CHROMSYMP. 701

GROUP SEPARATION OF OIL RESIDUES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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SUMMARY

The group separation by supercritical fluid chromatography of high-boiling residues (b.p. higher than 350°C) or North Sea oil is described. The chromatographic separation used a three-column system (cyano and silica and silver-impregnated silica) with column-switching and back-flushing with supercritical carbon dioxide as the mobile phase. The flame ionization detector could be used directly by placing the restrictor in the jet. The quantitative aspects are discussed in relation to the results obtained by liquid chromatographic methods.

INTRODUCTION

Deasphalted high-boiling petroleum residues can be separated into saturates, aromatics, and polars by liquid chromatography (LC). This separation usually requires a two-column system with column-switching and back-flushing[1]. However, quantitation is a rather difficult task owing to the lack of a suitable mass-sensitive detector in LC.

The interest in and use of supercritical fluid chromatography (SFC) have increased recently. When supercritical carbon dioxide (CO_2) is used as the mobile phase, it is possible to use flame ionization detection (FID) for quantitation, since the detector response is proportional to the mass of hydrocarbons. Noisy, spiked peaks, probably caused by condensation of the solute when the pressure is reduced have occasionally been observed in SFC[2,3]. The flame ionization detector for packed-column SFC, modified by Rawdon[4], was reported to be free of spiking.

Capillary SFC with FID has been used to separate petroleum samples[2,5,6]. Group separation of low-boiling petroleum fractions into saturates, olefins, and aromatics has been performed on packed silica and silver nitrate-impregnated silica columns in series, using supercritical CO_2 as the mobile phase and FID[7]. The objective of our investigation was to examine the possibility of using supercritical CO_2 as the mobile phase for the group separation of high-boiling petroleum residues (b.p. higher than 350°C). This paper describes the group separation of high-boiling residues of North Sea oil into saturates, aromatics, and polars by a three-column system with column-switching and back-flushing with supercritical CO_2 as the mobile phase.

EXPERIMENTAL

Materials

The liquid CO_2 was of standard grade from AGA Norgas, Oslo, Norway. Carbon disulphide was purchased from Rathburn (Walkerburn, U.K.) and the silver nitrate (purum p.a.) from Fluka (Buchs, Switzerland). The standards were obtained from different commercial sources. Crude oil and high-boiling distillation fractions and residues from North Sea oil were obtained from Statoil, Stavanger, Norway.

Instruments

A complete description of the pumping system has been published elsewhere[8]. Samples were injected with standard micro HPLC injectors (Rheodyne 7520 or Valco CI 4W). One UV detector (Perkin-Elmer LC-55) and one flame ionization detector (Hewlett-Packard 5790 A) were used. The quartz windows were tightened with extra springs so that the UV detector could be used at pressures up to 275 bar. The flame ionization detector was used at 350°C with a hydrogen flow-rate of *ca.* 40 ml/min and with a supply of oxygen (*ca.* 40 ml/min) instead of air. The restrictor was made by crimping the end of a piece of 0.4 mm O.D. 0.1 mm I.D. platinum tubing (Good-fellow Metals, Cambridge, U.K.). The restrictor was located 4–6 mm below the jet tip of the detector. One six-port, two-position valve was obtained from Valco and one from Waters (Automated Switching Valve). Both were operated manually. Peak integration was accomplished by a LDC/Milton Roy CI-10 integrator.

Columns

Two 250 × 1.3 mm I.D. CP-Spher silica (8 μm) columns were purchased from Chrompack (Middelburg, The Netherlands) and two 30 × 2.1 mm I.D. Spheri-5 cyano (5 μm) MPLC™ cartridge-type columns from Brownlee Labs. (Santa Clara, CA, U.S.A.). One of the 250 × 1.3 mm I.D. silica columns was impregnated with silver nitrate in the following way: one column volume of a 1% solution of silver nitrate in methanol (w/w) was pumped (0.1 ml/min) through the dry silica column. The methanol was removed by pumping *ca.* 1 column volume of hexane (0.1 ml/min) through the column, and the hexane was successively removed by allowing CO_2 at equilibrium pressure to flow through the column. Finally, the column was conditioned at the working pressure and temperature for at least 2 h.

Procedure

The high-boiling residues were deasphalted with *n*-hexane[1]. The standards, the residues, and the distillation fractions were dissolved in carbon disulphide for injection: an injection volume of 0.5 μl could be used on the microbore columns without loss of efficiency. Loss of efficiency and peak splitting were observed when 1 μl of tetrahydrofuran, which is a stronger solvent than carbon disulphide, was injected into the silica column. The injector temperature was kept above the critical temperature of CO_2 and below the boiling point of the injection solvent. The columns and the Valco valve were kept in the oven of the HP-5790 A gas chromatograph, while the Waters valve was connected through a hole in the inner wall of the oven, with the outer wall removed.

RESULTS AND DISCUSSION

Retention of alkanes and aromatics on silica

In order to study the possibility of using a silica column for the separation of saturates and aromatics in high-boiling petroleum fractions (b.p. > 350°C), the retention times of some references with supercritical CO_2 as the eluent were measured (Table I).

TABLE I

RETENTION TIME OF ALKANES AND AROMATICS ON TWO 25-cm SILICA COLUMNS WITH SUPERCRITICAL CO_2 AS THE MOBILE PHASE AT 60°C

Compound	t_R (min) at 240 bar (0.2 ml/min)	t_R (min) at 310 bar (0.3 ml/min)
n-C_{26}	3.8	2.8
Phytane	—	2.7
Squalane	—	2.8
Decalin	3.9	2.9
5-α-Cholestane	4.7	3.1
Nonadecylbenzene	5.1	3.4
Benzene	4.5	3.3
Naphthalene	6.0	4.0
Anthracene	8.9	5.4
Pyrene	11.4	6.7

The branched alkanes, phytane and squalane, were eluted with a retention time which was less than or equal to that of the n-alkane C_{26}, while the naphthenic decalin and cholestane had a greater retention time than n-C_{26}. The greater retention time of decalin compared with n-alkanes has also been observed by others[7]. The separation between cholestane and nonadecylbenzene was poor, compared with the LC separation with hexane as eluent.

The resolution of the n-alkanes was pressure-dependent. The retention time of n-C_{44} was minimal at 280 bar, but at lower pressures the large n-alkanes were retained compared with n-C_{20}, at 60°C.

At higher temperatures, the peaks became broad and asymmetric. The n-alkanes were partially separated at high temperatures, and this separation is not desired for group separation. These results show that temperatures above 100°C are not suitable for the group separation of large hydrocarbons within a normal operating pressure range.

With supercritical CO_2 as eluent, the silica column was highly activated, as observed by severe tailing of chrysene at 50°C. The activity of the silica could be decreased by adding water as modifier (less than 0.5%). However, this reduced the separation between cholestane and nonadecylbenzene. Water, which is one of the very few solvents compatible with a flame ionization detector, should be used with care as modifier. The effects of long-term use of small amounts of water on the silica columns were not studied, but mixtures of CO_2 with higher amounts of water resulted in irreversible loss of column efficiency, probably owing to dissolution of the packing.

High-boiling distillation fractions from C_{20} to C_{31} were chromatographed on two 25 cm silica columns. Both the UV detector and the flame ionization detector were connected in order to determine when the aromatics began to be eluted. There was no clear baseline separation between saturates and aromatics in any of the distillation fractions above C_{27}. A second peak, which had no UV absorption, is probably caused by naphthenes, since olefins are not present in high-boiling, naturally occurring petroleum fractions[9]. This implies that a longer column may separate paraffins, naphthenes, and aromatics in high-boiling distillation fractions.

Compared with the LC separation with hexane as mobile phase, the SFC separation of saturates and aromatics of high-boiling petroleum fractions on silica with supercritical CO_2 as mobile phase was much poorer. With cholestane and nonadecylbenzene as standards, the group separation on silica resembled the LC separation with hexane as mobile phase. However, with high-boiling residues, the group separation of saturates and aromatics was inferior with SFC, compared with LC. In order to obtain good reproducibility, a better separation was required.

Separation of saturates and aromatics on silver nitrate–impregnated silica

Silver-impregnated silica has been used to improve the separation of saturates and olefins both in LC[10,11] and SFC[7]. The retention is due to the formation of reversible π-complexes with the surface silver ions[12], resulting in good resolution of long-chain alkylbenzenes from aliphatic hydrocarbons[13].

A silver-impregnated silica column was prepared, as described in the Experimental section. This column gave strong adsorption of aromatic compounds. Nonadecylbenzene had a retention time of more than 1 h, compared with 3 min on the corresponding silica column. The retention time of cholestane was not influenced by the silver nitrate. Both nonadecylbenzene and chrysene could be backflushed from the silver-impregnated column with supercritical CO_2 as the mobile phase.

Almost all of the silver nitrate could be removed from the column by washing with water, but a small amount was left and produced greater adsorption of nonadecylbenzene than silica alone. However, since with this small amount of silver nitrate the linear capacity of the column was poor, it was decided to use a 1% coating. Compared with the results obtained on a 20% silver-impregnated silica column[7], this 1% coating gave a stronger adsorption of aromatic compounds. Unfortunately, the surface areas of the two silica materials are not available for comparison.

A complete separation of saturates and aromatics in distillation fractions and residues was obtained, as shown in Fig. 1. However, the adsorption of the aromatics was strong and the back-flushed peaks showed severe tailing, which evidently is not desirable for quantitation by integration. The tailing was reduced by adding a silica column ahead of the silver-impregnated column in order to prevent the compounds with the strongest adsorption from entering the silver-impregnated silica column before back-flushing (Fig. 2).

The possibility of using a smaller silver-impregnated column was also looked into. A 30 × 2.1 mm I.D. column was packed with 20% silver-impregnated silica (40 μm), and this column gave less tailing. However, owing to its low efficiency, it was not used for the group separation. A short and efficient silver-impregnated silica column ahead of a silica column would appear to be the best choice for a short analysis time.
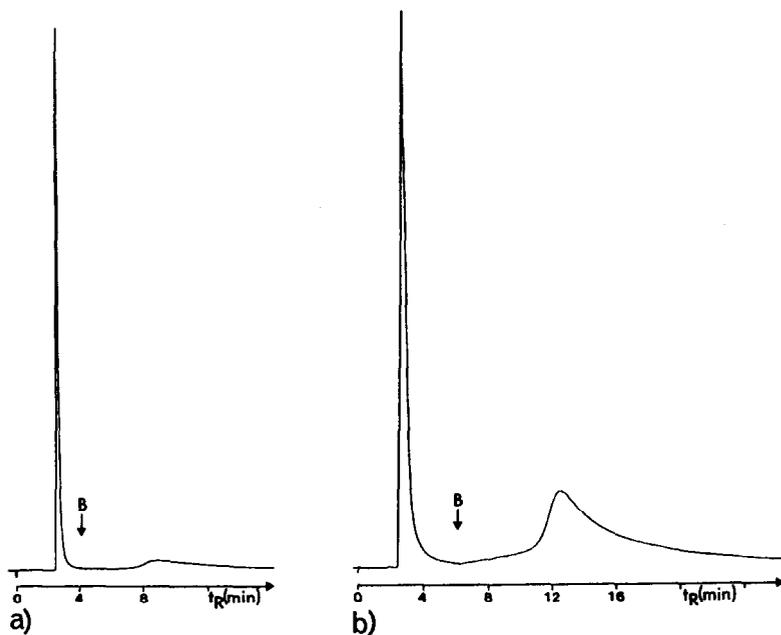
Fig. 1. Separation of distillation fraction C_{20} (a) and a deasphalted high-boiling residue (b) from North Sea oil on a 25-cm silver-impregnated silica column, eluted with supercritical CO_2 (0.2 ml/min) at 260 bar and 50°C. A volume of 0.5 μl of 1:5 (a) and 1:1 (b) diluted solutions was injected, and the flame ionization detector was operated at 350°C. Back-flushing started at B.
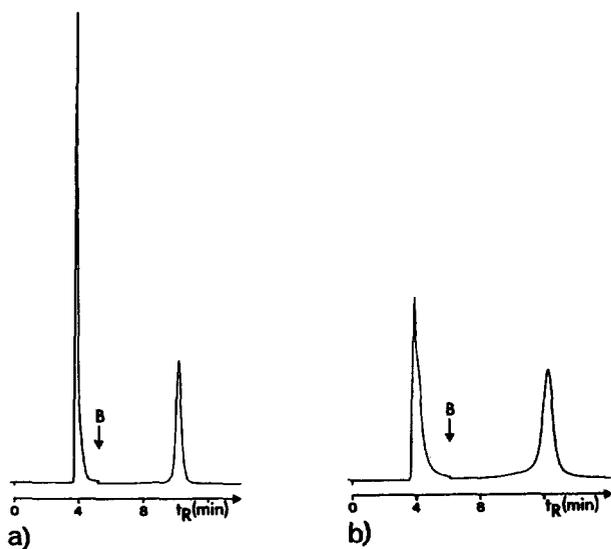

Fig. 2. Separation of distillation fraction C_{20} (a) and a deasphalted high-boiling residue (b) from North Sea oil on a 25-cm silica column plus a 25-cm silver-impregnated silica column, eluted with supercritical CO_2 (0.2 ml/min) at 270 bar and 50°C. A volume of 0.5 μl of 1:5 (a) and 1:1 (b) diluted solutions was injected, and the flame ionization detector was operated at 350°C. Back-flushing started at B.

In order to study how well the saturates and aromatics were separated on the coupled silica and silver-impregnated silica columns, the UV detector and the flame ionization detector were connected in series. There was no UV-absorbing (254 nm) material in the saturate fraction of the distillation fractions, residues, or crude oil. Owing to the UV absorption of the solvent, only C_{20} distillation fraction and crude oil could be examined at wavelenghts below 230 nm. No UV-absorbing (down to 200 nm) material was found in these samples before the columns were back-flushed.

Group separation of high-boiling fractions and residues

As in LC, the polar compounds will be strongly and irreversibly adsorbed on silica with supercritical CO_2 as eluent. A cyano column should be useful in trapping the polar compounds. Based on the results from group separation with LC[1], chrysene belonged to the aromatic fraction, whereas compounds with larger retention time on the cyano column were defined as belonging to the polar fraction. The retention order of polycyclic aromatic hydrocarbons (PAH) on a cyano column with super-critical CO_2 as mobile phase was the same as with hexane as mobile phase in LC. The column-switching system was the same as that used for the LC separation[1], with a silver-impregnated silica column included in addition to the silica column (Fig. 3). The silica plus silver-impregnated silica separates the saturates and aromatics, and the trapped polars are back-flushed from the cyano column. Polar compounds, such as acids (behenic acid) and amides (erucamide), could be back-flushed from the cyano column with supercritical CO_2 as mobile phase.
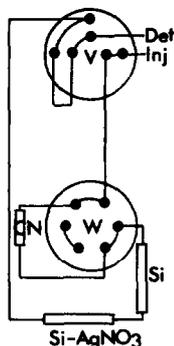

Fig. 3. Column system for group separation into saturates, aromatics, and polars. CN = 3 cm × 2.1 mm I.D. cyano column; Si = 25 cm × 1.3 mm I.D. silica column; Si-AgNO₃ = 25 cm × 1.3 mm I.D. silica column, impregnated with silver nitrate; V = Valco valve (back-flushing); W = Waters valve (column selection).

Fig. 4 shows the group separation of two high-boiling petroleum residues (b.p. > 350°C) with the column system shown in Fig. 3.

The retention time of chrysene was slightly different on two different cyano columns, indicating that the activity may vary. This is probably due to residual silanol groups, which should be kept to a minimum[14]. However, no significant difference in the quantitative results was obtained. The double peak shape of the back-flushed polars is probably due to the high diffusivity in supercritical CO_2 and voids at the column inlet.
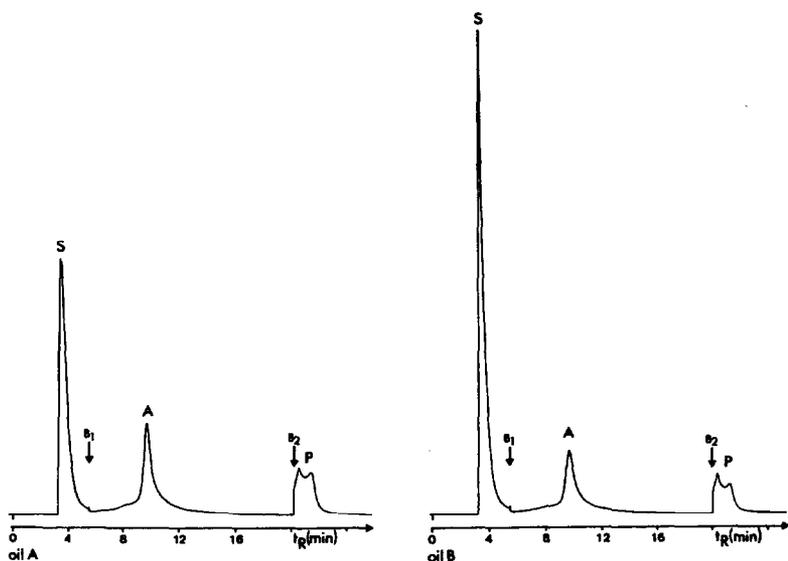
Fig. 4. Group separation into saturates (S), aromatics (A), and polar compounds (P) of two deasphalted high-boiling residues from North Sea oil, using the column-switching system in Fig. 3 with supercritical CO_2 (0.34 ml/min) at 270 bar and 50°C as mobile phase. Half a μl of 1:1 diluted solutions was injected, and the flame ionization detector was operated at 350°C. Back-flushing of the aromatics started at B_1 and of the polars at B_2.

Quantitation

Owing to the high viscosity of the high-boiling petroleum fractions ($>C_{22}$), a suitable solvent was needed for injection. For quantitative determinations, it is necessary to use a solvent producing no FID response. Carbon disulphide which is an effective solvent for the high-boiling fractions, is supposed to give no FID response, but a FID signal from the carbon disulphide used appeared in the void volume. By using a dilution of 1:5 or less, the addition to the FID signal of the saturates from the carbon disulphide was less than 1–2%.

The FID areas from the SFC group separation of two high-boiling petroleum residues were compared with the results (weight) from the corresponding LC separation and gravimetric determination (See Table II). The amount of polar com-

TABLE II

COMPARISON OF WEIGHT (LC) AND FID AREA (SFC) OF THE SATURATED, AROMATIC, AND POLAR FRACTIONS OF TWO HIGH-BOILING RESIDUES OF NORTH SEA OIL

Fraction	Oil A		Oil B	
	Weight (%)	FID area (%)*	Weight (%)	FID area (%)**
Saturated	44.5	45.6 ± 0.6	57.6	59.6 ± 0.6
Aromatic	35.4	35.3 ± 1.1	28.7	27.1 ± 0.6
Polar	20.0	19.1 ± 1.2	13.6	13.2 ± 1.1

* Based on thirteen measurements.
** Based on eight measurements.

pounds, determined by SFC, corresponded well with the amount determined by the LC method. Consequently, the polars can be back-flushed from the cyano column with supercritical CO_2 as the mobile phase. These results indicate that separation into saturates, aromatics, and polars can be performed by SFC with FID for direct quantitation.

CONCLUSION

Supercritical CO_2 can be used as the mobile phase for the group separation of high-boiling petroleum fractions, and direct quantitation can be obtained with an unmodified flame ionization detector. High-boiling petroleum fractions, residues, and crude oil can be separated into saturates, aromatics, and polars on a triple-column system (cyano plus silica plus silver-impregnated silica), with column-switching and back-flushing. The cyano column separates the polars and aromatics, and the silver-impregnated silica column gives a complete separation between saturates and aromatics, which is not obtained on a silica column alone. The silica column is included to reduce tailing of the back-flushed aromatics.

The amounts of saturates, aromatics, and polars in high-boiling residues of North Sea oil were determined and found comparable with the results obtained from gravimetric determinations after separation by LC.

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