length of the silver column is only 38 mm.

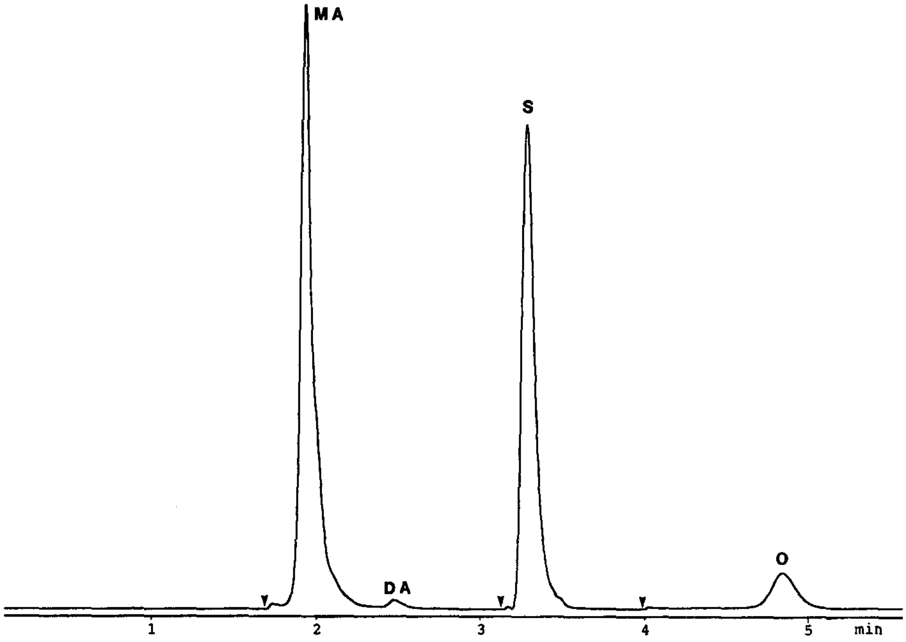

Fig. 4. Supercritical fluid chromatogram (FID) of gasoline F4 on the dual-column system. Columns: silica column as in Fig. 2 and a fused-silica column (38 mm × 0.25 mm I.D.) packed with Nucleosil 5 SA cation exchanger and modified *in situ* with silver nitrate. Conditions: 65°C and 300 atm. Switching points indicated with arrows.

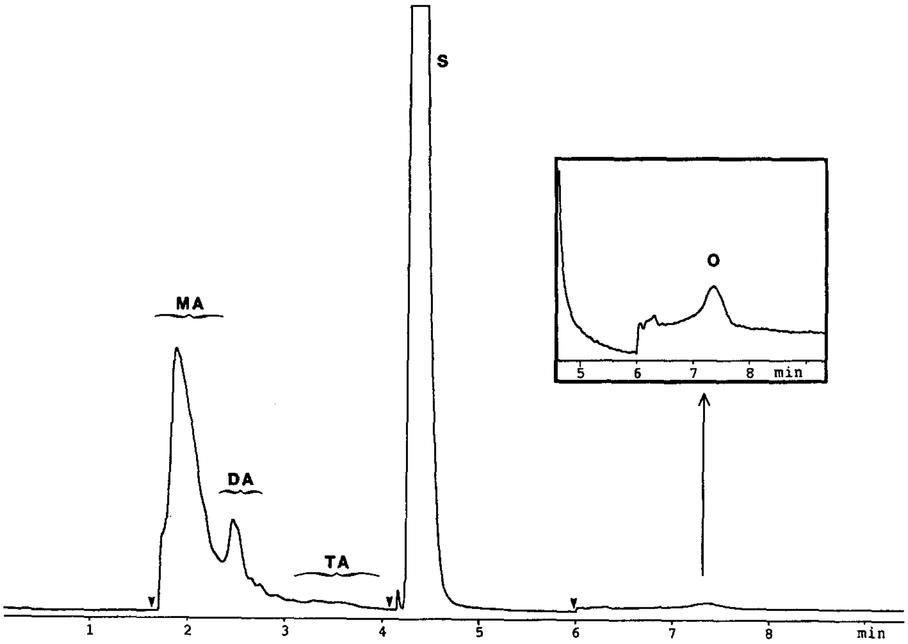

Fig. 5. Supercritical fluid chromatogram (FID) of diesel fuel D6. Columns and conditions as in Fig. 4. Switching points indicated with arrows. Inset magnified 17-fold.

Separation on the dual-column system

A quantitative determination of mono-, di- and triaromatics and the sum of aliphatics and alkenes was obtained on running the sample through the silica column. In addition, information concerning the appropriate switching times was achieved. It was necessary to take into consideration, however, that the linear flow-rate was lower when the argentation column was connected to the system.

Using the dual-column system, peak 1 (Figs. 2 and 3) was transferred to the argentation column for separation of saturates and alkenes. The resulting chromatograms from a gasoline and a diesel fuel are shown in Figs. 4 and 5.

When using 0.25 mm I.D. fused-silica micropacked columns, Skaar *et al.* [31] noted that the stability of the packed bed was inadequate for use with alternating flow directions. No such instability was experienced with the connectors used in this work. Further, columns of this type often broke when high pressure were applied [34], although this problem was overcome when we changed to thick-walled, fused-silica tubing. The flow of mobile phase is low in this type of column and this places stringent demands on the dead volumes of the connections, especially in systems where many connections are being applied.

Quantitative analysis

Quantitative data obtained with FLIA, HPLC and SFC–FID system used in this work are compared in Table III. The gasoline composition data obtained by FLIA are taken from ref. 36 and the diesel composition analysed by FLIA and HPLC–RI detection from ref. 37. The HPLC–RI analysis was performed according to ref. 14. An exact com-

TABLE III

COMPARISON OF SFC–FID WITH HPLC AND FLIA RESULTS FOR GASOLINE (F) AND DIESEL FUEL (D) SAMPLES

Fuel	Components[a]	FLIA (vol.%)	HPLC (vol.%)	SFC–FID (wt.%)
F1	S	71.3		64.1
	A	27.2		34.8
	O	1.5		0.7
F4	S	52.7		41.2
	A	42.6		53.3
	O	4.7		5.5
D1	S	95.6		97.3
	A	2.7	1.8	2.4
	O	1.4		0.1
D2	S	83.3		81.0
	A	14.7	16.9	18.7
	O	2.0		0.3
D6	S	71.2		69.1
	A	27.7	26.1	28.8
	O	1.0		0.5
D7	S	79.6		76.0
	A	19.8	20.0	23.8
	O	0.9		0.2
D8	S	80.4		77.3
	A	19.4	20.5	22.4
	O	0.2		0.3
D9	S	83.3		80.7
	A	16.0	17.3	19.0
	O	0.7		0.3

[a] S = saturates; A = aromatics; O = alkenes.

TABLE IV

SFC–FID REPEATABILITY STUDY WITH RELATIVE STANDARD DEVIATIONS (R.S.D.) (n = 8)

Fuel	S[a] (%)	R.S.D. (%)	MA[a] (%)	R.S.D. (%)	DA[a] + TA[a](%)	R.S.D. (%)	O[a] (%)	R.S.D. (%)
D6	69.1	0.4	22.6	1.0	6.2	6.2	0.5	8.4
F4	41.2	2.5	52.3	2.0	1.0	9.4	5.5	1.4

[a] MA = Monoaromatics; DA = diaromatics; TA = Triaromatics; S = saturates; O = alkenes.

parison of the results is difficult to make as FLIA and HPLC–RI results are reported in volume % and SFC–FID results in weight %. The results obtained with the different methods are, however, in relatively good agreement. A comparison made by Lee *et al.* [6] of the quantitative analysis of aromatics in diesel fuels by FIA and SFC–FID using a silica column showed much greater differences. The supercritical fluid chromatograms presented showed considerable overlap between saturates and monoaromatics, and that explains the observed differences.

The repeatability of the quantitative analysis is shown in Table IV.

Diesel fuels are often prepared from heavier distillates that have been cracked and hydrated. Using the method presented in this work, the hydration step can be monitored (Figs. 6 and 7).

Instrumental methods for quantitative analysis of fuels by means of HPLC or SFC are currently being developed. HPLC methods suffer from the lack of universal detectors. Further, they often give incomplete separations and long analysis times. The combination of a silica and a silver-loaded cation-exchange column in connection with a supercritical mobile phase and FID as described by Campbell *et al.* [29] is a promising approach. Their methodology, however, involves some drawbacks. First, it is

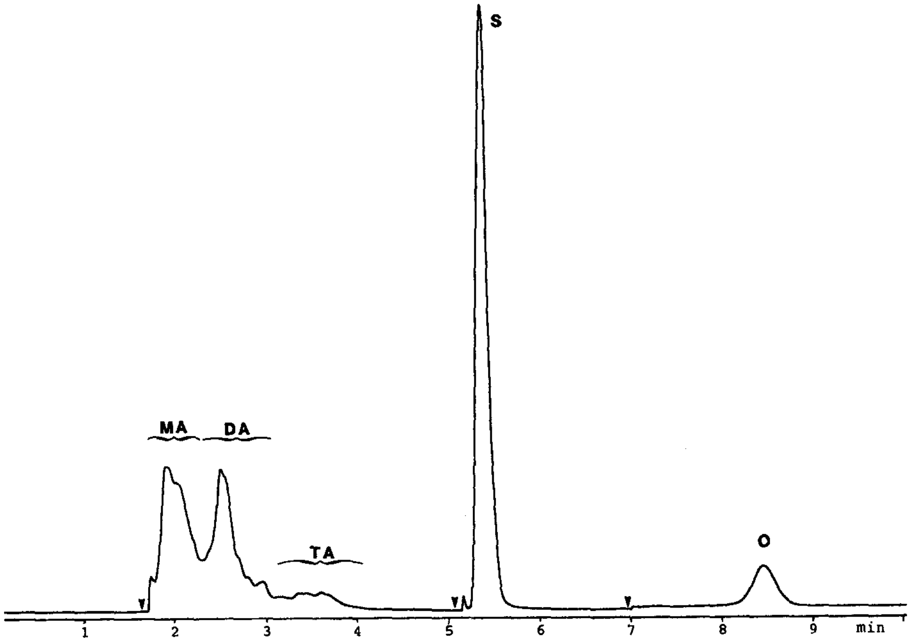

Fig. 6. Supercritical fluid chromatogram (FID) of feedstock. Columns and conditions as in Fig. 4.

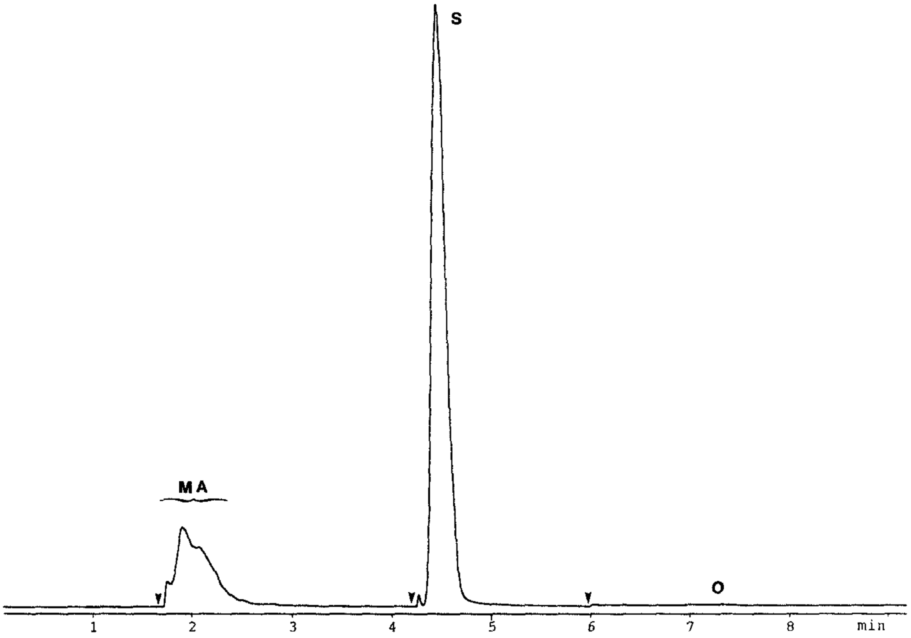

Fig. 7. Supercritical fluid chromatogram (FID) of feedstock after hydration. Columns and conditions as in Fig. 4.

complicated by the use of a mixed mobile phase, of 10% carbon dioxide in sulphur hexafluoride (SF_6). Second, the use of SF_6 as mobile phase necessitates the use of a gold-plated flame ionization detector. Third, even though the alkenes were back-flushed from the silver-impregnated column, long residence times were experienced. This resulted in broad peaks and long analysis times. Further, elution as such broad peaks makes the quantification of minor amounts of alkenes impossible. The silver column was kept at a low temperature, 40°C, and that, in combination with a weak mobile phase, is the reason for the broad peaks. The difficulties therefore increased when higher boiling distillates were analysed. It was erroneously thought that it was best to avoid heating the column in order to prevent degradation.

In this work, it has been demonstrated that saturates and alkenes can be separated from aromatics in SFC using neat carbon dioxide as mobile phase when capillary columns packed with small particles (4 μm) are being used. Moreover, the application of a relatively high temperature of the silver column, 65°C, resulted in short analysis time and minor amounts of alkenes in gasoline and diesel fuels could be quantified.

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