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Detailed analysis of crude oil group types using reversed-phase high-performance liquid chromatography

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Abstract

Different HPLC methods were developed for characterizing the one-, two-, three- and four-ring aromatic compounds from crude oils. The crude oils are separated in five different fractions and these fractions are then analysed by reversed-phase HPLC. This method of analysing crude oil could be of help in evaluating the origin of the corresponding oil. The methods described were applied to some crude oils.

1. Introduction

For the mineral oil industry and for research purposes it is very important to know the different group types in a given crude oil [1–5], which will contain different amounts of aliphatics, naphthenes, aromatics, naphthenoaromatics, heteroaromatics, polar compounds and colloids [6–10]. Efforts have been made to determine all of these groups quantitatively [11–14].

From the geochemical point of view, it is not enough to know the exact amounts of group types present in a crude oil. It is important to know the detailed constituents of the crude oil [10]. On the other hand, polycyclic aromatic hydrocarbons (PAHs) are well known components of petroleum and petroleum-derived products. PAHs are important environmental pollutants because of their carcinogenicity [15,16]. These compounds are routinely determined in industrial waste water, drinking water and ground water. Regulations on these toxic chemicals are already in effect in North America and Europe.

Many GC and HPLC methods are currently used for PAH determinations, most of which involve time-consuming extraction and clean-up steps [17–19]. The determination of PAHs from crude oil is usually a difficult task [20]; the mixtures are complex and the isolation of PAHs prior to analysis requires multi-step procedures [21], often involving tedious and time-consuming open-column chromatography and liquid–liquid extractions [22,23].

This paper describes improved methods based on (1) the preparative HPLC separation of group types from crude oils [14] and (2) the detailed analysis of collected group types fraction by reversed-phase HPLC. These HPLC methods allow the qualitative characterization of crude oils.

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2. Experimental

2.1. Solvents and chemicals

The solvents used were distilled *n*-hexane, chloroform, methanol and acetonitrile, all from Riedel-de Haën. Water was purified with a Millipore Q-filter system. The quality of this water is equal to that of triply distilled water. Standard model compounds were purchased from Aldrich and were used as received. The crude oils investigated were Suria, Shingli, Jakarta Arco and two north German crude oils. To compare the crude oils with fuels, a diesel fuel was also investigated. The specially prepared diesel fuel sample contains about 1% of sulphur compounds.

2.2. Instrumentation

We used a multi-step analysis. First the preparative separation of crude oils was performed based on previously published work [14], which was modified for preparative analysis. Five fractions were collected. The collected fractions were dried and dissolved in methanol or tetrahydrofuran and then fractions analysed on an analytical column.

The preparative HPLC system consisted of two pumps (Model 510), a UV detector (Model 484) and a refractive index (RI) detector (Model 410) (all from Millipore–Waters). Maxima 820 chromatography workstation software (Millipore–Waters) controlled the overall HPLC instrument. A high-pressure gradient system and an electronic backflush valve were used. The gradient system is shown in Table 1. The column used was LiChrosorb NH_2 from Merck (Darmstadt, Germany) (250 mm × 10 mm I.D.) with a particle size of 7 μm. To eliminate the resins and asphaltenes, the column was washed with chloroform in the backflush mode. This procedure was repeated once a day for about 2 h.

The analytical HPLC apparatus consisted of quaternary pump (1050 Ti-Series), an autosampler (1050 Series) and a degasser (1050 Series), all from Hewlett-Packard, and a UV detector (Merck–Hitachi L-4000). HPLC ChemStation (DOS Series) software (Hewlett-Packard) controlled the overall HPLC instrument. The gradient systems are shown in Table 2. The columns used were Nucleosil C_{18} (Macherey–Nagel) (125 mm × 4.0 mm I.D.) with a 30-mm precolumn (Macherey–Nagel) with a particle size of 5 μm (column system I) and Nucleosil C_{18} PAH (Macherey–Nagel) (150 mm × 4.0 mm I.D.) with an 11-mm precolumn from the same supplier with a particle size of 5 μm (column system II).

Table 1
HPLC gradient system (linear) for the preparative separation of crude oils

Time (min)	Stage	Flow-rate (ml/min)
0		3.0
17		3.0
20	Backflush	6.0
40		6.0
45	Re-equilibration	3.0
60		3.0

Column, NH_2 phase (250 mm × 10.0 mm I.D.); particle size, 7 μm; mobile phase, *n*-hexane.

3. Results

The major problem in the analysis of crude oils and crude oil fractions is the complexity of this natural mixture, containing hundreds of different compounds [14,24,25]. For example, one can find in the monoaromatic fraction all the possible substitutions on the aromatic ring and also the whole variety of chains with respect to type and length. A very limited selection of these compounds that belong to a single group type fraction (monoaromatics fraction) is given in Table 3. Separation of all the possible compounds present in crude oil is not possible [10,25].

To characterize a crude oil in detail, one has to analyse its group-type fractions to some extent [26,27]. RP-HPLC and GC are suitable for this purpose. The advantage of RP-HPLC over GC is its ability to separate even more condensed

Table 2
HPLC gradient system (linear) for the separation of crude oil fractions

Method	Time (min)	Mobile phase		Flow-rate (ml/min)	Column system
		Water (%)	Acetonitrile (%)		
1	Start	30	70	0.70	I
	5	30	70	0.70	
	10	20	80	0.70	
	25	0	100	0.70	
	50	0	100	0.70	
		Re-equilibration			
	55	30	70	0.70	
	70	30	70	0.70	
2	Start	40	60	1.00	II
	15	40	60	1.00	
	20	35	65	0.75	
	60	0	100	0.75	
	100	0	100	0.75	
		Re-equilibration			
	105	40	60	1.00	
	120	40	60	1.00	
3	Start	30	70	1.00	II
	12	30	70	1.00	
	15	15	85	1.00	
	25	15	85	1.00	
	30	0	100	1.00	
	45	0	100	1.00	
		Re-equilibration			
	50	30	70	1.00	
	65	30	70	1.00	
4	Start	20	80[a]	1.00	II
	25	20	80	1.00	
	50	0	100	1.00	
	70	0	100	1.00	
		Re-equilibration			
	75	20	80	1.00	
	90	20	80	1.00	
5	Start	20	80	1.00	II
	15	20	80	1.00	
	25	10	90	1.00	
	50	0	100	1.00	
	70	0	100	1.00	
		Re-equilibration			
	75	20	80	1.00	
	90	20	80	1.00	

[a] Mobile phase methanol.

aromatic compounds and long-chain aliphatic substituted aromatics. These compounds could not be measured using GC.

For studying the group-type fractions of crude oil, we analysed the crude oils on a preparative NH_2 column [14] and collected the five different fractions (see Fig. 1). The zero fraction (0) contains aliphatic compounds that can easily be

Table 3
HPLC retention times of monoaromatic model compounds

Substance	No. of substituents	No. of carbon atoms	Retention time (min)
Benzene	0	6	3.96
Toluene	1	7	4.74
Ethylbenzene	1	8	5.60
p-Xylene	2	8	5.72
Isopropylbenzene	1	9	6.55
1,2,3-Trimethylbenzene	3	9	6.79
o-Ethyltoluene	2	9	6.84
m-Ethyltoluene	2	9	7.19
p-Ethyltoluene	2	9	7.19
1,2,4-Trimethylbenzene	3	9	7.19
n-Propylbenzene	1	9	7.27
1,3,5-Trimethylbenzene	3	9	7.56
tert.-Butylbenzene	1	10	7.84
o-Diethylbenzene	2	10	8.43
1,2,3,4-Tetramethylbenzene	4	10	8.54
p-Isopropyltoluene	2	10	8.68
sec.-Butylbenzene	1	10	8.73
m-Diethylbenzene	2	10	8.82
p-Diethylbenzene	2	10	8.91
1,2,3,5-Tetramethylbenzene	4	10	8.96
1,2,4,5-Tetramethylbenzene	4	10	8.96
Isobutylbenzene	1	10	9.12
n-Butylbenzene	1	10	9.45
p-tert.-Butyltoluene	2	11	10.03
Pentamethylbenzene	5	11	10.61
2,2-Dimethylpropylbenzene	1	11	10.85
4-Methylbutylbenzene	1	11	11.32
1,3-Diisopropylbenzene	2	12	11.75
5-*tert.*-Butyl-*m*-xylene	3	12	11.75
n-Pentylbenzene	1	11	11.87
1,4-Diisopropylbenzene	2	12	12.11
Hexamethylbenzene	6	12	12.38
1,2,4-Triethylbenzene	3	12	12.39
1,3,5-Triethylbenzene	3	12	12.68
n-Hexylbenzene	1	12	14.37
1,4-Di-*tert.*-butylbenzene	2	14	14.64
3,5-Di-*tert.*-butyltoluene	3	15	15.89
1,3,5-Triisopropylbenzene	3	15	16.31
n-Heptylbenzene	1	13	17.00
1,3,5-Tri-*tert.*-butylbenzene	3	18	19.33
1,2,4,5-Tetraisopropylbenzene	4	18	19.35
n-Octylbenzene	1	14	19.58
n-Nonylbenzene	1	15	22.12
n-Decylbenzene	1	16	24.43
n-Dodecylbenzene	1	18	28.34

Column, C_{18} phase (125 mm × 4.0 mm I.D.); particle size, 5 μm; mobile phase, water–acetonitrile (see Table 2, method 1).

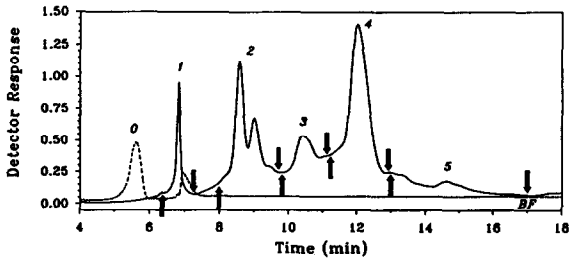

Fig. 1. Preparative HPLC of crude oil A dissolved in chloroform and filtered with a 0.25-μm filter. A 250-μl volume of the solution was injected. HPLC conditions are given in the text and Table 1. Solid line, UV detection (254 nm); dotted line, RI detection. ↑, Start of collecting the fraction; ↓, end of collecting the fraction.

determined by GC. The separation of this fraction has been published previously [14]. The first fraction (1) isolated in this work contains monoaromatic compounds, the second (2) contains diaromatic substances, the third (3) has a maximum amount of heteroaromatic compounds and the fourth (4) and the fifth (5) contain three- and four-ring aromatic hydrocarbon compounds [14].

For better reproducibility of the results, we collected the whole fractions manually as indicated in Fig. 1. The eluent was removed from these fractions carefully under vacuum to minimize the loss of compounds during the drying process.

Because in each fraction compounds with different chain length and substitution are present [5,14], we first investigated the chromatographic behaviour of some standard compounds. Table 3 gives retention data for some standard monoaromatic compounds along with the number of substituents and total number of carbon atoms (N_C). The HPLC traces of the substances are given in Figs. 2 and 3.

Most of the standard compounds are well separated. There is a noticeable substituent dependence of the retention time. The *ortho*-substituted compounds elute earlier than the corresponding *meta*- and *para*-substituted compounds. The straight-chain alkyl-substituted compounds elute later than most of the compounds having the same carbon number (see C_4-substituted benzene, e.g., tetra-, *sec*.-, iso- and *n*-butylbenzene all with $N_C = 10$). Similarly,

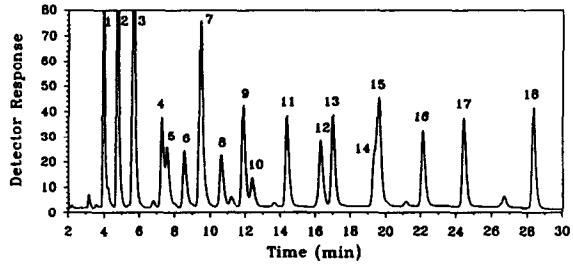

Fig. 2. HPLC of the monoaromatic model compounds. Solvent, methanol. A 10-μl volume of the solution was injected. Peaks: 1 = benzene; 2 = toluene; 3 = xylene and ethylbenzene; 4 = *n*-propylbenzene; 5 = 1,3,5-trimethylbenzene; 6 = 1,2,3,4-tetramethylbenzene; 7 = *n*-butylbenzene; 8 = pentamethylbenzene; 9 = *n*-pentylbenzene; 10 = hexamethylbenzene; 11 = *n*-hexylbenzene; 12 = 1,3,5-triisopropylbenzene; 13 = *n*-heptylbenzene; 14 = 1,3,5-tri-*tert*.-butylbenzene; 15 = *n*-octylbenzene; 16 = *n*-nonylbenzene; 17 = *n*-decylbenzene; 18 = *n*-dodecylbenzene. HPLC method 1 (see test and Table 2). UV detection at 254 nm.

n-octylbenzene ($N_C = 14$) elutes even later than 1,3,5-tri-*tert*.-butylbenzene and 1,2,4,5-tetraisopropylbenzene (both $N_C = 18$).

These few examples make it clear that the identification of all compounds present in a crude oil fraction just by comparing the retention times of the standard compounds is not possible. Even HPLC–MS would have problems in identifying hundreds of these compounds. For this

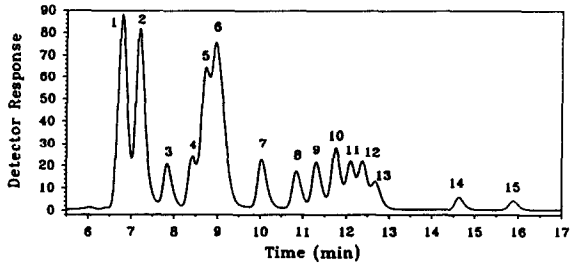

Fig. 3. HPLC of the monoaromatic model compounds. Solvent, methanol. A 10-μl volume of the solution was injected. Peaks: 1 = *o*-ethyltoluene; 2 = *m*-+*p*-ethyltoluene; 3 = *tert*.-butylbenzene; 4 = *o*-diethylbenzene; 5 = *sec*.-butylbenzene; 6 = *m*-+*p*-diethylbenzene; 7 = *p*-*tert*.-butyltoluene; 8 = 2,2-dimethylpropylbenzene; 9 = 3-methylbutylbenzene; 10 = 1,3-diisopropylbenzene; 11 = 1,4-diisopropylbenzene; 12 = 1,2,4-triethylbenzene; 13 = 1,3,5-triethylbenzene; 14 = 1,4-di-*tert*.-butylbenzene; 15 = 3,5-di-*tert*.-butyltoluene. HPLC method 1 (see text and Table 2). UV detection at 254 nm.

reason, we did not make any attempt to identify and quantify the peaks from crude oil fractions.

Our goal was to show the qualitative differences in crude oil fractions. Fig. 4 shows the differences in the compositions of a diesel fuel and two crude oils regarding monoaromatic compounds. We believe that each peak present in the chromatogram does not represent a single compound but contains many different substituted compounds.

Similarly, Figs. 5–8 show the differences for the two- three- and four-ring aromatic compounds and for the heteroaromatic compounds present in diesel fuel and in both crude oils. Fig. 6 shows the differences in the polar aromatic content of the samples. The diesel fuel contains, as mentioned above, about 1% of sulphur, crude oil A has 2.7% and crude oil B about 1.8% of sulphur. Fig. 6 includes not only the sulphur heteroaromatic compounds but also oxygen heteroaromatic compounds [28].

The preparative HPLC traces of diesel fuel, crude oil A and crude oil B do not differ very much (data not shown). On the other hand, the RP-HPLC traces (see Figs. 4–8) show substantial differences.

Fig. 4 shows, as expected, that not very many monoaromatic compounds are present in crude oils, compared with diesel fuel. The loss of short-chain substituted monoaromatic compounds is high because they are volatile (the oils used were not fresh oils). Diesel fuel is a distillation product, so it is rich in monoaromatic compounds.

It is worth mentioning that crude oil A is a so-called "heavy oil". This is also evident from Figs. 5–8. There are few peaks present in the shorter retention time region as compared with the diesel fuel and crude oil B, which indicates the absence of low-molecular-mass compounds.

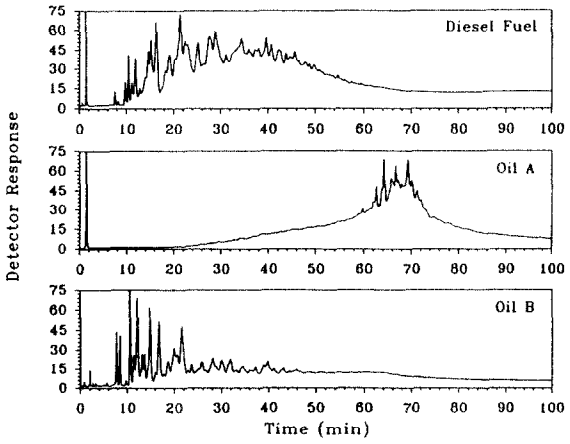

Fig. 5. HPLC of the second preparative fraction (two-ring aromatic compounds). Solvent, methanol. A 25-μl volume of the solution was injected. HPLC method 2 (see text and Table 2). UV detection at 254 nm.

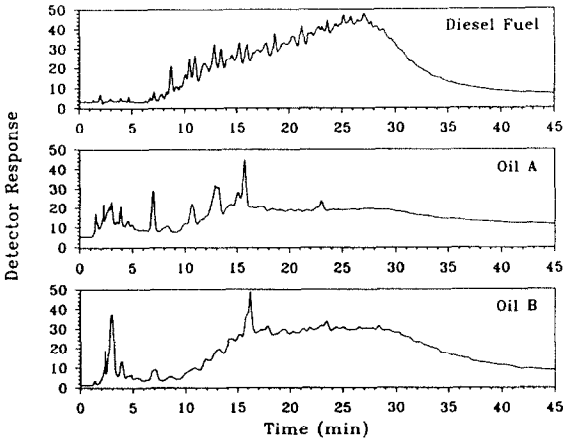

Fig. 4. HPLC of the first preparative fraction (monoaromatic compounds). Solvent, methanol. A 25-μl volume of the solution was injected. HPLC method 1 (see text and Table 2). UV detection at 254 nm.

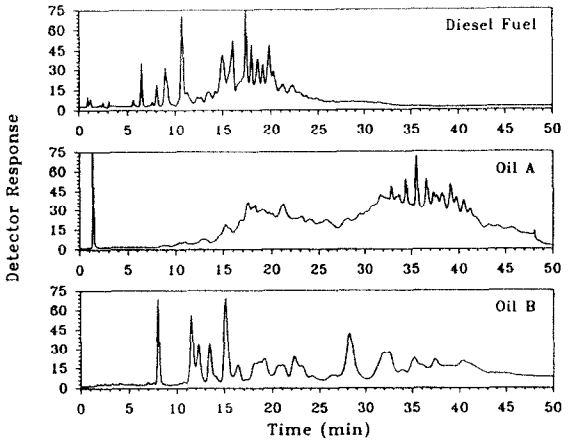

Fig. 6. HPLC of the third preparative fraction (heteroaromatic compounds). Solvent, methanol. A 25-μl volume of the solution was injected. HPLC method 3 (see text and Table 2). UV detection at 254 nm.

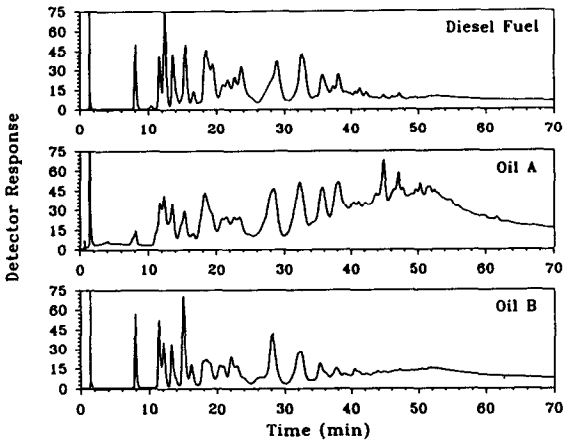

Fig. 7. HPLC of the fourth preparative fraction (three-ring aromatic compounds). Solvent, methanol. A 25-μl volume of the solution was injected. HPLC method 4 (see text and Table 2). UV detection at 254 nm.

It is obvious from the chromatograms that this oil produces more peaks at the higher retention time, which is in agreement with its higher molecular mass compounds.

4. Conclusions

The HPLC methods described allow the detailed separation of crude oils. The results help to characterize a crude oil. The crude oils are preparatively separated into the group types. The preparative chromatograms differ mostly in the peak area and not very much in shape [14]. The RP-HPLC methods with C_{18} and C_{18} PAH columns reflect the physical and chemical properties of the crude oils (molecular mass, contents of heteroaromatic compounds and the chain length of the substituents).

Efforts are in progress to establish a data bank of crude oils characterized with these methods. With the help of this data bank, it would be possible to establish the origin of an unknown crude oil sample, which is important in cases of soil and water pollution with crude oils. On the basis of these results, it should become possible to evaluate the environmentally relevant impact of soil and water contamination with crude oil.

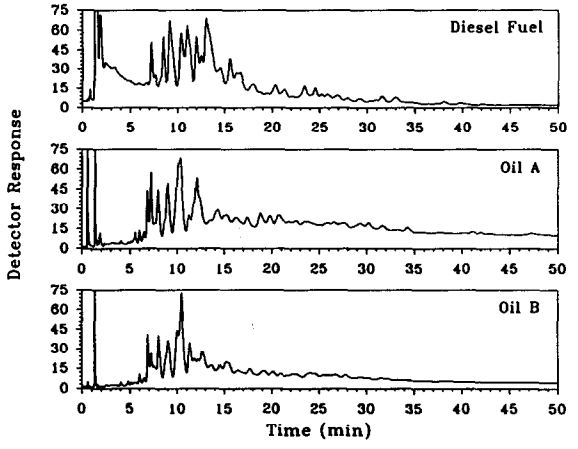

Fig. 8. HPLC of the fifth preparative fraction (four-ring aromatic compounds). Solvent, methanol. A 25-μl volume of the solution was injected. HPLC method 5 (see text and Table 2). UV detection at 254 nm.

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