

Rapid group-type analysis of crude oils using high-performance liquid chromatography and gas chromatography

Mohammed Shahid Akhlaq

Institut für Erdölforschung, Walther-Nernst-Strasse 7, W-38678 Clausthal-Zellerfeld (Germany)

(First received October 13th, 1992; revised manuscript received February 11th, 1993)

ABSTRACT

A simple, effective and rapid high-performance liquid chromatographic (HPLC) method was developed for the separation of crude oils into different group types. The method can be used to separate crude oils, kerosenes, gasolines, middle distillates, fuel oils, etc., into various classes of aliphatics (such as straight-chain, branched and cyclic), one-, two- and three-ring aromatics, polar compounds, resins and asphaltenes. A discussion of the experimental details and data from several samples is presented.

INTRODUCTION

Group-type analysis of a given mixture is useful, because often the separation of all the compounds is not necessary and may be impracticable [1–3]. For the mineral oil industry and for research purposes it is very important to know the different group types in a given crude oil, which will contain different amounts of aliphatics, naphthenes, aromatics, naphthoaromatics, heteroaromatics, polar compounds and colloids [4]. Efforts are made to determine all of these groups quantitatively. Doing this has following advantages: (1) with the crude oil characterization one can determine its quality and can adjust the process conditions; (2) with the knowledge of the starting material, the yield, structure and quality of the final products can be established; and (3) separation into group types can be used as pre-separation for further investigations to determine structures using HPLC, GC and mass and nuclear magnetic resonance spectrometry.

For this reason it is important to establish economical methods to characterize crude oils

more rapidly. Several HPLC methods [5–9] have been reported. The aliphatics are separated by HPLC and the remaining fractions are isolated as aromatics and polar compounds with back-flushing [6,10]. It takes about 200 min to separate a crude oil into five fractions [11]. Quantitative analyses of these fractions are carried out gravimetrically, which is very time consuming.

EXPERIMENTAL

Solvents and chemicals

The solvents used were distilled *n*-hexane and chloroform (Riedel-de Haën). Standard model compounds were purchased from Aldrich and were used as received. The crude oils used were Suria, Shingli, Matrum, Jakarta Arco and Scheerhorn oil.

Instrumentation

The HPLC system consisted of two pumps (Model 510), a UV detector (Model 484) and an RI detector (Model 410) (all from Millipore, Waters Chromatographie). Maxima 820 chromatography workstation software (Millipore, Wa-

ters Chromatographie) controlled the total HPLC instrument. A high-pressure gradient system and an electronic backflush valve were used. The gradient system is shown in Table I. The three columns used were μ Bondapak-NH₂ (Millipore, Waters Chromatographie) (300 mm \times 3.9 mm I.D.) with a particle size of 10 μ m, connected in series.

The gas chromatograph system was a Hewlett-Packard Model 5980 Series II, with flame ionization (FID) and thermal conductivity detection (TCD). A fused-silica (DB-5) capillary GC column (30 m \times 0.25 mm I.D., 0.25 μ m film thickness) was obtained from J&W Scientific. The GC oven was held 35°C for 5 min and then programmed at 5°C/min to a final temperature of 310°C, which was maintained for 10 min. A split-splitless injector was used in the split mode with a splitting ratio of 50 for all fractions.

Quantification

The relative percentages derived for each fraction required quantification by both HPLC and GC. We used an RI detector for HPLC

TABLE I

HPLC GRADIENT SYSTEM (LINEAR) FOR CRUDE OIL SEPARATION

Columns, 3 \times amino phase (300 mm \times 3.9 mm I.D.) connected in series. Mobile phase A = *n*-hexane; mobile phase B = chloroform.

Time (min)	Mobile phase		Flow-rate (ml/min)
	A (%)	B (%)	
Start	100	0	1.4
10	100	0	1.4
12	100	0	4.0
20	100	0	4.0
	Backflush		
24	90	10	4.0
32	90	10	4.0
35	50	50	2.0
60	50	50	2.0
	Re-equilibration		
75	100	0	3.0
85	100	0	3.0
90	100	0	1.4
100	100	0	1.4

because it responds to both aliphatic and aromatic compounds, whereas a UV detector will not respond to non-aromatics without an active chromophore. For the quantification of aliphatics, GC was used because it gives more reproducible results. For the GC calibration, all of the compounds in Table III were used. The response factor of the branched and cyclic aliphatics was assumed to be the same as for the corresponding normal aliphatics. To calibrate the HPLC one-ring aromatic fraction a mixture of ethylbenzene, *p*-isopropyltoluene and 1,3,5-trimethylbenzene (1:1:1, w/w/w) was used. The two-ring aromatic fraction was calibrated with naphthalene and 2-methylnaphthalene (1:1, w/w), the three-ring fraction with anthracene and phenanthrene (1:1, w/w) and the four-ring fraction with pyrene. Standard compounds for the polar and colloid fractions were not available, so these fractions were collected and the amounts of the substances present were determined gravimetrically after drying. With these amounts, the response factors were determined and accuracy was checked (Error <3%) with five different crude oils.

The HPLC or GC area counts for each fraction were multiplied by the average response factors obtained to give the relative amount of each fraction present.

RESULTS

The major problem in the analysis of crude oil is the complexity of this natural mixture, containing hundreds of different aliphatic and aromatic components [12,13]. The aliphatics consist of linear *n*-alkanes, branched-chain alkanes and cycloalkanes, while the major aromatic components are one-, two-, three- and four-ring alkylated derivatives [13]. In addition, crude oil also contains polar compounds, resins and asphaltene [11]. Most often it is useful to separate this mixture in group types. Because crude oil contains compounds from those with very low polarity such as aliphatics and naphthenes to very polar compounds such as acids and colloids, they cannot be separated and identified on one column. We used a backflush technique and

achieved the separation of crude oil into seven different fractions within 60 min.

Because in each fraction compounds with different chain lengths and substitution are present, we first investigated the chromatographic behaviour of some standard compounds. It has often been reported that the long-chain alkyl-substituted aromatics behave in chromatography like alkanes and no longer like aromatics [11]. Table II shows clearly that with the use of above method the separations of differently substituted benzene compounds occur in a very close elution range, but the pure alkane compounds separate earlier (Table III).

A standard mixture of 60 different compounds containing aliphatics (*n*-alkanes, isoalkanes and cycloalkanes), monoaromatics, diaromatics and poly- and heterocyclic compounds were selected to optimize the separation procedure. The components and their concentrations in the standard mixture were selected so as to simulate the complex chemical composition of crude oil. The separation tests carried out helped to develop and improve the analytical method.

First we investigated the 24 straight-chain compounds from C₇ to C₃₄, three branched and

TABLE II
HPLC RETENTION TIMES OF MONOAROMATIC MODEL COMPOUNDS

Substance	No. of substituents	No. of carbon atoms	Retention time (min)
Benzene	0	6	8.57
Toluene	1	7	8.67
Ethylbenzene	1	8	8.67
Hexylbenzene	1	12	8.42
Dodecylbenzene	1	18	8.23
Octadecylbenzene	1	24	8.10
<i>o</i> -Xylene	2	8	8.93
<i>m</i> -Xylene	2	8	8.93
<i>p</i> -Xylene	2	8	8.91
<i>p</i> -Ethyltoluene	2	9	8.87
<i>p</i> -Isopropyltoluene	2	10	8.86
1,3,5-Trimethylbenzene	3	9	8.96
Tetralin	–	10	9.03

TABLE III
HPLC RETENTION TIMES OF STRAIGHT-CHAIN, BRANCHED-CHAIN AND CYCLIC ALIPHATIC MODEL COMPOUNDS

Substance	No. of carbon atoms	Retention time (min)
Cyclohexane	6	7.03
<i>n</i> -Heptane	7	7.04
Cycloheptane	7	7.03
<i>n</i> -Octane	8	7.05
Isooctane	8	7.02
Cyclooctane	8	7.04
<i>n</i> -Nonane	9	7.06
<i>n</i> -Decane	10	7.06
<i>n</i> -Undecane	11	7.07
<i>n</i> -Dodecane	12	7.07
<i>n</i> -Tridecane	13	7.08
<i>n</i> -Tetradecane	14	7.09
<i>n</i> -Pentadecane	15	7.09
<i>n</i> -Hexadecane	16	7.11
<i>n</i> -Heptadecane	17	7.12
<i>n</i> -Octadecane	18	7.12
<i>n</i> -Nonadecane	19	7.13
Pristane	19	7.12
<i>n</i> -Eicosane	20	7.14
Phytane	20	7.12
<i>n</i> -Heneicosane	21	7.15
<i>n</i> -Docosane	22	7.16
<i>n</i> -Tricosane	23	7.18
<i>n</i> -Tetracosane	24	7.19
<i>n</i> -Pentacosane	25	7.21
<i>n</i> -Hexacosane	26	7.22
<i>n</i> -Octacosane	28	7.23
<i>n</i> -Triacontane	30	7.25
<i>n</i> -Dotriacontane	32	7.26
<i>n</i> -Tetracontane	34	7.28

three cyclic alkanes. Table III shows the retention times of all these compounds, which are very close ($\Delta t = 0.3$ min). As expected, the long straight-chain aliphatics elute slightly later than the short-chain aliphatics. Further, the branched-chain aliphatics separate slightly earlier than the corresponding straight-chain compounds (see octane, nonadecane and eicosane in Table III). Nevertheless, all these compounds elute very close to each other.

Better resolution of the aliphatic fraction can be achieved by GC [14–16]. A gas chromatogram of the aliphatic fraction is shown in Fig. 1.

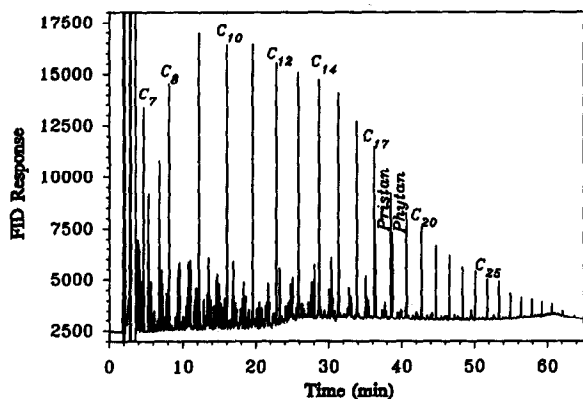


Fig. 1. Capillary gas chromatogram of the aliphatic fraction of a crude oil. Solvent, dichloromethane. A 1- μ l volume of the solution was injected in the split mode. GC conditions are given in the text.

The straight-chain compounds are separated very well, along with the branched and cyclic compounds.

Crude oils contain many different substituted benzenes. For this reason we investigated thirteen different one-ring aromatics individually. The HPLC results are given in Table II. There is a noticeable substituent dependence of the retention time. Up to a propyl substituent single and multiple substitution causes longer retention times whereas longer chains [8], such as hexyl, give short retention times.

The two-, three- and four-ring aromatic compounds are listed together with their retention times in Table IV. The compound classes are very well separated. It is noticeable that the condensed compounds need more time to elute from the column (see naphthalene and biphenyl and also anthracene and triphenylmethane). The aromatic sulphur and oxygen heterocyclic compounds are eluted as expected with the corresponding aromatic fraction. Quantification of the heterocyclic compounds is not possible because they are not well separated from the corresponding aromatic fraction. They are treated as aromatics.

We did not make any attempt to separate aromatics with more than four-ring systems, because these compounds are not expected to be present in high concentrations in crude oils (<1%). These components are eluted together

TABLE IV

HPLC RETENTION TIME OF TWO-, THREE- AND FOUR-RING AROMATIC MODEL COMPOUNDS

Substance	No. of aromatic rings	No. of carbon atoms	Retention time (min)
Naphthalene	2	10	11.82
2-Methylnaphthalene	2	11	11.95
3-Methylnaphthalene	2	11	12.03
Biphenyl	2	12	11.78
Bibenzyl	2	14	12.31
Xanthene	2	13	13.25
Dibenzothiophene	2	12	14.09
Anthracene	3	14	16.06
Phenanthrene	3	14	15.39
Triphenylmethane	3	19	15.28
Pyrene	4	16	19.67

with polar compounds in the backflush fraction. NH-, SH- and OH-substituted compounds are very polar and for this reason they eluted after the backflushing of the column. Resins and asphaltenes are also eluted in the backflush fraction, but with a mobile phase containing 50% chloroform.

This method was used to separate and characterize different crude oils. Fig. 2 shows a reproducibility test with different amounts of crude oil injected. The peaks were characterized quantita-

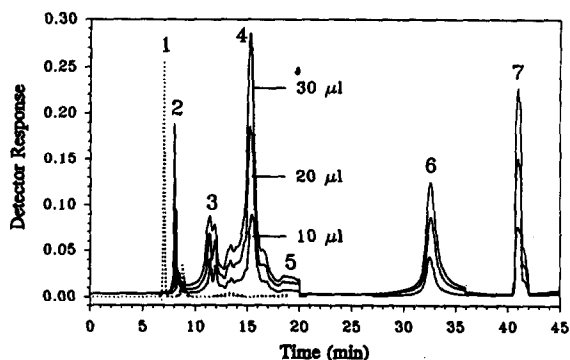


Fig. 2. HPLC of a crude oil dissolved in chloroform and filtered with a 0.25- μ m filter. Volumes of 10, 20 and 30 μ l of the crude oil solution were injected. Peaks: 1 = alkanes; 2 = one-ring aromatics; 3 = two-ring aromatics; 4 = three-ring aromatics; 5 = four-ring aromatics; 6 = polar compounds (NH-, SH-, OH-substituted compounds); 7 = colloids (asphaltene and resins). HPLC conditions are given in the text. Solid lines, UV detection (254 nm); dotted line, RI detection.

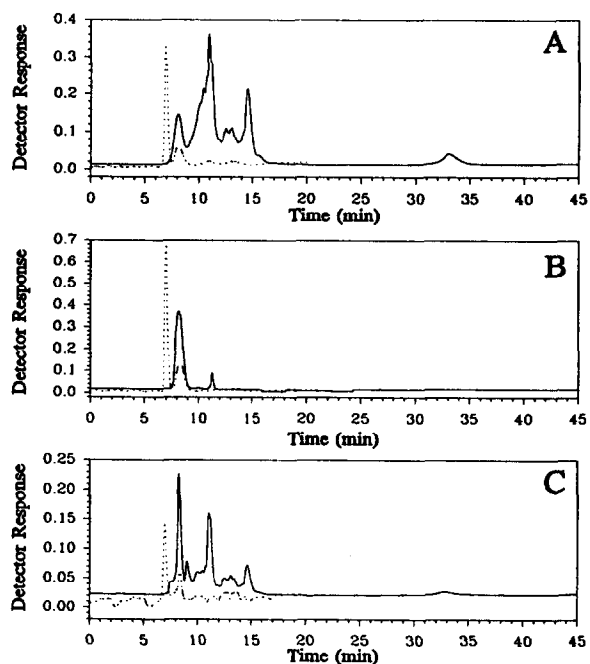


Fig. 3. HPLC of (A) diesel fuel, (B) petroleum fraction with b.p. <190°C and (C) middle distillate. A 1- μ l volume of the undiluted fuel was injected. HPLC conditions are given in the text. Solid lines, UV detection (254 nm); dotted lines, RI detection.

tively with integration and the use of response factors. Fig. 3 shows chromatograms of (A) diesel fuel, (B) a petroleum fraction with b.p.

<190°C and (C) a middle distillate. All these chromatograms show the same group-type separation as in Fig. 2 for crude oil except for the colloid-fraction. Colloids are not present in gasolines, kerosenes, middle distillates and fuel oils.

All the crude oil fractions from Fig. 2 were quantified and their relative percentages are given in Table V. We compared the results with those obtained using other methods, such as chemical separation with solvents [17] (ethyl acetate, pentane and toluene) and with column chromatography [18–20]. The results agreed very well with the classical methods, to within 10%.

CONCLUSIONS

The method described allows the separation of crude oil, fuel oil and middle distillate in their group types within 60 min. With this method one can characterize the samples quickly and without great expenditure. It is also possible to collect each fraction and effect a separation by HPLC or GC [21] (see Fig. 1), and to characterize them by infrared or NMR spectrometry or GC-MS.

Quantification of the fractions is done by integration of the corresponding peaks and using the response factors. This method is much more convenient and accurate than gravimetric meth-

TABLE V

RELATIVE QUANTITATIVE COMPOSITION (%) OF A CRUDE OIL DETERMINED USING THE HPLC METHOD AND DATA OBTAINED FROM CHEMICAL SEPARATION WITH SOLVENTS (ETHYL ACETATE, PENTANE AND TOLUENE) AND BY COLUMN CHROMATOGRAPHY (SEE TEXT)

Crude oil fraction	HPLC/GC	Chemical separation	Column chromatography
Low-boiling fraction	–	6.8	6.8
Naphthenic and paraffinic fraction	16.9	–	15.3
One-ring aromatics	54.4	–	–
Two-ring aromatics	2.2	–	44.7
Three-ring aromatics	0.4	–	–
Four-ring aromatics	0.4	–	–
Polar compounds	3.0	–	3.2
Disperse medium	–	66.3	–
Colloids (asphaltenes and resins)	24.1	27.4	25.6
Insoluble residue	2.3	–	1.9
Total %	103.7	100.5	97.5

ods, because with the latter one has to eliminate the eluent first. Quantitative elimination of the eluent is difficult and it is possible to lose some of the compounds from the one- and two-ring aromatic fractions in the drying process.

REFERENCES

- 1 N.G. Johanasen, L.S. Etre and R.L. Miller, *J. Chromatogr.*, 256 (1983) 393.
- 2 R.L. Miller, L.S. Etre and N.G. Johanssen, *J. Chromatogr.*, 264 (1983) 19.
- 3 H. Engelhardt, *Erdöl Kohle Erdgas Petrochem.*, 30 (1977) 405-411.
- 4 M.S. Akhlaq, in *11. Königsteiner Chromatographietage*, GIT Verlag, Darmstadt, 1991, pp. 392-397.
- 5 S.C. Lamey, P.A. Hesbach and K.D. White, *Energy Fuels*, 5 (1991) 222-226.
- 6 J.C. Suatoni, H.R. Garber and B.E. Davis, *J. Chromatogr. Sci.*, 13 (1975) 367-371.
- 7 J.C. Suatoni and H.R. Garber, *J. Chromatogr. Sci.*, 14 (1976) 546-548.
- 8 P.L. Grizzle and J.S. Thomson, *Anal. Chem.*, 54 (1982) 1071-1078.
- 9 N.J. Tate, in G.B. Crump (Editor), *Petroanalysis '81*, Wiley, Chichester, 1982, pp. 268-284.
- 10 C.E. Östman and A.L. Colmsjö, *Fuel*, 68 (1989) 1248-1250.
- 11 A. Hollerbach, V. Meyn, G. Pusch, C. Kayser, D. Kessel, R. Meyn and I. Swaid, *DGMK-Ber.*, 202-4/2 (1989) 29-32.
- 12 I.L. Davies, K.D. Bartle, P.T. Williams and G.E. Andrews, *Anal. Chem.*, 60 (1988) 204-209.
- 13 J. Bundt, W. Herbel, H. Steinhart, S. Franke and W. Francke, *J. High Resolut. Chromatogr.*, 14 (1991) 91-97.
- 14 J.A. Apffel and H. McNair, *J. Chromatogr.*, 279 (1983) 139-144.
- 15 I.L. Davies, K.D. Bartle, G.A. Andrews and P.T. Williams, *J. Chromatogr. Sci.*, 26 (1988) 125-130.
- 16 F. Munari, A. Trisciani, G. Mapelli, S. Trestianu, K. Grob, Jr., and J.M. Colin, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 601-606.
- 17 J. Wilkens and H.J. Neumann, *Bitumen Teere Asphalte Peche*, 25 (1974) 246-247.
- 18 H.H. Oelert and H.J. Neumann, *Erdöl Kohle Erdgas Petrochem.*, 29 (1976) 309.
- 19 H.H. Oelert and H.J. Neumann, *DGMK-Ber.*, 4508 (1974) 1-50.
- 20 F.P. Burke, R.A. Winschel and D.L. Wooton, *Fuel*, 58 (1979) 539-541.
- 21 M.S. Akhlaq, *J. Chromatogr.*, in preparation.