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Detailed analysis of hydrocarbon groups in diesel range petroleum fractions with on-line coupled supercritical fluid chromatography–gas chromatography–mass spectrometry

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Abstract

A supercritical fluid chromatographic column was coupled to a capillary gas chromatography (GC) system, corresponding to a two-dimensional separation scheme. The good compatibility of supercritical fluid extraction (SFC) with GC is emphasised: a simple coupling device including a heart-cut valve, a T-piece and a restricted capillary transfer-line was necessary. The system was applied to the analysis of diesel-range petroleum fractions to obtain a more detailed characterisation of these types of samples. Group-type separation of the samples was performed by SFC using a silica-packed column, according to ASTM method D 5186-95. The eluate was monitored with flame ionisation and UV diode array detectors. The separated groups were then transferred to the GC column for detailed analysis. Compounds separated with capillary GC were identified using mass spectrometry (MS). The SFC–GC–MS analysis carried out on a fluid catalytic-cracking product resulted in characterisation of the compounds present in diaromatic and polyaromatic groups, while identification of peaks in the saturate and monoaromatic groups was not possible because of the coelutions of the huge number of components present in these fractions. Results achieved by the SFC–GC–MS system are similar to those provided by LC–GC, but the great advantage of the SFC–GC system is that the SFC solvent (CO_2) can be easily eliminated and has no disturbing effect on the GC separation and detection.

Keywords: Petroleum; Interfaces, SFC–GC; Hydrocarbons

1. Introduction

The great challenge in the analysis of diesel-range petroleum fractions is to separate the huge number of hydrocarbon compounds present in the sample. The number of possible hydrocarbons in this (C_{10} to C_{25}) range is in the order of millions.

High-performance liquid chromatography (HPLC) methods (IP 391/95) [1] and supercritical fluid chromatography (SFC) packed column methods (ASTM D 5186-91) [2] usually applied for the analysis of gas oil samples give only the saturates/aromatics group-type composition and the aromatic ring-number distribution data of the samples.

Coelutions in any single-step chromatographic separation make the detailed analysis, identification and quantitation of target compounds impossible.

Combined separation schemes [HPLC–gas chromatography (GC), GC–GC, GC×GC (i.e. two-dimensional GC) SFC–GC, SFC–SFC, etc.] were applied [3–18] to get more information about the composition of these samples.

The SFC–GC system [19] is very simple: using a

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capillary to transfer the SFC flow into the GC injector seems to be adequate, because this technique allows total sample transfer from SFC to GC, as well as compatible with various detectors.

Our SFC–GC–MS system meets the criteria of orthogonal separation scheme: SFC group-type separation (according to polarity) is combined with GC separation (according to boiling-point). Flame ionisation detection (FID) and UV diode array detection (DAD) provided continuous monitoring of the separation on the SFC column enabling us to set cutting times correctly. The FID system was optimised for determination of gas oil samples [20].

However, using these sophisticated methods, we have to keep in mind that for reliable characterisation of oil fractions – either for product quality, or for refinery processes – group-type classification is more important than structure elucidation of the particular isomers.

Transferring the groups separated on the SFC packed silica column to the GC–MS system ensured that components of a well defined group were

Table 1
Experimental conditions

Instrument	Hewlett-Packard G 1205A SFC system Hewlett-Packard 5890 Series II GC system Hewlett-Packard 5972A mass-selective detector Hewlett-Packard Vectra 486/66VL personal computer
Software	HP SFC G1855A HP MSD Chem Station G1034C
Injector	HP 7673 autosampler, Rheodyne 7410-072 injector valve
Sample	MCB C_{10}–C_{23}, S: 1255 ppm, N: 468 ppm
Loop	1 μl
Heart cut valve	Rheodyne 7010-082
SFC column	HP Hydrocarbon Group Sep., 5 μm silica 250×4.6 mm I.D.
SFC column temperature	35°C
SFC eluent	CO_2 5.3 (Linde)
CO_2 flow-rate	2.5 ml/min
CO_2 output pressure	15.2 MPa
FID restrictor	HP integral high flow, 30 ml/min, 15.2 MPa
FID	350°C, 30 ml/min CO_2 (expanded) 30 ml/min air makeup, 60 ml/min H_2, 420 ml/min air
HP 1050 DAD	λ=320 nm, spectrum: 230–450 nm
Restrictor in the injector	HP integral high flow, 20 ml/min, 15.2 MPa
GC injector	Split 1/100 Temperature: 200°C Septum purge: 3 ml/min
GC column	Supelco SPB-1 30 m×0.32 mm, 0.25 μm film
GC column temperature	35°C for 10 min after the heart cutting, 50°C/min rate to 100°C, 5°C/min rate to 250°C, 250°C for 5 min
GC head pressure	62.05 kPa
GC carrier	Helium 6.0 (Linde)
MSD interface	Direct, 250°C
Ionisation	Electron impact, 70 V
Detection	Scan mode
Mass range	50–600 m/z

analysed in a particular GC run, which made their MS identification a bit easier.

2. Experimental

The analyses were performed on a Hewlett-Packard SFC system, comprising an HP G1205A SFC pump and an HP 5890 GC system, equipped with FID, HP DAD and HP quadrupole MS detection systems.

The packed SFC column (HP Hydrocarbon Group Sep., 5 μm silica, 250 mm×4.6 mm) was taken out from the oven and mounted in a separate heated housing. The SFC oven was used as GC oven. The SFC worked in downstream mode to carry out group-type analysis on the C_9-C_{25} range fraction of the refinery fluid catalytic-cracking (FCC) main column bottom (MCB) plant product.

Instrumentation and analytical conditions are summarised in Table 1. The instrument set-up is shown in Fig. 1.

Supercritical CO_2 eluted from the SFC silica column, passed through the heart-cut valve to the FID and UV-DAD systems, respectively.

Switching the heart-cut valve the supercritical CO_2 flow was directed to a T-piece. A small part of the stream was transferred from the T-piece into the GC injector via a capillary tube with a fixed restrictor at its end. The GC injector was used in split mode.

Major part of the flow from the T-piece proceeded on to the FID and DAD systems, for simultaneous monitoring of the groups separated on the SFC column, enabling us to check the cutting points. Spikes on the FID and DAD traces mark the cutting on/off actions.

SFC and GC runs started at the same time. The different cuts were trapped by the 35°C capillary

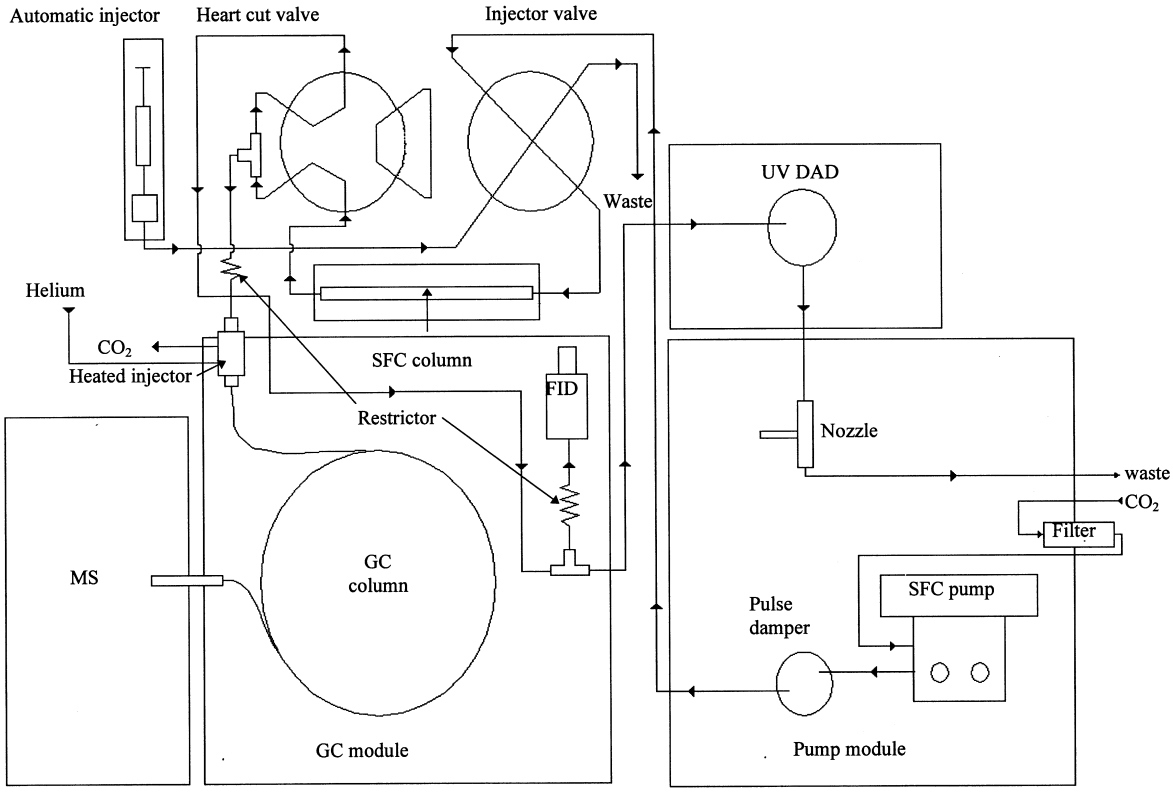

Fig. 1. Schematic diagram of SFC–GC–MS system.

column (Supelco SPB-1 30 m×0.32 mm, 0.25 μm film) during the 10 min initial time of GC run, then temperature program started the elution of the fraction retained by the column. The components of the heart-cut groups were separated according to boiling point on the non-polar capillary GC column. The peaks from the GC column were detected by a quadrupole mass spectrometer. Group-type of the particular SFC-cut, mass spectra and retention data of the peaks were used for identification of the compounds.

3. Results and discussion

Fig. 2 shows the SFC separation of the 170–350°C fraction of refinery FCC plant product on a single packed silica column with parallel FID and DAD. Cut point settings based on these traces are marked on the chromatograms. Mass percentage data of the cuts were calculated using the FID peak area values.

Figs. 3–8 show the GC–MS total ion chromatograms of the different cuts from the SFC chromatogram. Time scale is identical for all the chromatograms, so they can be overlaid for evaluation.

No peak broadening was observed for the peaks started with nonanes.

Chromatograms did not show any disturbing effects of CO_2 on either separation or detection process. This indicates that in the injector supercritical conditions do not exist any more, that is CO_2 readily evaporated and cleared away through the injector split and 35°C capillary column. There was no need to use an additional retention gap or venting-valve contrary to LC–GC coupled systems.

This allowed us to set SFC and GC parameters independently. GC conditions used in our experiments were optimised for polycyclic aromatic hydrocarbon (PAH) separation.

The GC separation of the so called saturate fraction, cut 1, shows the carbon-number distribution marked by the C_{11} to C_{23} *n*-alkanes (Fig. 3).

The separation power of the capillary column was

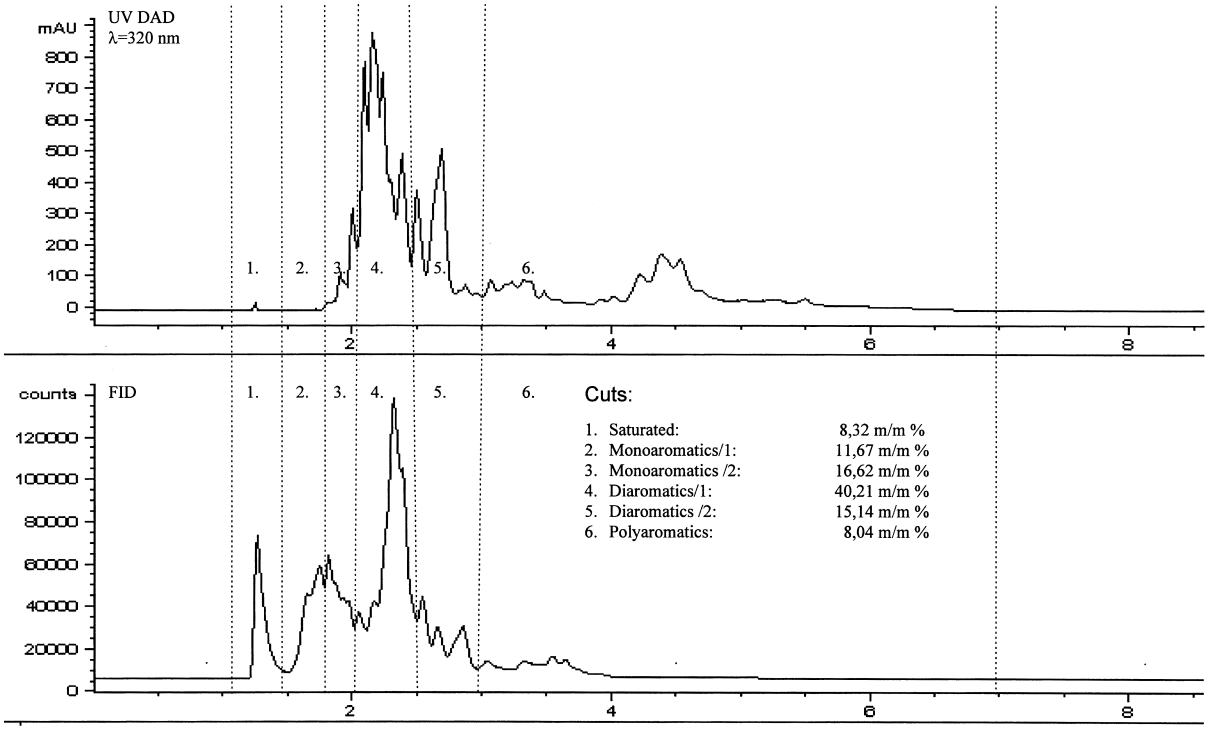

Fig. 2. SFC separation of MCB sample on packed silica column. Time in min.

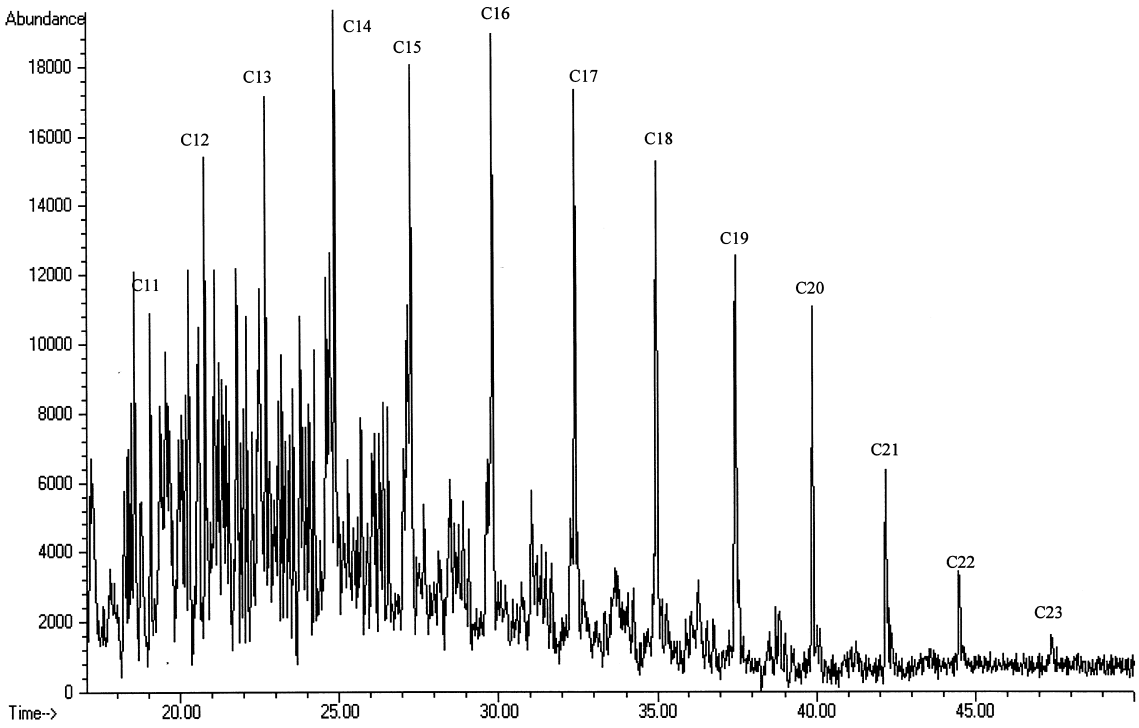

Fig. 3. Total ion chromatogram of saturated fraction (cut 1). Time in min.

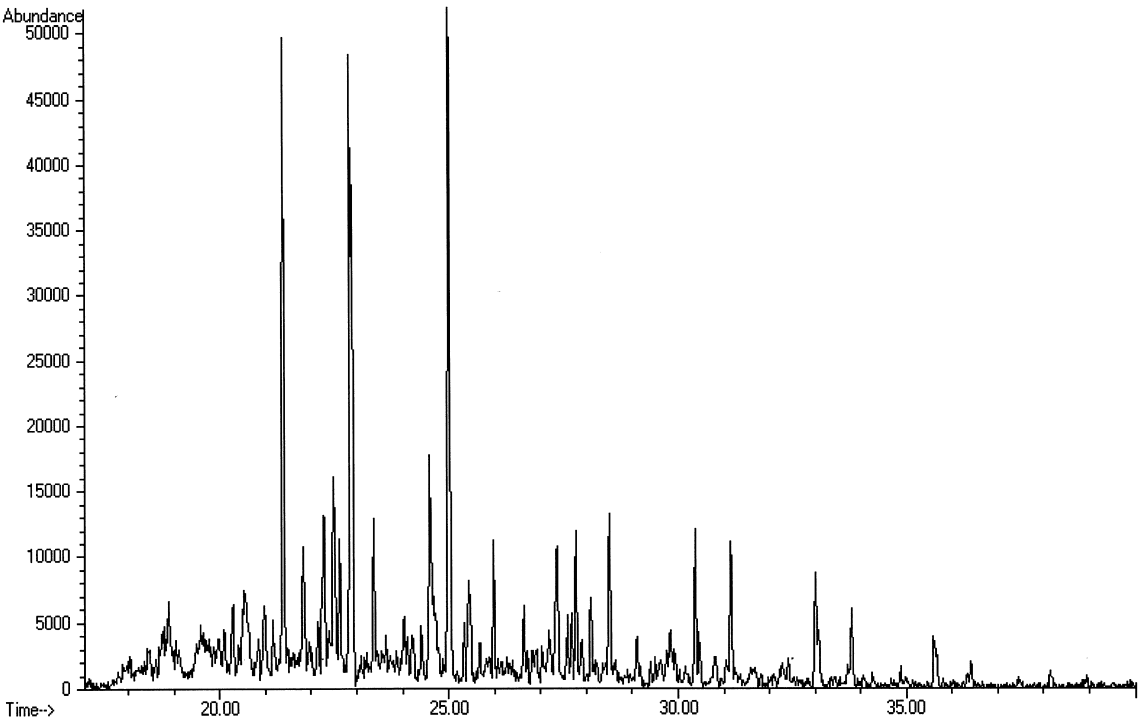

Fig. 4. Total ion chromatogram of monoaromatic fraction 1 (cut 2). Time in min.

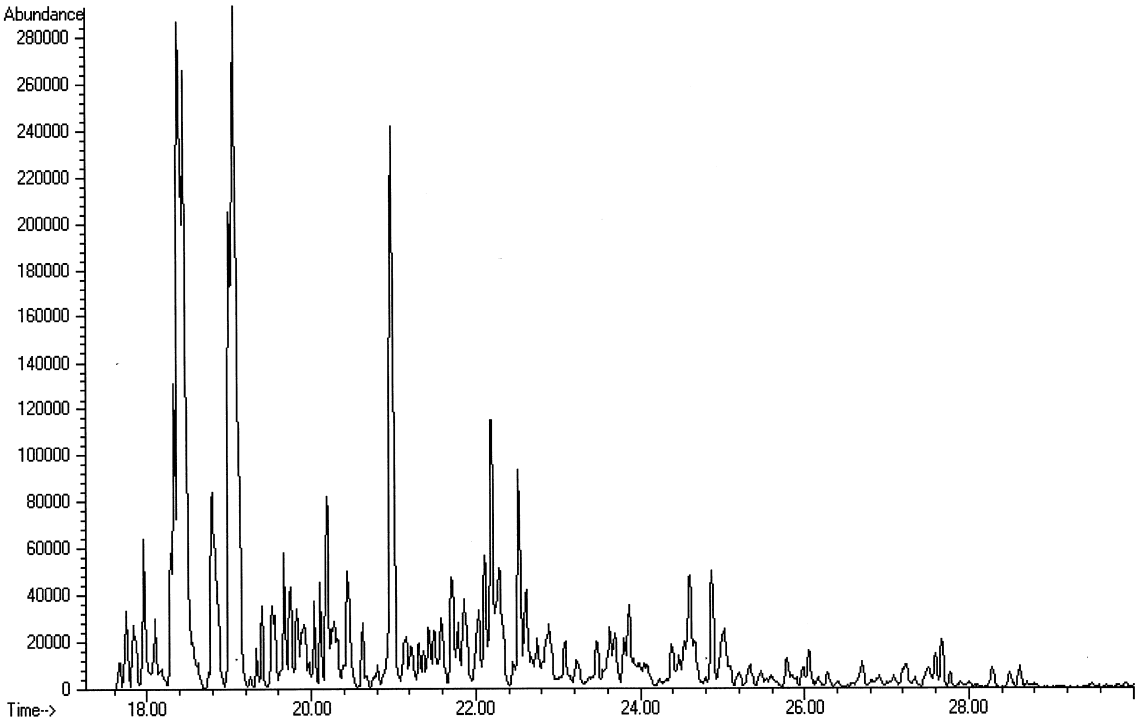

Fig. 5. Total ion chromatogram of monoaromatic fraction 2 (cut 3). Time in min.

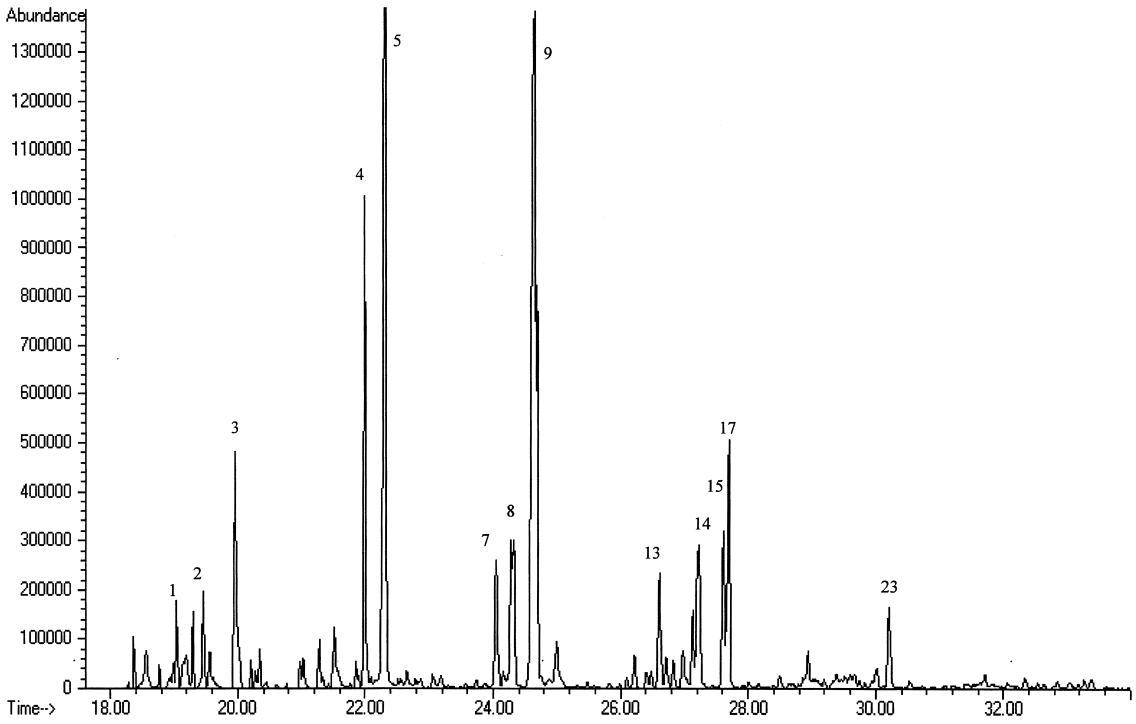

Fig. 6. Total ion chromatogram of diaromatic fraction 1 (cut 4). Compound names are presented in Table 2. Time in min.

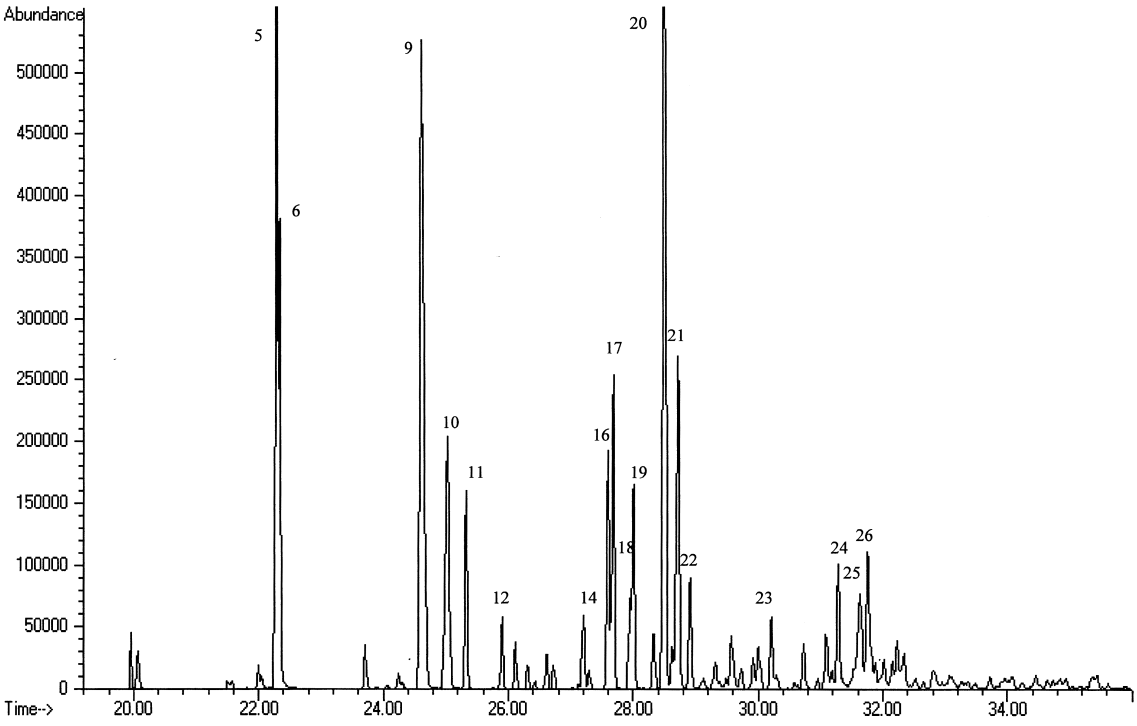

Fig. 7. Total ion chromatogram of diaromatic fraction 2 (cut 5). Compound names are presented in Table 2. Time in min.

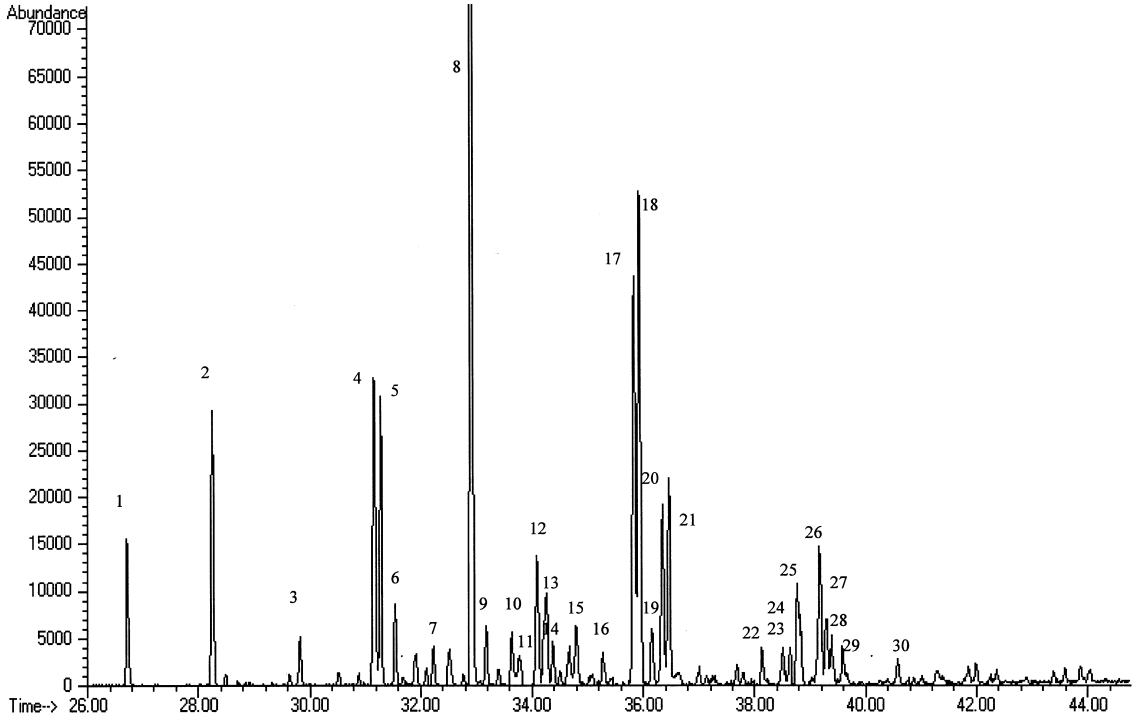

Fig. 8. Total ion chromatogram of polyaromatic fraction (cut 6). Compound names are presented in Table 3. Time in min.

Table 2
Identified compunds of diaromatic fractions, cuts 4 and 5

1	Tetramethylbenzene
2	2,3-Dihydro-5-methyl-1H-indene
3	Naphthalene
4	2-Methylnaphthalene
5	1-Methylnaphthalene
6	Methylnaphthalene
7	Ethylnaphthalene
8	2,6-Dimethylnaphthalene
9	1,3-Dimethylnaphthalene
10	1,7-Dimethylnaphthalene
11	2,3-Dimethylnaphthalene
12	Acenaphthene
13	2,3,6-Trimethylnaphthalene
14	1,4,6-Trimethylnaphthalene
15	1,6,7-Trimethylnaphthalene
16	2-Isopropylnaphthalene
17	2,3,5-Trimethylnaphthalene
18	Trimethylnaphthalene
19	Trimethylnaphthalene
20	3-Methyl1,1′-biphenyl
21	Benzene, [1(2,4-cyclopentadien-1-ylidene)ethyl]
22	2-Methyl1,1′biphenyl
23	7-Ethyl-1,4-dimethylazulene
24	2,3′-Dimethyl1,1′-biphenyl
25	3,3′-Dimethyl1,1′-biphenyl
26	4,4′-Dimethyl1,1′-biphenyl

Table 3
Identified compunds of cut 6

1	Dibenzofuran
2	9H-Fluorene
3	4-Methyldibenzofuran
4	1-Methyl-9H-fluorene
5	2-Methyl-9H-fluorene
6	Methyl-9H-fluorene
7	Dibenzothiophene
8	Phenanthrene
9	Anthracene
10	9H-Fluorene-9-one
11	Dibenzocycloheptadiene
12	2,3-Dimethyl-9H-fluorene
13	2-Phenyl-2,3-dihydroindene
14	1,1′-Biphenyl, 2(1-azido-1-methylethyl
15	Methyldibenzothiophene
16	4,4′-Methylenebisbenzenamine
17	1-Methylanthracene
18	9-Methylphenanthrene
19	2-Methylanthracene
20	3-Methylphenanthrene
21	Methylphenanthrene
22	1,4-Dimethylanthracene
23	9-Ethylphenanthrene
24	2-Ethylphenanthrene
25	9,10-Dimethylanthracene
26	3,6-Dimethylphenanthrene
27	2,5-Dimethylphenanthrene
28	Dimethylphenanthrene
29	2,7-Dimethylphenanthrene
30	Pyrene

not enough to give a more detailed picture of this complex fraction: containing *n*-alkanes, isoalkanes, cycloalkanes and olefins as well. Identification of the poorly resolved peaks was hopeless. This stands for the monoaromatics fraction, cuts 2, and 3 in Figs. 4 and 5, respectively.

Total ion chromatograms of cuts 4 and 5 from diaromatic fraction, (Figs. 6 and 7) contain far less peaks, so we made an attempt to identify the major components of these fractions, based on their mass spectra and retention data. Results of this identification process are summarised in Table 2.

The chromatogram of the polyaromatics fraction (cut 6) in Fig. 8 shows fairly well separated peaks enabling us to identify 30 of the most abundant PAHs in the sample. These are listed in Table 3.

4. Conclusions

(1) It was relatively simple to couple and run SFC–GC separations: (i) there was no need for special interface system (retention gap, pre-column and solvent vent), the GC injector and capillary column provided all these functions. Quite simply: a restricted capillary tubing (normally used in SFC) was pierced through the septa into the GC injector. (ii) Continuous monitoring enables to cut any segment of the SFC chromatogram. (iii) SFC and GC parameters can be optimised almost independently. (iv) Splitless GC mode for trace analysis is also possible. (v) Upgrading with a stop-flow valve allowed us to analyse the whole sample in one injection. (2) Components of diaromatic and polyaromatic SFC fractions were separated and identified for detailed PAH analysis of diesel fuels. (3) Some major components (e.g., *n*-alkane distribution) can be analysed in the saturates and monoaromatics cuts, but detailed GC–MS identification was not possible, due to coelutions of the large number of compounds present in these fractions.

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