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Note

Reversed-phase separation of alkanes in high-boiling fractions of crude oil

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Distillates of most crude oils contain *n*-alkanes in relatively high amounts. The concentration of *n*-alkanes affects important properties of the distillate fuels, such as engine knocking, freezing point, pour point and viscosity. Two common approaches for isolating *n*-alkanes from other hydrocarbons are urea adduction and adsorption in molecular sieves. The latter method is used in the PNA (paraffins, naphthenes, aromatics) analysis, but can be used only for naphtha with boiling points below 210°C[1]. Since the urea adduction method is highly time-consuming and also of questionable analytical value, there is a need for fast methods which can be applied to all kinds of petroleum samples.

The most likely method of choice today would appear to be some kind of high-performance liquid chromatography (HPLC), such as the work of Alfredsson[2,3] which separated paraffins from naphthenes in gasoline range petroleum on an experimental polystyrene–divinylbenzene support (40 Å). However, this separation can not be achieved with higher boiling fractions. Bearing in mind the complexity and wide size range of a crude oil, separation of different groups of saturates can realistically be obtained only in limited cuts or fractions. Since reversed-phase materials are known to separate *n*-alkanes on the basis of chain length[4,5], we decided to examine the possibility of using reversed-phase columns for separation of saturated hydrocarbons of high-boiling (above 350°C) fractions of crude North Sea oil.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) of HPLC grade (Rathburn, Walkerburn, U.K.) was passed over basic Al_2O_3 (superactive 1 from Woelm) to remove peroxides. Water was deionized and glass-distilled. Prior to use, all HPLC solvents were degassed by helium. Alkane standards were obtained from Alltech (Deerfield, IL, U.S.A.). High-boiling distillation fractions from a North Sea oil were obtained from Statoil, Norway. The saturates of each distillation cut were separated from the rest of the material by normal phase chromatography on a cyano column (Spherisorb 5 μm CN, 150 × 7.8 mm I.D.) with hexane as the mobile phase.

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Instruments and columns

The HPLC equipment consisted of a solvent delivery system (Waters 6000 A), a valve-loop injector (Rheodyne 7125) and an RI detector (Waters R 401). The oven of a DuPont 830 liquid chromatograph was used for thermostatting. Two of the columns were of the MPLC™ cartridge type (Brownlee Labs., Santa Clara, CA, U.S.A.). One 100 × 4.6 mm I.D. column was packed with RP-18 (5 μm) and one 220 × 4.6 mm column was packed with Aquapore RP-300 (10 μm). A 250 × 4.6 mm I.D. LC-18-DB (5 μm) column was obtained from Supelco (Bellafonte, PA, U.S.A.).

Procedure

The samples were dissolved in THF. The samples and the syringe were warmed if necessary to keep the sample soluble. Owing to the low sensitivity of the RI detector the concentration of each alkane was greater than 1 μg/μl. The injector volume was kept at 20 μl or less. The separations were performed at different temperatures. Mixtures of THF and water were used as mobile phases. The injector, column and the optical part of the RI detector were placed in the thermostatted oven. A 2-ml tubing coil in front of the injector was thermostatted as well to ensure constant temperature of the mobile phase.

RESULTS AND DISCUSSION

Separation of standards

Preliminary examinations showed that a stronger eluent than methanol was needed for the elution of large *n*-alkanes from an RP-18 column. THF, which is soluble in water in all proportions, was chosen.

The first experiments were performed on a Brownlee RP-18 column at room temperature. The large *n*-alkanes eluted as broad peaks, if at all, with the THF–water mixture that was needed for the separation of even-numbered *n*-alkanes from C_{20} to C_{44}. To determine whether the broad peaks were due to pore exclusion effects, the *n*-alkanes were also injected on to an Aquapore RP-300 column. This column has a pore size of 300 Å and should not exclude C_{44}. However, the broad peaks were also obtained with this column. A higher percentage of water was necessary for adequate retention of *n*-alkanes on the column, probably because of a lower carbon content of the packing. Increasing the temperature to 60°C improved the peak shapes, but the large *n*-alkanes were not eluted at a THF–water ratio necessary for retention of C_{20}. When the amount of THF in the mobile phase was increased the large *n*-alkanes were eluted as sharp peaks from both columns.

Since increasing the temperature also improved the peak shape of the larger *n*-alkanes, this implies that the main problem is the solubility of the large *n*-alkanes. In order to be able to use a higher percentage of THF, a reversed-phase material with a higher carbon content was desirable. The separation of even-numbered *n*-alkanes on the LC-18-DB column is shown in Fig. 1. This separation was obtained with a THF content of 85% in the mobile phase, which on the two previous columns resulted in inadequate retention. The solubility of C_{44}, as based on peak shape, became less satisfactory when the THF content was lowered to 80%, where baseline separation was obtained for the rest of the mixture. In such a classical case for

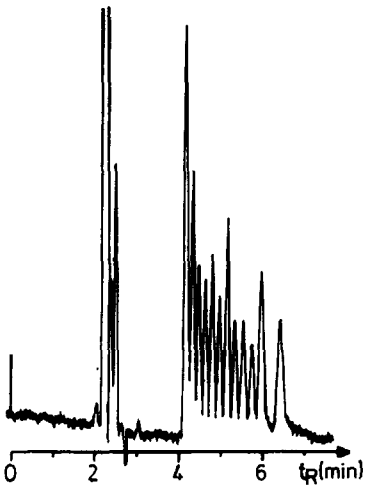

Fig. 1. Reversed-phase separation of *n*-alkane standards on a LC-18-DB (5 μm) column. The mobile phase was THF–water (85:15) (0.5 ml/min) and the temperature was 50°C. The sample size was 5 μl and contained *ca.* 15 μg of each of C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36}, C_{38}, C_{40} and C_{44}.

gradient elution it is very unfortunate that the RI detector cannot be used with gradient elution.

The relationship between log k' and carbon number is close to linear (Fig. 2); this linearity is well documented in the literature[6]. The naphthenic cholestane ($C_{27}H_{48}$) had a retention time equal to the C_{22} *n*-alkane on this column. Owing to lack of standards, further effects of cyclization and branching could not be studied. However, these compounds will in general be expected to have shorter retention times than the corresponding *n*-alkanes.

Separation of the saturates of high-boiling distillation fractions

Based on the previous results separation of *n*-alkanes from branched alkanes and naphthenes in high-boiling petroleum residues cannot be obtained, unless a frac-

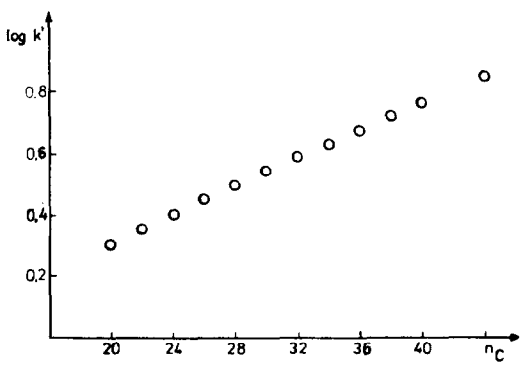

Fig. 2. Log k' *vs.* carbon number (n_C) for *n*-alkanes on a C_{18} bonded phase in THF–water (80:20) (50°C).

tionation in narrow distillation cuts is performed first. The saturate fractions from distillation cuts corresponding to C_{20} to C_{31} were chromatographed on the LC-18-DB column with THF–water as the mobile phase. The separation of fraction C_{27} is shown in Fig. 3. Comparison with standards and gas chromatographic analysis showed that the two late-eluting peaks corresponded to the C_{26} and C_{27} *n*-alkanes. The same pattern was revealed in the other distillation cuts. The material eluted in front of the *n*-alkanes is a mixture of naphthenes and branched alkanes.

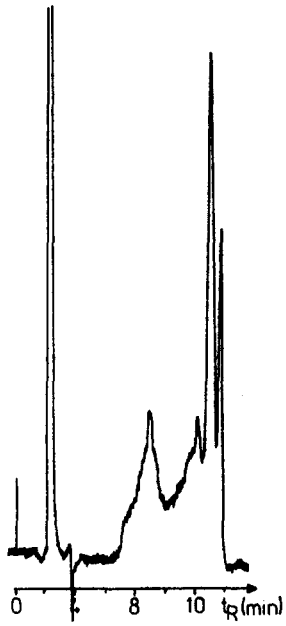

Fig. 3. Reversed-phase separation of the saturate fraction (*ca.* 600 μg in 10 μl) of a C_{27} distillation cut from a North Sea Oil on a LC-18-DB (5 μm) column. The mobile phase was THF–water (73:27) (0.5 ml/min) and the temperature was 50°C.

The amount of *n*-alkanes in each distillation cut could be determined by integration of the RI signal, since the RI response has been shown to correspond to the amount of material in the saturate fraction of the high-boiling petroleum crudes[7].

CONCLUSION

Reversed-phase chromatography can be used for the separation of saturated hydrocarbons of high-boiling petroleum fractions. Owing to the complexity of the saturate material of high-boiling petroleum residues, this method can be applied only to narrow distillation cuts. In this case, *n*-alkanes can be separated from other alkanes. The reversed-phase material must have a high carbon content to allow a high amount of organic modifier in the mobile phase, which is necessary to solubilize the large hydrocarbons. Increasing the temperature above room temperature was also necessary.

REFERENCES

1 I. M. Wittemore, in K. H. Altgelt and T. H. Gouw (Editors), *Chromatography in Petroleum Analysis*, Marcel Dekker, New York, 1979, p. 72.
2 T. V. Alfredsson, *J. Chromatogr.*, 218 (1981) 715.
3 T. V. Alfredsson, *Ger. Offen.*, DE 3,330,858 (Cl. GO1N 31/08) (1984); *U.S. Appl.*, 413,557 (1984); *C.A.*, 100 (1984) 177636w.
4 A. Tchapla, H. Colin and G. Guiochon, *Anal. Chem.*, 56 (1984) 621.
5 N. E. Hoffman and J. C. Liao, *Anal. Lett.*, A11 (1978) 287.
6 W. R. Melander and Cs. Horváth, *Chromatographia*, 15 (1982) 86.
7 E. Lundanes and T. Greibrokk, *J. Liquid Chromatogr.*, in press.