Journal of Chromatography, 641 (1993) 347–355
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 115

Characterization of fuels by multi-dimensional supercritical fluid chromatography and supercritical fluid chromatography–mass spectrometry

P.E. Andersson, M. Demirbüker and L.G. Blomberg*

Department of Analytical Chemistry, Arrhenius Laboratories for Natural Sciences, Stockholm University, S-106 91 Stockholm (Sweden)

(First received December 24th, 1992; revised manuscript received March 23rd, 1993)

ABSTRACT

A multi-dimensional supercritical fluid chromatographic (SFC) system was evaluated for the determination of saturated compounds, alkenes, mono-, di- and triaromatics and polar compounds in diesel fuel distillates. The system consisted of three packed microcolumns, which were packed with cyano-modified silica, silica and *in situ* silver ion-impregnated cation exchanger. Further, an interface for SFC–electron impact MS was constructed. The application of direct fluid introduction was possible when packed microcolumns of 50 μm I.D. were employed. The different groups of organic compounds were readily separated, with the exception of alkanes/alkenes and monoaromatics. This separation became increasingly incomplete as the boiling range of the distillates was increased. Using SFC–MS, it was found that the lack of baseline separation depended solely on the tailing of the alkane/alkene peak. However, for most diesel distillates, only a minor part of the alkane/alkene peak co-eluted with the monoaromatics. In addition, examination by SFC–MS provided data for the proper selection of integration limits. The determination of aromatics was in good agreement with the results obtained using the HPLC method IP 391/90.

INTRODUCTION

It has been demonstrated that there may be a strong correlation between the composition of a fuel and the exhaust that is formed on combustion [1]. In this context, chemical characterization of fuels has become of increasing importance. Several methods have been used for such characterizations [2]; however, the most promising results in recent years have been achieved by supercritical fluid chromatography (SFC) [3–13].

In general, the chromatographic analysis concerns the contents of some different groups of hydrocarbons, *e.g.*, alkanes, alkenes, mono-, di- and triaromatics and polar compounds. For such a group separation, SFC in a multi-column mode is very suitable [2–4,6,7,10,12]. Further, quantification in such systems is facilitated by the use of flame ionization detection (FID).

The objective of this work was to evaluate and improve the performance of a multi-dimensional SFC system for the analysis of diesel fuels. A satisfactory separation of alkanes/alkenes from monoaromatics was, in most instances, achieved on columns packed with silica of pore size 60 Å and particle size 4 μm. For distillates having a broad boiling range, the separation became less complete. In this work, the composition of the co-eluting section of the chromatogram and the separation of the different classes of aromatics was studied by SFC–MS. This study was intended to serve as a basis for the selection of proper switching times in the multi-dimensional system and to establish the appropriate integration limits for quantitative analysis. Further, the

* Corresponding author.

0021-9673/93/$06.00

occurrence in diesel fuels of some other types of compounds, *e.g.*, biphenyls and dibenzothiophenes, was examined by SFC–MS.

EXPERIMENTAL

Instrumentation and columns

The analytical system consisted of a Lee Scientific (Salt Lake City, UT, USA) 600 Series SFC instrument, connected to an ELDS (Kungshög, Sweden) data system. Three different columns were used, the first being packed with Deltabond-SFC, cyano-bonded, 5 μm (Keystone Scientific, Bellefonte, PA, USA), length 25 mm, the second with Superspher Si 60, 4 μm (Merck, Darmstadt, Germany), length 290 mm, and the third with Nucleosil 5 SA (Macherey–Nagel, Düren, Germany), impregnated *in situ* with $AgNO_3$, length 100 mm. All these columns had an I.D. of 250 μm. The columns were connected to the injector, two Valco (Houston, TX, USA) N6W six-port switching valves and the flame ionization detector by means of fused-silica capillary tubing, of 22 μm I.D. (Polymicro Technology, Phoenix, AZ, USA). A frit restrictor (Lee Scientific) (50 μm I.D.), adjusted to give a linear flow-rate of 5.5 mm/s, was used. 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.

Column preparation

Columns were prepared from fused-silica capillary tubing, 250 μm I.D. and 430 μm O.D. or 50 μm I.D. and 375 μm O.D. (Polymicro Technology). The columns were packed using a slurry packing techique, the packing material being suspended in a solvent [toluene–cyclohexanol (4:5, v/v)] for the cation exchanger and acetonitrile for CN-silica and silica; generally, 0.25 g of packing material was slurried in 2.5 ml of solvent. The slurry was transferred to a packing reservoir that could be magnetically stirred, thus applying an approach suggested by Kennedy and Jorgenson [14]. The reservoir was pressurized with acetonitrile to 350 atm (1 atm = 101 325 Pa); packing was performed downwards using a Varian (Walnut Creek, CA, USA) Model 8500 syringe pump. During packing, the bed was supported by a glass-fibre filter, which in turn was supported by a piece of fused-silica capillary (20 mm × 100 μm I.D.). The supporting capillary was attached to the column by MVSU/004 and MDGF/005 graphite ferrule mini-unions (SGE, Ringwood, Victoria, Australia). Polyimide ferrules (FS.25; Valco) could also be used, but graphite ferrules are less expensive and they can be used three or four times. After packing, a glass-fibre filter was applied to the capillary on top of the packing. The filter was kept firmly attached to the packed bed by the injector transfer line, which was attached by mini-unions (SGE). Similarly, the detector transfer line was attached to the column outlet. The cation exchanger was modified with $AgNO_3$ as described previously [15]. Finally, the columns were dried in the chromatograph under carbon dioxide at 275 atm and 115°C.

The preparation of columns of I.D. 50 μm was done in the same way, except that the glass-fibre filter at the column end was secured between the column and a butt-connected capillary. Further, as the packed bed was physically very stable, it was unnecessary to use a filter on the injector side.

In columns packed with silica, the bed had to be compacted in order to achieve sufficient physical stability. This was accomplished by treatment with carbon dioxide at 65°C and 300 atm. After the treatment, depressurization was carried out very gently, to avoid disturbing the bed. The pressure was thus released overnight through the split. Compaction of the bed in columns packed with cation exchanger was achieved by water treatment. If necessary, the columns were shortened after compaction.

Samples

A series of diesel distillates obtained from BP International (Sunbury-on-Thames, UK) were analysed.

Conditions

Separations were performed at 375 atm and 75°C (0.81 g/ml). Injection of the sample was on

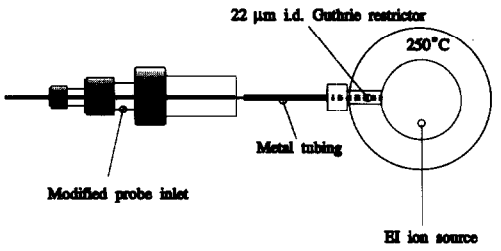

Fig. 1. Schematic diagram of SFC–MS interface.

the cyano-bonded column, where polar compounds were retained; aromatics were retained on the silica column, while alkanes and alkenes were retained on the silver-impregnated column. The last column was then switched out of the system and the aromatics were eluted from the silica column to the detector. Next, the polar compounds were back-flushed from the cyano-bonded column, after which the saturates were eluted from the silver-impregnated column. Finally, the alkenes were back-flushed from the silver-impregnated column. Peak areas (%) were used for quantification.

SFC–MS

SFC–MS was performed on a Lee Scientific 600 Series instrument connected to a Jeol JMS-D 300 magnetic sector instrument. A simple interface via the probe inlet was used for the connection (Fig. 1). The rod of the interface was heated by the ion source heater. Capillaries (350 mm × 50 μm I.D.) packed with Superspher Si 60, 4 μm (Merck), were used for the separation. The restrictor was of the Guthrie type [16], prepared from a piece of fused-silica capillary of 22 μm I.D. The conditions were 50°C and 220 atm (0.81 g/ml). Injection was by timed split (0.07 s) and a split of 1:20 was applied. Electron impact (EI) ionization at 70 eV was used, and the ion source temperature was 250°C. Masses were scanned over the m/z range 52–400, scanning time 1 s.

RESULTS AND DISCUSSION

Packed bed stability

Back-flushing is a precondition for the successful performance of the present multi-column system. Difficulties have been reported concerning the use of packed microcolumns in the back-flush mode. Skaar *et al.* [10] reported that their packed capillary columns did not withstand alternating flow directions, and Hirata [17] proposed that back-flushing should be avoided for packed capillary columns. Compaction of the bed when the column is being used is a major reason for poor bed stability. This effect can be eliminated by proper column conditioning. After such a conditioning, the bed should be secured by a suitable end fitting. Compaction of the bed by means of water treatment has been described by Konishi *et al.* [18].

The physical stability of the packed bed is considerably increased when the ratio of column and particle diameters is decreased. Capillary columns having an I.D. of 50 μm and which are packed with 4- or 5-μm particles can thus be attached to the injector in the same fashion as 50-μm open-tubular columns. However, as the first section of the column would then be situated outside the oven on the Lee Scientific instrument, we preferred to use a transfer capillary also in this instance.

Chromatographic system

A column packed with cyano-modified silica was incorporated in the system. This column protects the silica column from analytes that would be irreversibly adsorbed. Further, this column facilitates the elution of polar compounds by back-flushing. This has been demonstrated previously by Greibrokk and co-workers [4,6,10].

If true baseline separation is not achieved, analytes will be entrained in the transfer capillary. In the present system, this will happen after the first switch (Fig. 2). The loop which is closed in position B will contain sample components. Before applying position C, the system is switched to position A for 4 s, and the sample contained in the transfer capillary will thereby be transferred into the silver-impregnated column. Such a double switch results in two small switch peaks (Fig. 3). Narrow-bore transfer capillaries of 22 μm I.D. were employed in order to diminish the dead volumes. As a consequence of the extra time in position A, the length of the silver-impregnated column had to be increased

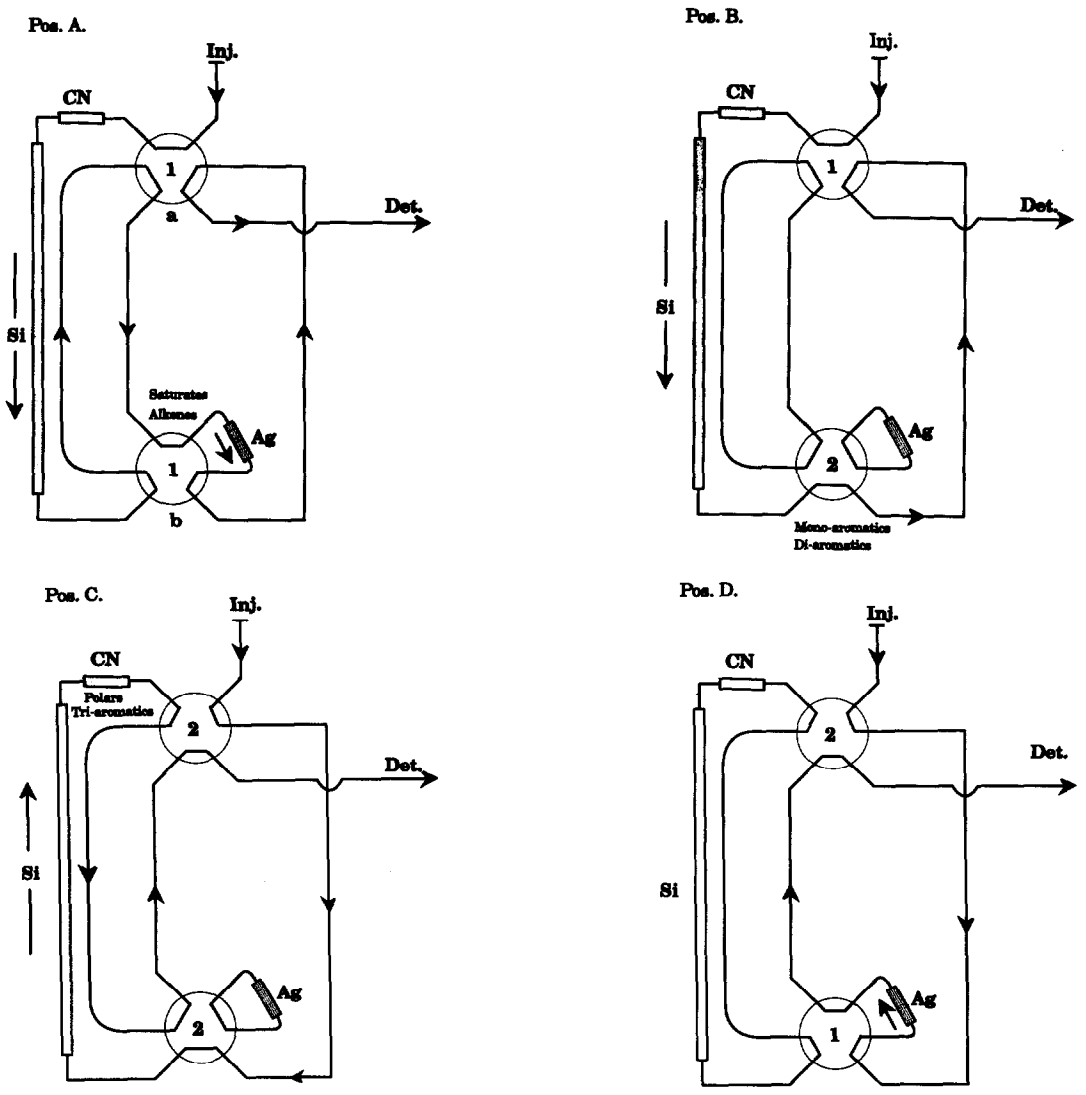

Fig. 2. Schematic diagram of the column-switching system. (A) Separation on the CN and Si columns, polar compounds retained on the CN column, saturates and alkenes transferred to the Ag column; (B) aromatics transferred from Si column to flame ionization detector; (C) polar compounds back-flushed from the CN column; (A) saturates eluted from the Ag column; (D) alkenes back-flushed from the Ag column.

to prevent elution of alkanes at this time. As a result, it was necessary to increase the column temperature in order to ensure the proper elution of the alkenes from the silver-impreganted column. The temperature was thus increased to 75°C, and to maintain the density at 0.81 g/ml the pressure was increased to 375 atm.

When switching from position C to A, both valves had to be switched. In order to prevent back-flushing of the silver-impregnated column, valve a was switched just before valve b, resulting in double switch peaks (Fig. 3). Finally, switching to position D led to a small elevation of the baseline (Fig. 3). This can be explained by the decrease in pressure drop over the system.

Mass spectrometry

The separation achieved on the column packed with silica was studied by EI-MS. The purpose was to obtain a basis for column switch-

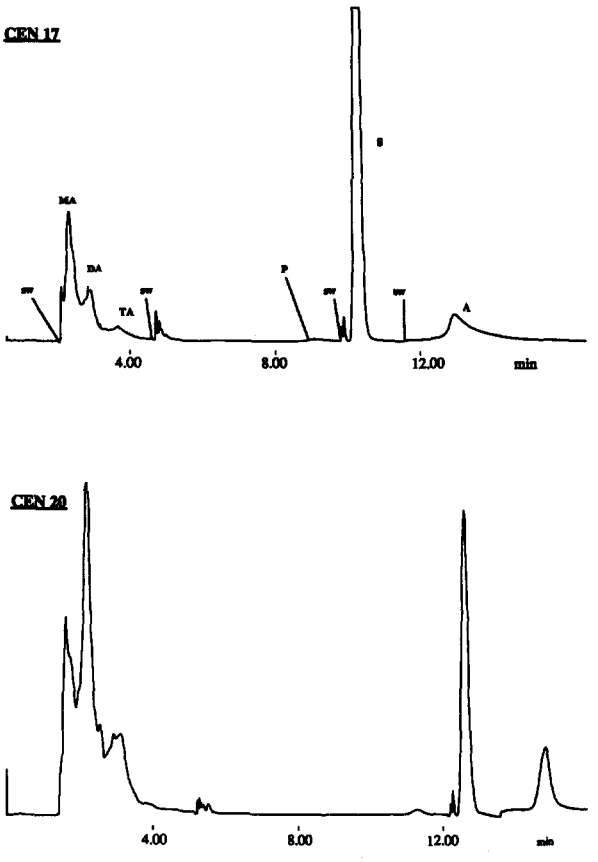

Fig. 3. Supercritical fluid chromatogram (FID) of two diesel fuels, CEN 17 and 20, obtained with the coupled system. Columns: fused silica (25 mm × 0.25 mm I.D.), packed with Deltabond-SFC, cyano-bonded, 5 μm; fused silica (290 mm × 0.25 mm I.D.), packed with Superspher Si 60, 4 μm; fused silica (100 mm × 0.250 mm I.D.), packed with Nucleosil 5 SA and impregnated *in situ* with $AgNO_3$. Mobile phase, carbon dioxide at 75°C and 375 atm. Peaks: MA = monoaromatics; DA = diaromatics; TA = triaromatics; P = polar compounds; S = saturated compounds; A = alkenes. Switching points are indicated by sw.

ing and selection of integration limits. Further, it was of interest to demonstrate the presence of some different types of aromatics in the fuels.

Polycyclic aromatic compounds have been extensively studied by GC–MS [19] and SFC–MS has been applied to some extent [8,20,21]. For our purposes, it was necessary to design a system for SFC–MS that would give EI mass spectra. For the connection of open-tubular SFC with MS, it has been reported that the ion source pressure will become too high at elevated column pressures [22]. As a consequence, the sensitivity was much decreased, and chemical ionization (CI) took place in addition to EI, thus leading to mixed EI and mass CI spectra. Some different attempts have been made to solve this problem. Lower mobile phase flow-rates have thus been applied [23], a split between the column and the mass spectrometer has been used [23–25], the MS pumping has been improved [26] or a moving belt technique has been applied [27]. The approach taken in this work was to apply packed narrow-bore separation columns that would give extremely low flow-rates. The columns used here give a flow-rate of expanded carbon dioxide of *ca.* 50 μl/min (at atmospheric pressure). With such low flow-rates, the heating of the restrictor can be performed in a very simple way. Further, the ion source pressure was, without instrument modifications, kept at $1.8 \cdot 10^{-5}$ Torr (1 Torr = 133.322 Pa), thus providing EI conditions. The exit of the restrictor was placed about 2 mm from the ion source. When the restrictor protruded into the ion source, CO_2 clustering was observed. The heating was obviously unsatisfactory in this instance.

Selection of switching points

As alkanes/alkenes and monoaromatics are not fully separated, the selection of the switching point may be critical. In diesel distillates, having a broad range of boiling points, highly substituted monoaromatics and long-chain alkanes will co-elute. The broader the boiling range, the poorer the separation will be.

In order to investigate the nature of the overlapping compounds, the separation on a column packed with silica was studied by SFC–MS. It was found that, for broad distillates, alkanes/alkenes were, to a small extent, eluted after the valley between the peaks, and no part of the monoaromatics tended to be eluted before that valley (Fig. 4). For this type of distillate, switching in the valley would therefore, in quantitative analysis, lead to too high values of the content of monoaromatics. It should be noted, however, that the alkane/alkene peak in Fig. 4 is high and the degree of overlap, when using the present stationary phase, is relatively small. The switching has to be made on the basis of time only. A UV detector could be installed after the column, although when the detector responds to

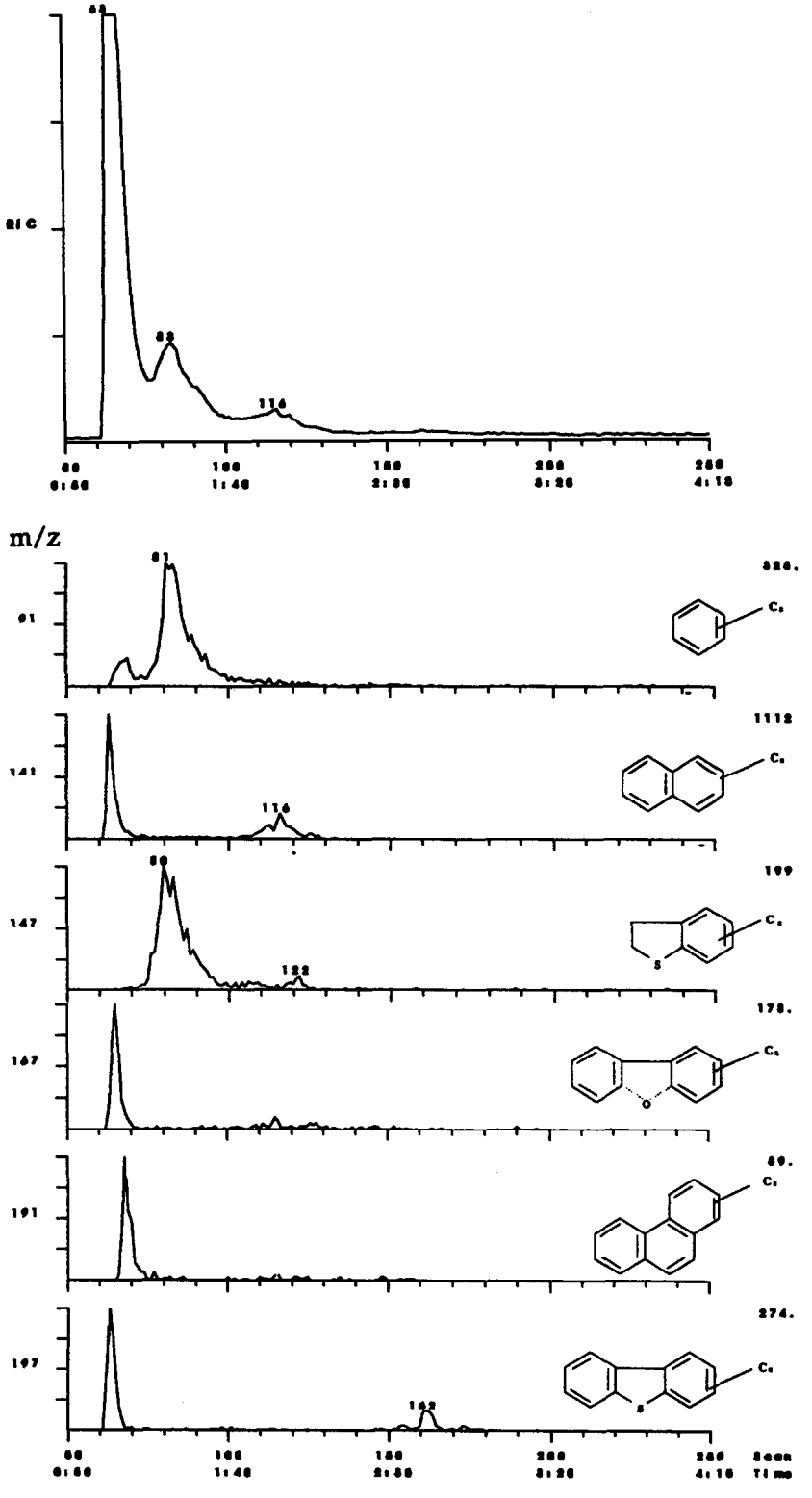

Fig. 4. Total ionization chromatogram and mass chromatograms of a diesel fuel (CEN 17) obtained by SFC–MS. Column, fused silica (350 mm × 50 μm I.D.) packed with Superspher Si 60, 4 μm. Mobile phase, carbon dioxide at 50°C and 220 atm. Electron impact ionization at 70 eV; ion source temperature, 250°C. Time in min:s.

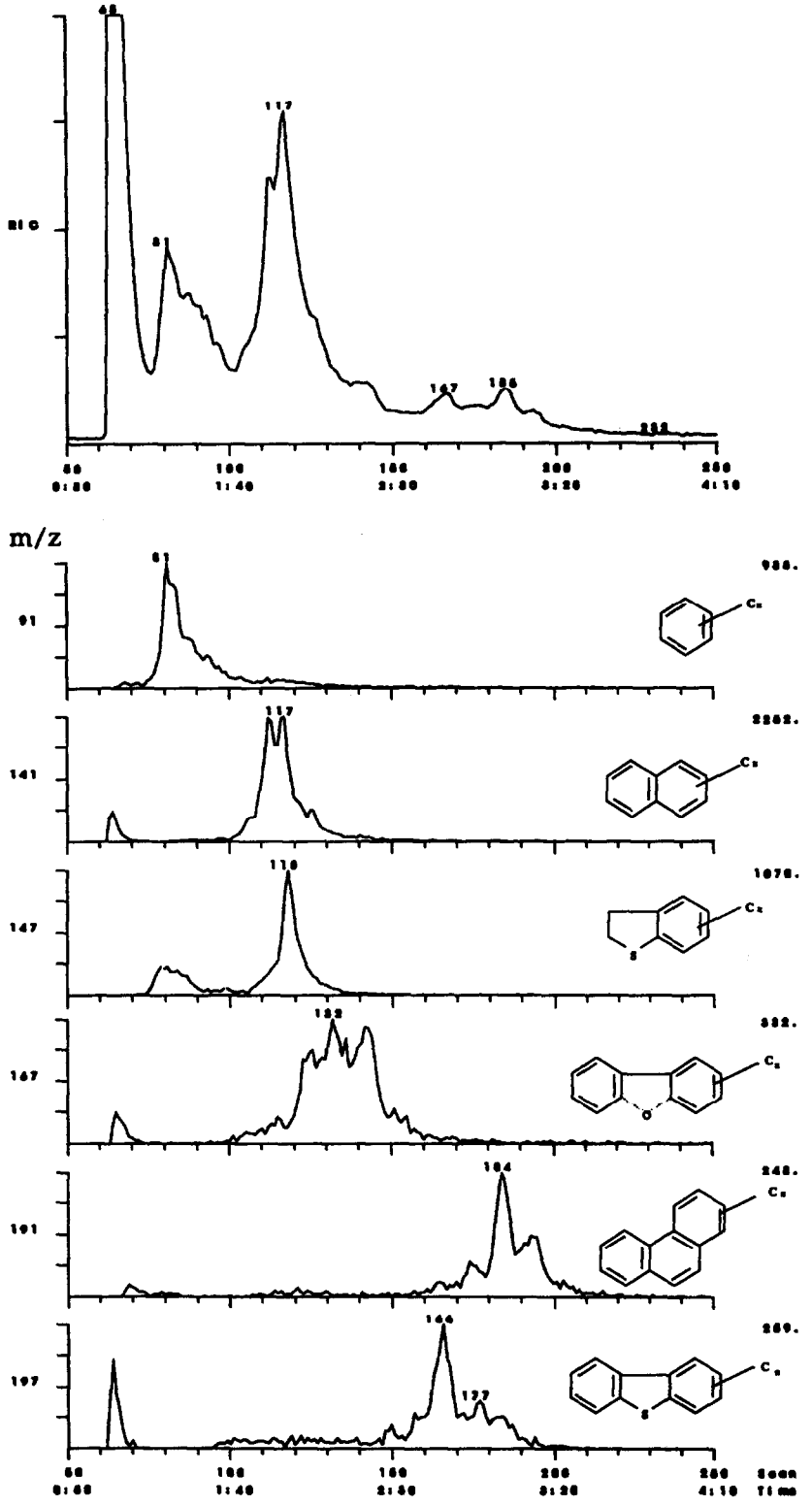

Fig. 5. Total ionization chromatogram and mass chromatograms of a diesel fuel (CEN 20) obtained by SFC–MS. Column and conditions as in Fig. 4.

the first aromatics it is already too late for switching.

Selection of integration limits for quantitative analysis

In order to establish proper integration limits for the determination of aromatics, the separation was studied by SFC–MS (Fig. 5). There was almost no overlap between mono- and diaromatics. For practical reasons, the same conditions could not be applied with SFC–MS as with SFC–FID. However, the conditions applied with SFC–FID resulted in the most complete separations. In samples containing relatively large amounts of high-boiling substances, several minor peaks could be discerned after the main peak emanating from diaromatics (Fig. 5). Mass spectrometric examination at m/z 147, 167 and 197 indicated the presence of several sub-groups of aromatics. These mass numbers are not totally selective [19], hence several peaks were observed in the mass chromatograms. Substances such as

TABLE I

COMPOSITIONS OF SOME GAS OILS OF THE DIESEL FUEL BOILING RANGE

Fuel	Components	HPLC (vol.%)	SFC–FID (mass%)
CEN 17	Monoaromatics	15.7	16.0
	Diaromatics	8.7	8.0
	Triaromatics	2.1	2.3
	Polar compounds		0.6
	Saturated compounds		65.8
	Alkenes		7.2
CEN 18	Monoaromatics	17.5	17.2
	Diaromatics	11.6	11.6
	Triaromatics	5.9	7.8[a]
	Polar compounds		0.7
	Saturated compounds		55.4
	Alkenes		7.2
CEN 19	Monoaromatics	27.4	28.7
	Diaromatics	12.5	14.3
	Triaromatics	4.0	6.1
	Polar compounds		0.4
	Saturated compounds		46.6
	Alkenes		3.8
CEN 20	Monoaromatics	20.6	19.0
	Diaromatics	33.7	37.8[b]
	Triaromatics	11.9	16.2[c]
	Polar compounds		0.5
	Saturated compounds		19.6
	Alkenes		6.8
CEN 21	Monoaromatics	28.8	27.9
	Diaromatics	5.9	6.4
	Triaromatics	0.9	1.1
	Polar compounds		–
	Saturated compounds		56.8
	Alkenes		7.7

[a] Gives a response at m/z 198, dibenzothiophenes and naphthothiophenes.

[b] The value includes peaks, corresponding to 6.4 mass%, giving a response at m/z 167, biphenyls, acenaphthenes and dibenzofurans.

[c] The value includes peaks, corresponding to 6.2 mass%, giving a response at m/z 198.

biphenyls, benzothiophenes and dibenzothiophenes were thus detected. When the retention of these compounds is known, their occurrence will be accounted for separately (Table I).

Comparison of methods

A series of samples of gas oils of the diesel fuel boiling range were analysed and the results were compared with those of aromatic-type (vol.%) analyses by HPLC (IP 391/90) [28]. Although our data are given in mass%, good agreement was found (Table I). The repeatability of the analysis by SFC was in the same range as reported previously [2]. The determination of compounds present at high and moderate concentrations thus gave a relative standard deviation (R.S.D.) of 1.5–2.4%, whereas minor components, typically polar compounds, gave R.S.D. $\approx$ 11%. The precision of the HPLC method was poorer [28]. Further, SFC gives, as discussed earlier, shorter analysis times than HPLC [2]. The main drawback of HPLC in fuel analysis, however, is the lack of universal detectors. A refractive index detector is used in method 391/90, but the response of such a detector will vary greatly with the nature of the solutes. The merit of FID is that it provides a relatively uniform response for the organic compounds present in the fuels.

In this work, packed microcolumns were used. Using such columns, the costs of the stationary and mobile phases will be low. It seems that the main expense in the application of the present method will concern instrumentation.

ACKNOWLEDGEMENTS

This work was financially supported by Neste (Porvoo, Finland). Samples were kindly provided by Dr. I. Roberts (BP Research, Sunbury-on-Thames, UK). S. Hoffmann, S. Smith and A. Christensen are acknowledged for their contributions in the initial stages of the development of the SFC–MS interface.

REFERENCES

1 R. Westerholm and K-E. Egebäck, *Impact of Fuels on Diesel Exhaust Emissions*, Report 3968, Swedish Environmental Protection Agency, Solna, 1991.
2 P.E. Andersson, M. Demirbüker and L.G. Blomberg, *J. Chromatogr.*, 595 (1992) 301.
3 T.A. Norris and M.G. Rawdon, *Anal. Chem.*, 56 (1984) 1767.
4 E. Lundanes and T. Greibrokk, *J. Chromatogr.*, 349 (1985) 439.
5 H.E. Schwartz and R.G. Brownlee, *J. Chromatogr.*, 353 (1986) 77.
6 E. Lundanes, B. Iversen and T. Greibrokk, *J. Chromatogr.*, 366 (1986) 391.
7 R.M. Campbell, N.M. Djordjevic, K.E. Markides and M.L. Lee, *Anal. Chem.*, 60 (1988) 356.
8 B.W. Wright, H.R. Udseth. E.K. Chess and R.D. Smith, *J. Chromatogr. Sci.*, 26 (1988) 228.
9 S.W. Lee, B.J. Fuhr, L.R. Holloway and C. Reichert, *Energy Fuels*, 3 (1989) 80.
10 H. Skaar, H.R. Norli, E. Lundanes and T. Greibrokk, *J. Microcol. Sep.*, 2 (1990) 222.
11 F.P. Di Sanzo and R.E. Yoder, *J. Chromatogr. Sci.*, 29 (1991) 4.
12 B.J. Fuhr, L.L. Klein, C. Reichert and S.W. Lee, *LC·GC Int.*, 4 No. 1 (1991) 36.
13 M. Ashraf-Khorassani, J.M. Levy and L.A. Dolata, *Am. Lab.*, 24 No. 8 (1992) 29.
14 R.T. Kennedy and J.W. Jorgenson, *Anal. Chem.*, 61 (1989) 1128.
15 M. Demirbüker and L.G. Blomberg, *J. Chromatogr.*, 550 (1991) 765.
16 E.J. Guthrie and H.E. Schwartz, *J. Chromatogr. Sci.*, 24 (1986) 236.
17 Y. Hirata, *J. Microcol. Sep.*, 2 (1990) 214.
18 M. Konishi, Y. Mori and T. Amano, *Anal. Chem.*, 57 (1985) 2235.
19 M.L. Lee, M.V. Novotny and K.D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds*, Academic Press, New York, 1981, pp. 242–289.
20 M.L. Lee and K.E. Markides (Editors), *Analytical Supercritical Fluid Chromatography and Extraction*, Chromatography Conferences, Provo, UT, 1990.
21 B.W. Wright, H.R. Udseth, R.D. Smith and R.N. Hazlett, *J. Chromatogr.*, 314 (1984) 253.
22 E.C. Huang, B.J. Jackson, K.E. Markides and M.L. Lee, *Chromatographia*, 25 (1988) 51.
23 H.C. Chung, J.C. Aldridge and D.S. Moore, *Anal. Instrum.*, 19, Nos. 2 and 3 (1990) 99.
24 G. Holzer, S. Deluca and K.J. Voorhees, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 528.
25 M. Takeuchi and T. Saito, in K. Jinno (Editor), *Hyphenated Techniques in Supercritical Fluid Chromatography and Extraction (Journal of Chromatography Library*, Vol. 53), Elsevier, Amsterdam 1992, pp. 47–63.
26 S.D. Zaugg, S.J. Deluca, G.U. Holzer and K.J. Voorhes, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 100.
27 A.J. Berry, D.E. Games and J.R. Perkins, *J. Chromatogr.*, 363 (1986) 147.
28 *IP Standard Methods for Analysis and Testing of Petroleum Products*, Designation IP 391/90, Institute of Petroleum, London, 1990.